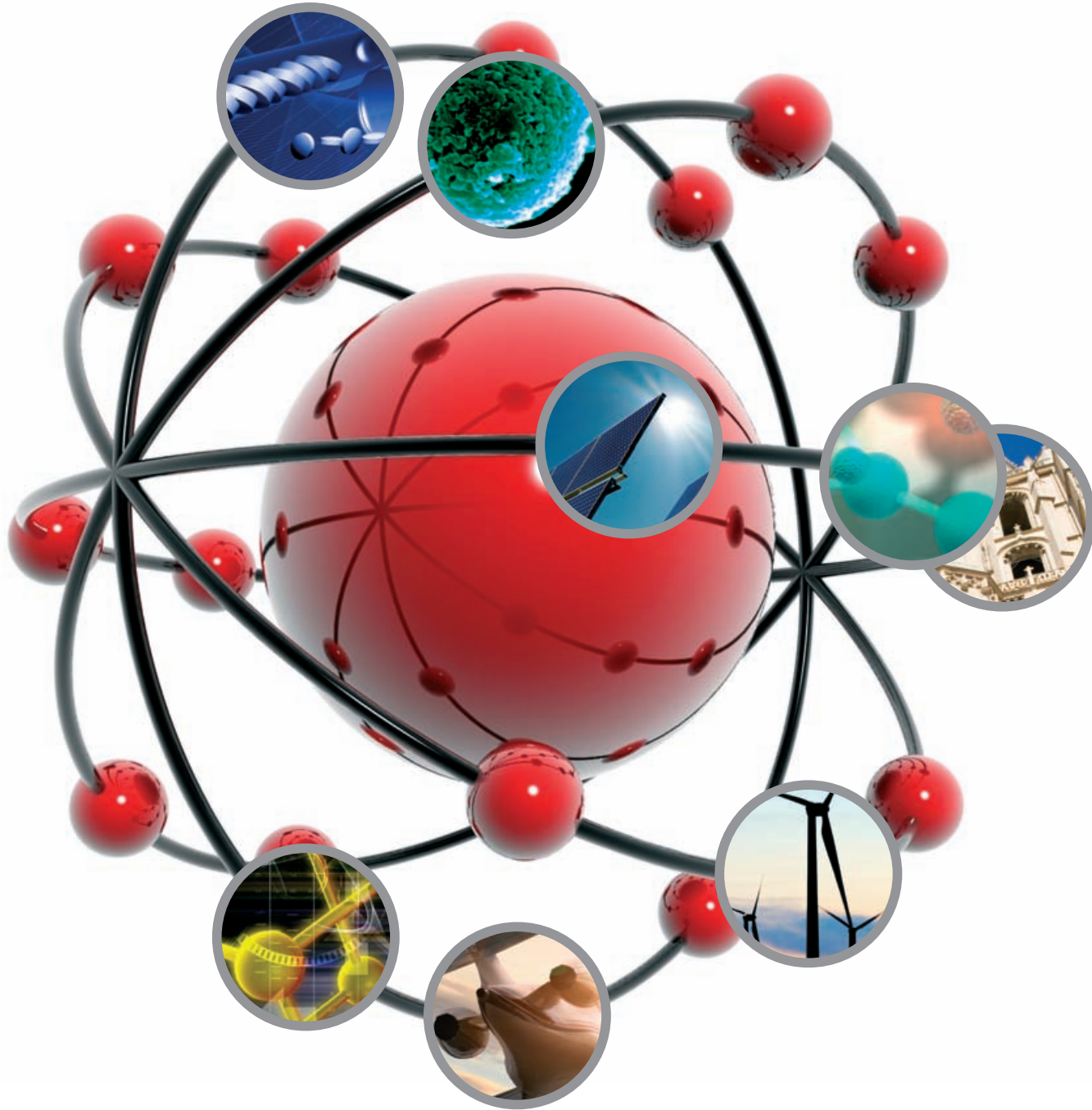


Neutrons
reveal
all
A compilation
of divulgative articles



ESS
bilbao

Neutrons reveal all



All rights reserved. No part of this publication may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopy, recording or any information storage and retrieval system, without permission in writing from the copyright owner(s).

ISBN: 978-84-692-4285-8
Dep. Legal: 00000

Response to the Questionnaire of the ESFRI Working Group on ESS Siting (EWESS), *ESS-Bilbao* 02

Prologue, *J. Campo* 04

Smart Materials

1

Structure and Dynamics of Responsive Microgels, *E. López Cabarcos & J. Rubio Retama* 08

Molecule Based Magnets, *F. Palacio* 11

Metal Matrix Composites, Residual Stress and Neutrons, *G. González Doncel* 15

Neutron Reflectometry and Functionalized Surfaces and Interfaces, *V. Lauter* 19

Health and Biotechnologies

2

Understanding Molecular and Cellular Processes using Neutron Scattering Experiments, *S. Magazù* 26

Neutrons: A Gentle Probe for Gentle Materials, *A. De Francesco* 32

Neutron Scattering as a Tool in the Development of Magnetic Bionanoparticles for Therapy and Diagnosis, *A. Millan* 36

Nanotechnologies

3

Research on Nanoparticles using Neutron Scattering, *L. Fernández Barquín* 42

Neutron Spectroscopy of Isolated Magnetic Molecules, *G. Chaboussant* 46

Nanocomposites for Structured Light Materials: the Input of SANS, *F. Boué* 50

Nanomagnets for Quantum Computation, *F. Luis Vitalla* 55

Cultural Heritage and Archeometry

4

Neutrons in Archaeometry and Conservation Science: the Contribution of Neutron Scattering to Cultural Heritage, *G. Artioli* 60

Neutron Study of Ancient Paper: an Example of early Biomaterials, *C. Mondelli* 64

Neutron Scattering Applications to Cultural Heritage Materials and Artefacts, *R. Rinaldi* 67

Transport Technologies

5

Residual Stresses with Neutrons in Automotive, Aeronautic and Railway Industries, *J. Ruiz Hervias* 74

Neutron Radiography and Tomography in Engines and Rockets, *M. Ceretti* 78

The Importance of Neutrons to assess the Quality of Welds, *G. Bruno* 82

The Use of Neutron for the Study of Composite Materials used for Engines, *G. Garcés* 85

Environment

6

Neutron Scattering and in situ Catalyst Studies, *T. Ramírez-Cuesta* 90

Novel Materials for Magnetic Refrigeration: the Role of Neutron Techniques, *E. Palacios* 93

Neutron's Contribution to more Safe Radioactive Waste Management, *M.M. Castellote Armero* 96

Energy

7

Application of Neutron Scattering to the Development of better Organic Solar Cells, *A. Urbina* 102

Hydrogen Storage Materials and Neutron Scattering Experiments, *J. Hernández Velasco* 105

New Basic Science

8

Quantum Phenomenology, *R. Ballou* 110

Spin Dynamics of Heavy Fermions/Valence Fluctuation Systems at Thermal and Epithermal Neutron Energies. *A. P. Murani* 113

Cold Neutrons, Gravitation, and Forces in the Universe, *H. Abele* 117

Neutron Science and the Hydrogen Bond in Water, *L. R. Falvello* 123

Magnetism without Static Magnetic Moments: Quantum Spins and Low Dimensionality, *J. E. Lorenzo, L.P. Reganult* 128

Synergy between Neutron Scattering and Complementary Experimental Techniques, *J. A. Blanco* 132

Response to the Questionnaire of the ESFRI Working Group on ESS Siting (EWESS)

The scientific impact of a high intensity, long pulse Spallation neutron source has been well documented in a number of recent reports (The ESS Project, Vol.II, New Science and Technology for the 21st Century, The European Spallation Source Project, 2002, available at:

http://neutron.neutroneu.net/n_documentation/n_reports/n_ess_reports_and_more/102. A Second Target Station at ISIS, RAL-TR-2000-032, 2000, available at: <http://ts-2.isis.rl.ac.uk/scienceCase/>: Medium to Long Term future Scenarios for Neutron Based Science in Europe (ESFRI 2003).

Furthermore the scientific potential of instrumentation based on a long pulse design was evaluated in the Engelberg (Engelberg 2002) and Rencurel (Rencurel 2008) workshops.

The rationale for choosing a long pulse option for the first target station of ESS is based on a number of technical advantages:

- The use of long pulse (of the order of a millisecond) reduces significantly the effects of cavitation in the mercury target even at the high energies per pulse set forth in the reference design (~300kJ per pulse).
- A long pulse target station eliminates the need for an accumulator ring and associated beam chopping and hence allows more power to be delivered to the target. This is also more cost effective.
- The long neutron pulse also allows greater flexibility for the design of scattering instrumentation using appropriate band width selection and repetition rate choppers to optimize to the required resolution.
- The long-proton pulse also provides better optimization of the target-moderator-reflector configuration that lead to additional increases in the neutron beam intensities in particular for cold neutrons.

The reports referenced above show three major themes appearing throughout the discussions of forefront science. The first is the desire to extend current capabilities to be able to answer more difficult questions. These may involve extending measurements in the presence of a more difficult sample environment and concomitant restrictions to smaller samples, or measurements made to higher precision to look for subtle intensity variations or line shape effects. The second is the desire to extend most types of measurements to parametric studies exploring ranges of compositions, external fields such as temperature or pressure, or time scales, as in kinetic studies. The third is the general tendency toward the study of systems exhibiting greater complexity, such as the complex chemical systems that occur in many soft matter studies, aspects of macromolecular functionality important in biology that can be explored using neutron scattering, or the multi-component systems important to the geophysical properties and functions relevant to earth sciences. These trends are all evident today as scientists stretch the capabilities of existing neutron sources and instrumentation to try to extend their measurements into some of these areas. The long pulse ESS will provide major capabilities that support these three themes and significantly extend the types of scientific problems that can be fruitfully addressed with neutron scattering. By focusing on and optimizing for the production of cold neutrons this new facility will provide much higher cold-neutron intensities than heretofore available on any pulse neutron source. These higher fluxes translate into the ability to study much smaller samples, more-weakly-scattering processes, and /or higher-rate kinetic behaviors. They also translate into the ability to extend measurements to study of large length scales and slower dynamical processes.

For example, higher intensities permit tightening the resolution to provide an order-of-magnitude extension of neutron scattering dynamical studies to probe longer time scales (slower motions) at longer length scales (times up to 10 microseconds at distances up to 1 micron). This order-of-magnitude range extension will lead directly to new insights into forefront highly complex and difficult problems, for example elucidating the detailed processes and molecular drivers leading to the folding of proteins that is essential for them to carry out their biological role.

Another example can be found in the field of neutron reflectometry, which has long been a unique and powerful tool for probing the atomic or magnetic density normal to surfaces and layered materials. In principle, lateral structures in such systems can also be probed in neutron reflectometers, using grazing-incidence techniques such as grazing-incidence diffraction or grazing-incidence small-angle neutron scattering (SANS). However, the extremely weak signals have made the use of such techniques very difficult, if not impossible, with the neutron beam intensities that have been available up to now. The much higher intensity of cold neutrons, coupled with emerging new techniques such as spin-echo resolved grazing-incidence scattering, will enable the full capabilities of neutron (isotopic sensitivity, magnetic moment) to be brought to bear in the study of such lateral surface structures at length scales of about 10 to 1.000 nanometers or more. This exciting prospect will open up broad forefront scientific areas to study with neutrons, including lateral structures in lubricating or adhesive layers, wetting phenomena, block copolymer or liquid crystal layers on surfaces, artificial biomembranes or biomimetic systems, self-assembly of nanoparticles on surfaces templates and perhaps even real biological membranes.

A third example of new capabilities lies in the use of very highly focused neutron beams. At present, neutron focusing devices easily achieve focused beam sizes of <100 microns, and focused neutron beams ~10 microns in size will be possible in the near future. The neutron intensity that will be available in such focused beams will be enough to measure the very weak absorption or scattering produced by the relatively small number of sample atoms illuminated by a beam of this size. This, of course, will permit the study of such very small samples, and should also create opportunities to develop instrumentation for various types of scanning neutron probes for exploring minute regions of large samples. The availability of intense neutron beams of this size will generate new techniques that will open up totally new scientific

fields with an ultimate potential that is at present only dimly imagined.

As a final example of new scientific capabilities provided by the ESS, we mention the area of kinetic studies. The unprecedented fluxes will allow all structural and dynamical measurements to be made much faster. This will, of course, facilitate parametric measurements probing material structure and dynamics as functions of environmental conditions such as temperature, pressure, applied magnetic or electrical field, or changing chemical composition of the environment. However, perhaps even more exciting, these rapid measurements will allow structural measurements (at length scales ranging from hundreds of nanometers down to fractions of one nanometre) to be made in a few seconds or less, allowing the kinetics of relaxation processes or the approach to chemical equilibrium to be followed on such time scales. This will enable much more extensive neutron exploration of the behavior of systems far from equilibrium and the approach to equilibrium than has previously been possible. In favorable cases pump-probe or other sample modulation techniques can extend these types of measurements down to a few microseconds allowing much more detailed study of the initial relaxations in far-from equilibrium conditions in a wide variety of systems.

In summary, the quantum jump in performance brought by the ESS will provide researchers with the means to probe distance and time scales that have hitherto been unavailable, but are critical to answering some of the grand challenge questions facing our society. Extending the range of measurement to longer distances and slower time scales enables the study of systems exhibiting greater complexity, such as the complex chemical systems that occur in many soft matter studies, aspects of macromolecular functionality important in biology that can be explored using neutron scattering, or the multi.-component systems important to the geophysical properties and functions relevant to earth sciences. Furthermore the unprecedented high intensities will also enable very short measurements times with the routine use of parametric studies to explore systems far from equilibrium, in transient states, or in approach to equilibrium. In addition to these unique capabilities, the high intensities of cold neutrons will enable smaller samples to be measured, under more complex environments, thereby providing information on materials under extreme conditions hitherto unattainable.

ESS-Bilbao

April 25th, 2008

Prologue

The scientific case of the ESS project, presented in Bonn in 2002, was elaborated by a large number of European scientists over a period of several months. This and other subsequent reports gather most of the information related to the characteristics of neutron scattering techniques and show what makes them an essential tool for the advancement of science and technology today.

Therefore, ESS-Bilbao considers that it is not necessary to completely remake the scientific case. However, ESS-Bilbao would like to initiate an important communication exercise to share with the society why “neutron sources for science”, and in particular the ESS, are essential to maintain and increase our quality of life. Thus, an additional effort to popularize the scientific case, using language adapted for the general public with the ability to penetrate the present society is necessary.

For this reason, the ESS-Bilbao Consortium asked the neutron scattering Spanish scientists to lead this task, counting on the participation of some international specialists too. This is the first but not the last action planned with respect to the popularization objectives.

Moreover, it was not our goal to produce an exhaustive compilation of the numerous neutron science applications. Thus, only a reduced number of specialists were contacted. In order to give to the reader a quick overview of the vision of each area we have tried to limit the length of each contribution.

As a result we have generated this short document which is structured in eight sections according to certain aspects which concern society most today: transport technologies, smart materials, health and biosciences, energy, sustainable development and environment and cultural heritage. A special consideration to fundamental science and nanotechnology applications is also included in this compendium. The authors were asked to incorporate the important aspects, contributions, or achievements made by neutron scattering techniques relevant for society as well as new ideas or experiments within each area that could only be implemented with the ESS.

The use of technical jargon was avoided as much as possible to facilitate a more effective communication to the general public, possibly, with a limited knowledge in the science field. We recognize that writing a paper with all these limitations has been a very difficult mission and, in some cases, an almost impossible task.

Finally, the ESS-Bilbao Consortium would like to express its gratitude to all the participants to this interesting project that will, without any doubt, serve to spread the neutron scattering techniques to society.

Dr. Javier Campo

ESS-Bilbao & Materials Science Institute of Aragón

Smart materials

Health and Biotechnologies

Nanotechnologies

Cultural Heritage and Archeometry

Transport Technologies

Environment

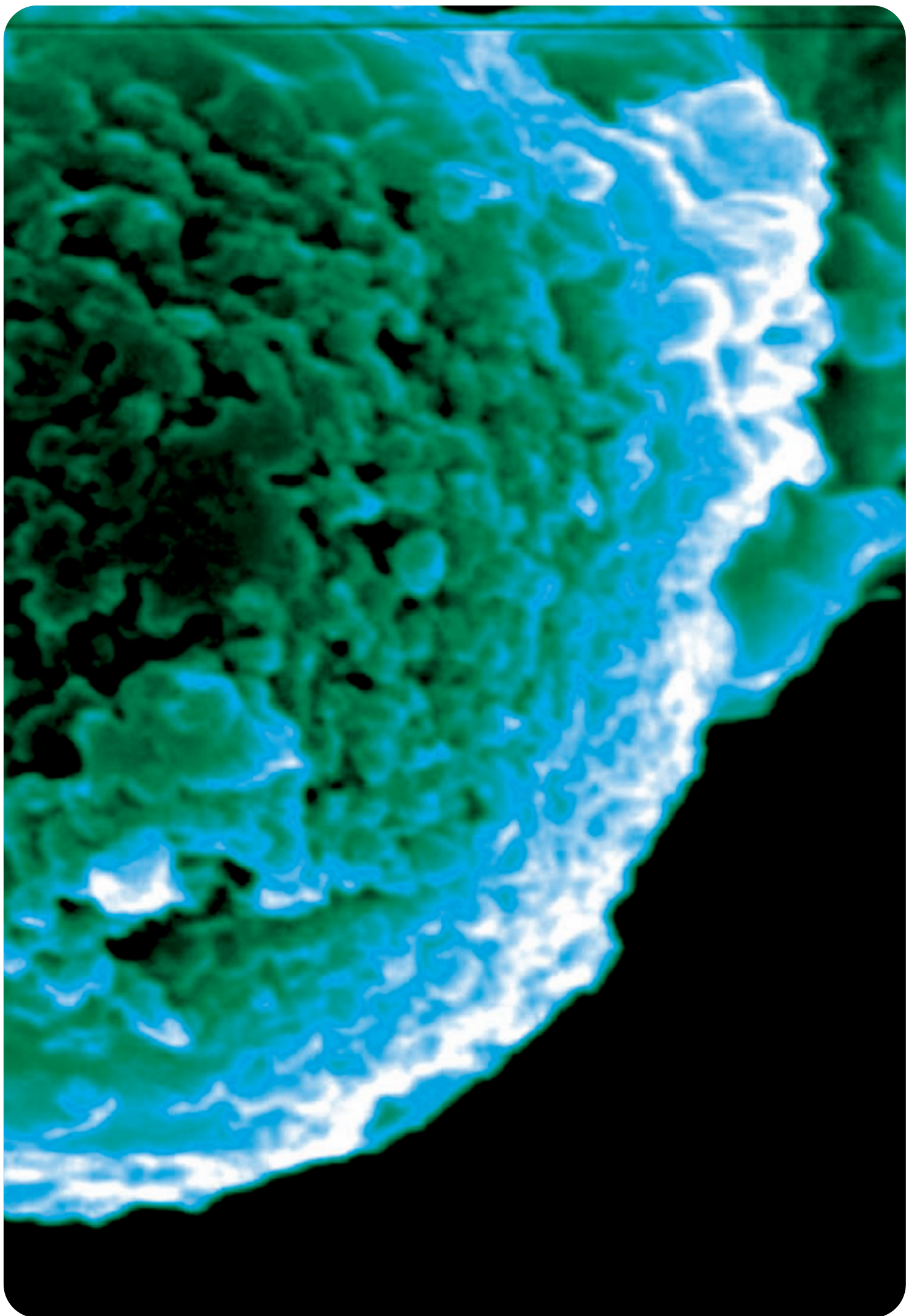
Energy

New Basic Science

Smart Materials

1

- | | | |
|------------|---|--|
| 1.1 | Structure and Dynamics of Responsive Microgels | E. López Cabarcos & J. Rubio Retama |
| 1.2 | Molecule Based Magnets | F. Palacio |
| 1.3 | Metal Matrix Composites; Residual Stress and Neutrons | G. González Doncel |
| 1.4 | Neutron Reflectometry and Functionalized Surfaces and Interfaces | V. Lauter |



Structure and Dynamics of Responsive Microgels

E. López Cabarcos & J. Rubio Retama



In recent years “smart” materials have been studied in numerous publications and there is growing interest in these systems. Smart material means a material able to respond to tiny changes in the environment changing its dimensions or emitting a signal. One example is constituted by gels formed by a network of interconnected polymer chains immersed in a solvent that swell or shrink in response to minimum changes of temperature, pH or solvent composition. These gels could be used to absorb pollutants, drugs or enzymes that would be released when the gel expands in response to a change in pH or temperature. However, for the gel to expand or contract, the solvent has to diffuse through the polymer network, and this takes time if the gel dimensions are large. By preparing gels of micron size (microgels) the solvent diffusion time reduces to seconds or even milliseconds, which make them attractive systems as switchable materials.

The gel’s thermal response manifests itself in large size variations around a characteristic transition temperature (the so called volume transition) that involves conspicuous changes in the structure and dynamics of the

polymer network, which have been studied using small angle neutron scattering (SANS) and quasielastic neutron scattering (IQNS) respectively. The suitability of neutrons for these purposes arises from their wavelengths being similar to interatomic distances and their energies being comparable with the energies required for molecular motions. These features allow us to obtain both spatial and temporal information about spatial inhomogeneities and molecular motions which is important not only in polymers and gels but also in chemistry and biology. Another important characteristic of neutrons that can be used to great advantage in the study of gels is that isotopes of the same atom may have very different scattering strengths. In particular, hydrogen scatters quite differently from its isotope deuterium. Generally, the gel structure includes a large number of hydrogen atoms in both the polymer network and in the solvent that is commonly water. Thus, by replacing ordinary water with deuterated water is possible to separate in both, SANS and IQNS patterns, the contributions arising from the polymer network and from the solvent.

Some relevant experiments performed with neutrons in the last years

Poly(magnesium acrylate) microgel with pomegranate structure for bioreactors.

A novel poly(magnesium acrylate) microgel (PAMGA) was synthesized for application as enzyme immobilization system. The variation of the monomer concentration employed in the synthesis permitted to tune up the shape and size of the microgels in such a way that using 1.5 mol l^{-1} , microgels of average size $40 \mu\text{m}$ formed by smaller subunits of around $1 \mu\text{m}$ are produced (Fig.1). This fact confers the microgels a pomegranate-like structure that increases the specific surface of the system.

Glucose Oxidase (GO_x) was immobilized within PAMGA microgels with different cross-linking content with the aim of using them as bioreactors. Cross-linking introduced inhomogeneities in the polymer matrix that greatly influenced

Fig.1 Scanning electron microscopy micrograph of PAMGA microgel

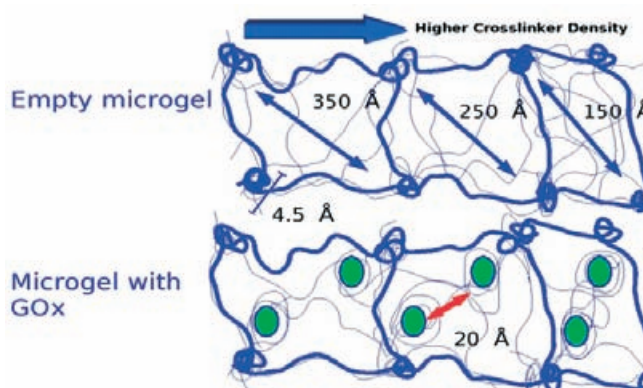
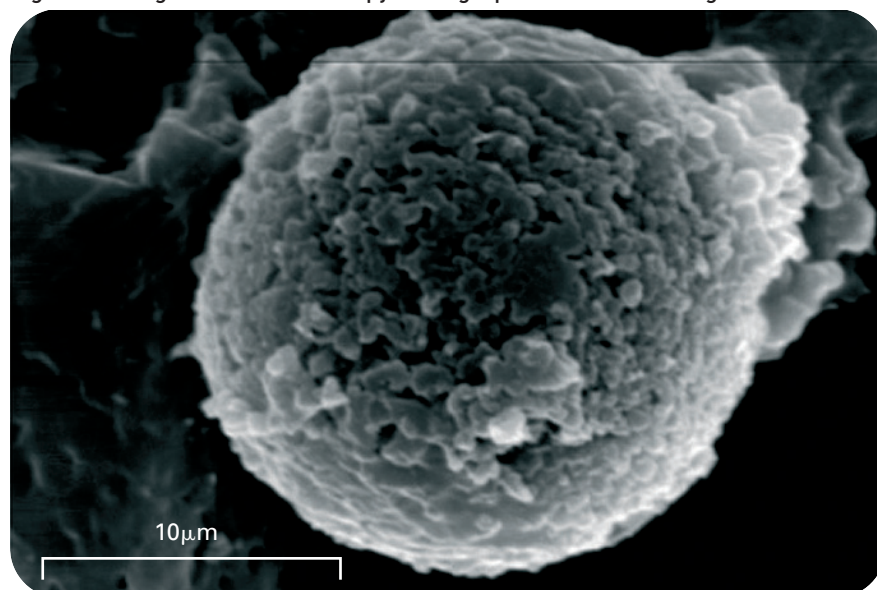


Fig.2 Schematic representation of PAMGA microgels with GO_x . The dimensions were obtained with SANS technique.

the polymer structure. At the nano-scale, the cross-linker concentration induced changes in the fractal dimensions and the correlation lengths of the microgels, whereas at macroscopic-scale modified the swelling degree. **The incorporation of GO_x was detected due to the slight increase of the polymer network provoked by the accommodation of the enzyme and the appearance of a new correlation length (20 \AA) in the neutron scattering pattern (Fig.2).** It was found that the entrapped GO_x increased the swelling of the microgels due to the osmotic effect of the enzyme, and the activity of the entrapped GO_x depends on the microgel cross-linking content.

Elucidation of the core-shell structure of poly(N-isopropylacrylamide) microgel.

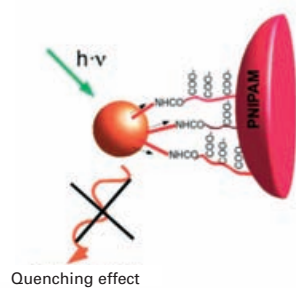
In the group of responsive-polymer based systems, poly(N-isopropylacrylamide) (PNIPAM) is certainly one of the most interesting materials. PNIPAM microgels swell at temperatures below 33°C and keep collapsed at higher temperatures. The microgels can be covered with luminescent CdTe nanocrystals covalently immobilized on their surface. The chemical environment around the CdTe nanocrystals can be modified by changing the temperature, provoking a steep variation in the nanocrystal luminescence intensity in such a way that below 36°C luminescence is quenched whereas above this temperature the microgel becomes strongly luminescent (Fig.3).

This should allow the use of these systems as optical switches with temperature as input signal. The structure of the PNIPAM microgels was investigated using SANS and a core-shell model was proposed with the core containing most of the cross-linker molecules and the shell controlling the whole particle swelling. Furthermore, the dynamics of the polymer chains was studied with IQNS and two diffusion motions in the swollen microgels were identified: i) a slow component associated with the highly cross-linked core and ii) a fast component arising from the low cross-linked shell region.

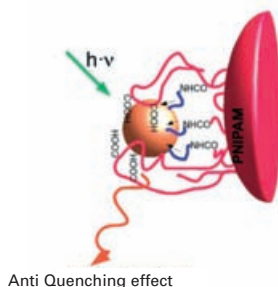
Biosensors based on polyacrylamide microgels with entrapped redox enzymes

Redox enzymes such as glucose oxidase, tyrosinase, and choline oxidase were immobilized in polyacrylamide (PA) microgels with the aim to prepare electrodes for biosensors. The electrode response is derived from the redox process of the enzymatic reaction product at the reading potential. The reduction of the gel size to mesoscopic dimensions has several advantages when serves as enzymatic container for biosensors: i) it decreases the device time response by orders of magnitude; ii) very often, the encapsulated enzyme is protected against inactivation by the polymer matrix; iii) high enzymatic activity, since the high surface-to-volume ratio facilitates the enzyme accessibility; iv) possibility of incorporating functional groups during the synthesis of the particles to improve the analytical properties of the devices. Modifications of the structure and dynamics of the microgel by the presence of the redox enzymes and the incorporation of conducting polypyrrole were investigated with SANS.

Swelling State at 25°C



Collapsed State at 40°C



Future experiments with responsive hybrid particles using neutron scattering

Hybrid particles attracted scientific interest due to the possibility of combining different properties in individual particles with different compositions. These particles are commonly defined by a core-shell structure. The core often responds to an external field whereas the shell stabilizes the core, makes it compatible with the environment and provides additional responsive properties (Fig.4). Many interesting technological applications can be foreseen for these materials, including separation technology, catalysis (nanoreactors), biochemistry (conjugates of quantum dots and antibody), medicine (drug targeted delivery), etc.

One example of hybrid material would consist in a core constituted by an optical active nanoparticle encapsulated in a microgel. This new particle could also exhibit magnetic properties when the polymer shell serves as a carrier of magnetic nanoparticles. Thus the whole system will be optically active and could be located in a convenient position using a magnet to form regular structures for microgrids. Another example would consist of using magnetic nanoparticles covered with biocompatible polymers for targeted drug delivery. **For these applications the thorough knowledge of the structure and dynamics of the shell layers, obtained by neutron scattering, is of paramount importance since it helps to predict particles' behavior and to improve their design.**

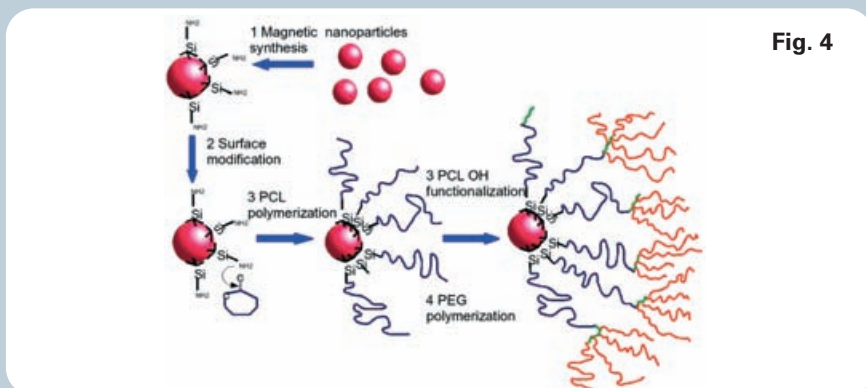


Fig. 4

Fig. 4. Scheme that summarizes the synthesis of some hybrid nanoparticles: i) core of magnetic nanoparticles, ii) the surface of the nanoparticles is covered with a silane molecule required for initiating the poly(ϵ -caprolactone) open ring polymerization, and iii) polymerization of an outer layer of poly(ethyleneglycol) forming a dendritic shell.



FURTHER READING

- A. Fernandez Barbero, I.J. Suarez, B. Sierra, A. Fernandez Nieves, F.J. Nieves, M. Marquez, J. Rubio Retama, E. López Cabarcos, *Advances in Colloid and Poner* "Interf. Sci. 147 (2009) 88
- J. Rubio Retama, F.M. Tamimi, M. Heinrich, E. López Cabarcos, *Langmuir* **23** (2007) 8538
- M. Agrawal, J. Rubio Retama, N. Zafeiropoulos, N. Gaponik, S. Gupta, V. Cimrova, V. Lesnyak, E. López Cabarcos, S. Tzavalas, R. Rojas-reyna, A. Eychmüller, M. Stamm, *Langmuir* **24** (2008) 9820
- A. Fernandez Barbero, A. F. Nieves, I. Grillo, E. López Cabarcos. *Phys. Rev. E* **66** (2002) 051803
- J. Rubio Retama, B. Frick, T. Seydel, M. Stamm, A. Fernandez Barbero, E. López Cabarcos, *Macromolecules* **41** (2008) 4739
- J. Rubio Retama, B. López Ruiz, E. López Cabarcos, *Biomaterials* **24** (2003) 2965
- J.P. Hervás, M. Sanchez Paniagua, E. López Cabarcos, B. López Ruiz, *Biosensors and Bioelectronics* **22** (2006) 429

Molecule-Based Magnets

F. Palacio

Ubiquitous magnets, from the very necessary ones in motors, transformers and actuators to the handy souvenirs we stick to our refrigerator door to hold memos and shopping lists, are commonly made from metals, alloys or metallic oxides. Some, like magnetite, are known since more than two thousand years ago others are more recent but all them have become essential to our current way of life. From electricity production to cars, from computers to domestic appliances they are silent albeit fundamental components in almost every aspect of our technologies. **As a whole, magnets constitute a multitrillion dollar global industry and generate the second largest cash flow in world economy.**

About thirty years ago, a new kind of magnets based on molecules was discovered. Instead of being hard, heavy, opaque and insoluble, they can be soft, light, flexible, transparent and soluble. Moreover, molecule-based magnets offer other interesting properties, like the possibility to modify their magnetism using light or that of tuning their properties by minor modifications in their molecular composition. They can also combine several properties, like optical, conducting and magnetic, in a multifunctional material. Using

molecules it is possible to have a magnet without metals and several interesting examples of organic magnets have been discovered. Last but not least, they can be reduced to the size of a single molecule. Accepting that single molecule magnets are not real magnets, they in many ways behave as such, e.g., they have hysteresis cycle and show memory effects.

Molecular Magnetism has grown as an important multidisciplinary field in science and is raising strong expectations in the benefit of industry and society. As size can be reduced to the molecular scale they open the way to a new class of information storage materials. Multifunctionality enables materials for opto-magnetic gates, molecular spin valves and molecular spintronics. Under very mild external interactions, like pressure and temperature changes or the presence of water molecules, some molecular magnetic materials abruptly change their spin state making them valuable materials for new kinds of sensors. Indeed, the miniaturised Mössbauer spectrometer MIMOS-II which was part of the instrumental payload of NASA's Mars explorer rovers "Spirit" and "Opportunity" incorporated a water sensor based on such changing spin materials.

The role of neutron scattering on molecular magnetism research

Neutrons are a most valuable tool to investigate magnetic materials, particularly if they are molecular. The wavelengths of thermal neutrons compares well with atomic spacing so they can provide accurate structural information ranging from the precise positions of hydrogen atoms to those of large molecules. Moreover, neutrons *see the nuclei* as they interact with them *via* strong interactions instead of the interactions of x-rays with matter *via* the atomic electron cloud. This has important benefits with respect to more

conventional x-ray structural determinations, like to be able to see light atoms, particularly hydrogen, and to differentiate isotopes and neighbouring elements. As neutrons bear magnetic moment, they are ideal probes to determine magnetic structures and magnetic fluctuations. Neutrons are highly penetrating in matter, so they enable complex environments and extreme conditions around the sample, e.g., cryostats, furnaces, pressure cells, reactors and other. They can provide bulk information of processes, transitions and reactions under realistic conditions.

The high value of neutron scattering experiments on molecular magnets can be highlighted in the following examples.

Determination of magnetic density distribution in organic magnets.

In conventional magnets based on metals and alloys, the magnetic moments responsible of the material magnetism are all localised in the metal atoms as they arise from the spins of unpaired electrons in their atomic orbitals. In the case of organic magnets the strong covalent bonds impose the formation of *molecular orbitals*, where electrons are delocalised at molecular level. In consequence magnetic moments can be delocalised through several molecular atoms each having different moment density. **The knowledge of such moment distribution is of utmost importance to understand the mechanisms involved in the development of the bulk magnetic state. Polarised neutron diffraction is the only technique sensitive enough to investigate such density moment distribution** as exemplified in Fig. 1 where it is shown how a single spin moment is delocalised in the five-member ring, -CNSSN, ring of the *p*-cyano- tetrafluorophenyl-dithiodiazolyl free radical. These are the molecular orbitals responsible for the magnetism of the compound. This molecule in the solid state constitutes the organic magnet with the highest magnetic ordering temperature, ten times higher than any other organic magnet.

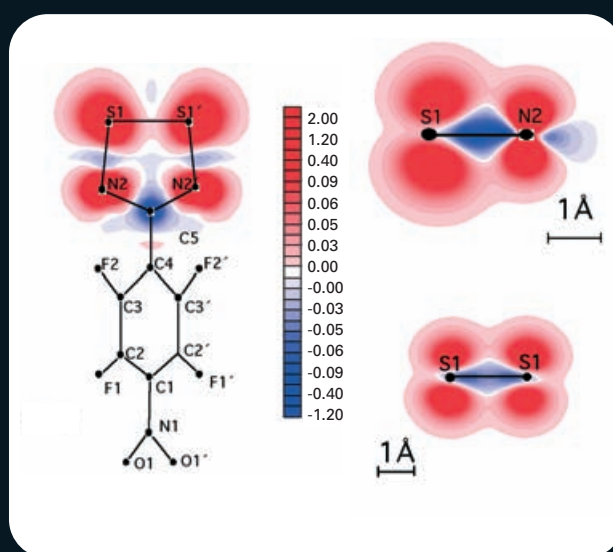


Fig. 1. Distribution of the magnetic moment density of the unpaired spin in the *p*-cyano- tetrafluorophenyl-dithiodiazolyl free radical

Structural transformations in photo-induced magnetic transitions.

Spin crossover materials can be defined as switchable molecular materials. Under external excitation they tend to change their spin state, i.e., the number of unpaired electrons, in a way that very often implies memory effects. The transformation correlates with structural changes that are difficult to investigate in detail using conventional x-ray techniques. The compound $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ (ptz=1-*n*-propyltetrazole) is the best representative light-induced spin crossover material. Upon cooling, it can transform from the colourless high-spin state (HS) to the purple low-spin (LS) one at about 128 K. The transformation is accompanied by a change in the compound crystal structure that can be reverted while warming the compound above 135 K to the HS state. There is, therefore, a memory effect of about 7 K in the process. Moreover, by irradiating the

compound while in the LS state and at the liquid helium temperature it is possible to reach the HS state through a photo-induced process. Similar and even larger memory effects have been observed in related compounds whose transitions occur at room temperature and above. The memory effects of these materials are being investigated to develop displays and memory cards. The structural behaviour of the compound during the transition process between LS and HS and vice versa was and open question of both fundamental and practical importance that neutron experiments have helped to solve recently. **Neutron diffraction experiments done in samples under visible light illumination have permitted to observe a continuous shift, which clearly rules out a mechanism of nucleation and growth of like-spin domains during the phase transformation. It also shows the basically homogeneous character of the photo-excitation process.**

Long-range ferromagnetism in single molecule magnets.

Magnetic clusters of molecular nature, the so called **Single Molecule Magnets** (SMM), are ideally monodispersed nanomagnets that have attracted interest because of the new physics they help to unveil but also because their potential importance as components of massive computer memories and in quantum computation. The archetypical SMM and by far the most studied one is the Mn_{12} acetate, commonly referred as Mn_{12} , whose total spin is $S=10$ and can be grown as a single crystal where all the molecules are chemically identical (**Fig. 2**). Magnetisation in this compound can be induced by the application of an external magnetic field. At room temperature and upon reversal of the field direction the magnetisation will closely follow the change by also reversing its direction. However, at temperatures of the liquid helium and below, it is observed that the magnetisation following of field changes tends to slow down and proceed through complex mechanisms with strong memory effects. At a given temperature it eventually becomes blocked and cannot follow the field reversal anymore.

There are several important problems in this system that can only be addressed using neutron scattering techniques. The first is the precise understanding of the electronic energy states at molecular level. The energy of the cold and thermal neutrons is within the required range to induce electronic transitions between these molecular states, which have been determined by inelastic neutron scattering experiments. In these experiments neutrons can be considered an spectroscopic probe that induce electronic transitions by transferring energy to the molecular electrons at well defined energy values. The energy absorptions are clearly observed because of the smaller number of neutrons arriving to the detector as shown in the ripples of **Fig. 3**.

Another important information that only neutrons can provide is the accurate knowledge of the density distribution of magnetic moments in this molecule. For it, polarised neutron diffraction experiments have been used in a manner similar to the one explained in the first highlight.

The slowing down of the magnetisation reversal and its eventual blocking is a process that occurs at the molecular level. In principle, neighbour molecules do not interfere this process independently that they all undergo it at the same time. **An open question that has recently been addressed with the help of neutron tools is whether a crystal lattice of these single molecule magnets can interact with each other interact with each other and undergo magnetic ordering.** The experiments, which first required to inhibit the blocking of the magnetisation motion, evidenced the formation of a *supermagnet*, or more precisely a *superferromagnet* where all the large molecular magnetic moments align spontaneously parallel to each other. They also evidenced the limitations of current neutron sources as it will be explained in the next section.

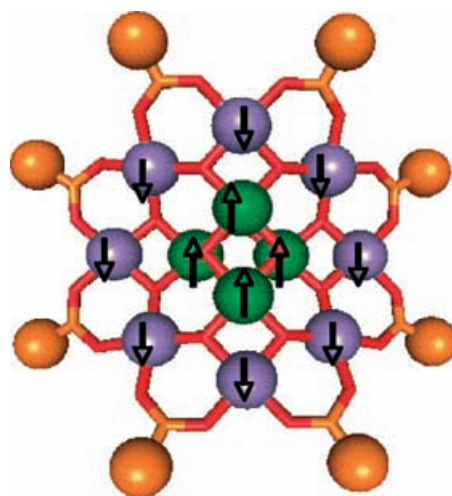


Fig. 2. Simplified view of the molecule $[\text{Mn}_{12}\text{O}_{12}(\text{Acetate})_{16}(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$ where most of the non-magnetic atoms have been masked for simplicity. Mn^{3+} ($S=2$) atoms are represented by purple beads while Mn^{4+} ($S=3/2$) are represented by green beads.

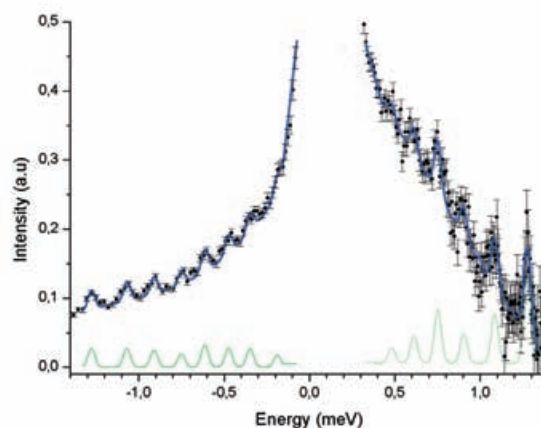


Fig. 3. Inelastic neutron scattering results showing the counting of neutrons in the energy range of magnetic transitions between molecular orbital energy states in the Mn_{12} molecule.

New opportunities to be addressed with the ESS

Major current limitations in neutron sources are all related to insufficient time average neutron flux at the sample. Neutron scattering in current sources is at the threshold of the necessary sensitivity for many experiments in molecular magnetism. This is so because of the difficulties for growing large single crystals in most molecular materials. A third generation neutron source like the ESS, which will also include instrument innovations beyond current state of the art, will offer 100 to 1000 times more sensitivity than any other neutron facility. This will open new opportunities in the research of molecular magnets, such as:

- A characteristic property of many molecular magnets is they can be multifunctional and readily processed. This has enabled the discovery of multilayered materials formed by layers of different functionality, e.g., magnetic, conducting, etc., and prepared following a *bottom up* approach. Since layers are molecular and they are developed at the molecular level they can be
- exceedingly thin. These *molecular superlattices* have shown very large magneto-resistance and are at the dawn of molecular spintronics. Spintronics is an emerging technology which exploits the intrinsic spin of electrons and its associated magnetic moment, in addition to its fundamental electronic charge, in solid-state devices. Hard drives and read heads in modern computers are based on this technology. Molecular spintronics can further improve storage density and reading efficiencies. A most necessary tool to investigate such *molecular superlattices* and measure their spin wave spectra is neutron scattering. The ESS will offer the capability of measuring the spin wave spectra in such molecular systems.
- Molecular nanomagnets are an important area in molecular magnetism. They can either be single molecule magnets, as explained above, or they can consist in more conventional inorganic nanomagnets prepared and grown from its components in a controlled manner. This is like using molecules as handy tools to develop particles and their

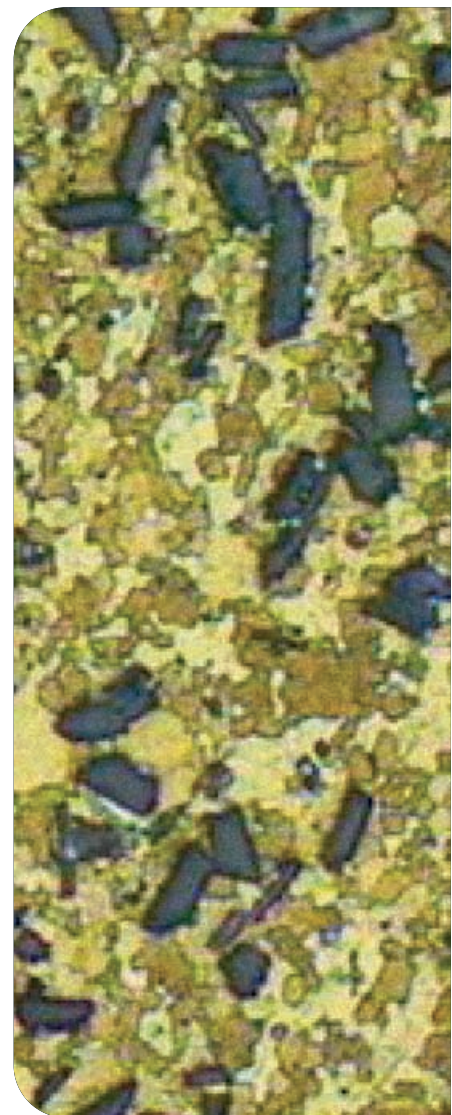
molecular environment. An important application of this technique is the growing on magnetic nanoparticles in polymeric matrices to lead to ferrofluids. Proper tailoring of polymers and chemical conditions can produce biocompatible ferrofluids formed by encapsulated magnetic particles with the necessary anchoring elements to incorporate biomolecules, drugs, antibodies or other therapeutic elements. A mayor barrier between successful results at the laboratory scale and their practical use is the scaling up in the production of these complex materials. **This include accurate understanding of the kinetic processes in which particles are grown. Small angle neutron scattering can be an unique technique to follow such processes provided it has the adequate sensibility to tune experimental times to reaction times.** This is not possible with current neutron sources but it will be possible with the proposed time average neutron flux in the ESS.

To summarise, the ESS will lead to new important results as

- it will provide access to new problems, new materials and new questions
- it will provide instrumental sensitivities and data quality beyond current state of the art allowing a more accurate understanding and modelling of phenomena and processes
- it will provide new experimental setups that will open the access to new research possibilities.

Metal Matrix Composites, Residual Stress and Neutrons

G. González Doncel



Metal matrix composites, MMCs, constitute a prominent class of metallic materials. The term MMCs often refers to composites with discontinuous reinforcement, to distinguish them from the composites with long or continuous fibers. These MMCs are formed in essence by a metallic matrix (generally a commercial aluminum alloy, but other alloys are also possible) in which micrometric ceramic particles of Al_2O_3 , SiC or other ceramic or inter-metallic material, are homogeneously embedded, (Fig. 1). The addition of a hard and resistant phase to a soft and tough metal was found to be the appropriate method for increasing significantly the stiffness (elastic modulus) of metals, which is not possible by any other microstructural modification. Furthermore, it was soon found that other important properties such as their mechanical resistance (yield

stress), wear behavior, thermal stability, and their behavior at high temperature (creep) were also improved. From a practical point of view, these composites are very attractive and promising: due to the discontinuous nature of the reinforcement, the current and widely-used industrial metallurgical procedures used for the processing /transformation of metals (such as casting, powder metallurgy, forming operations, rolling, extrusion, machining, welding, etc.), can, if employed appropriately, also be also used on these materials. This means that the ultimate implantation of MMCs in the industrial sectors does not require, in principle, substantial reconversion of present day infrastructures for metals' transformation.

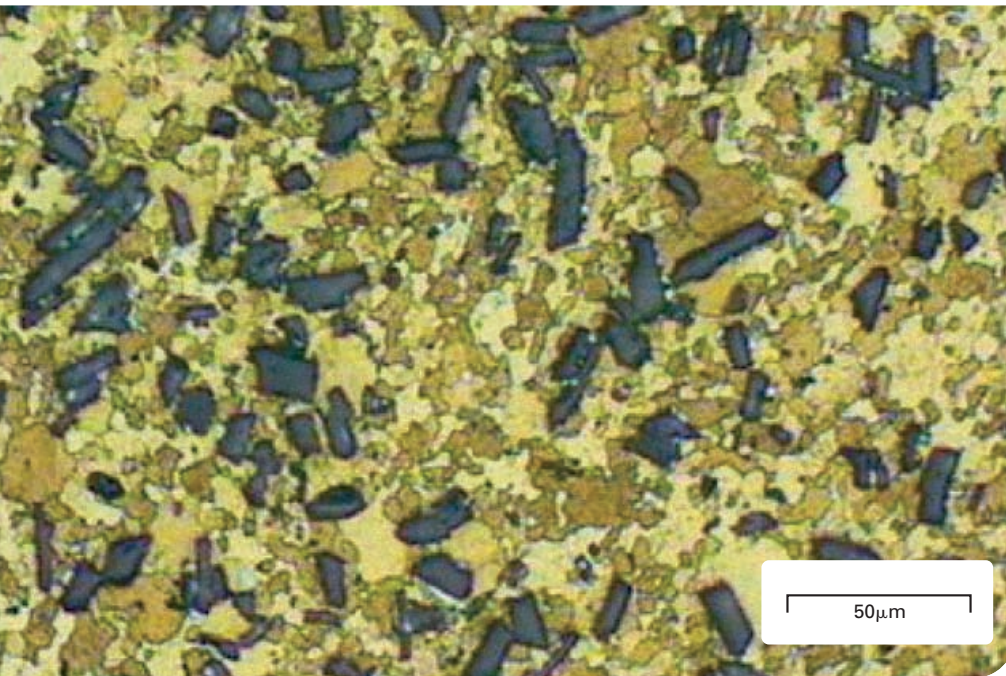


Fig. 1. Typical microstructure of a metal matrix composite. In this case, the material is a 2014Al alloy reinforced by 15vol% of Al_2O_3 particles (dark regions). The grain structure in the aluminum matrix alloy is also visible. This material was fabricated by ingot metallurgy.

This advantage, the opportunity to fabricate MMCs at competitive costs, their attractive mechanical properties, and the little increase in weight that the ceramic addition causes (better properties for a similar weight), make these composites very attractive structural materials in the transportation (ground, aerospace, and naval) sectors. In fact, several automotive companies are already using them for automobile components (diesel pistons, rear wheel hubs, drive shafts, brake rotors, etc.)

A massive use of these MMCs would bring a substantial weight reduction in vehicles and, hence, lower fuel consumption. The immediate social impact of this benefit would be a significant decrease in green-house effect gas emissions, resulting in a direct, and very desirable, reduction in current environmental degradation. It should be borne in mind that the transport sector is responsible for about 30% of the total

green-house effect gas emissions produced in the world's industry.

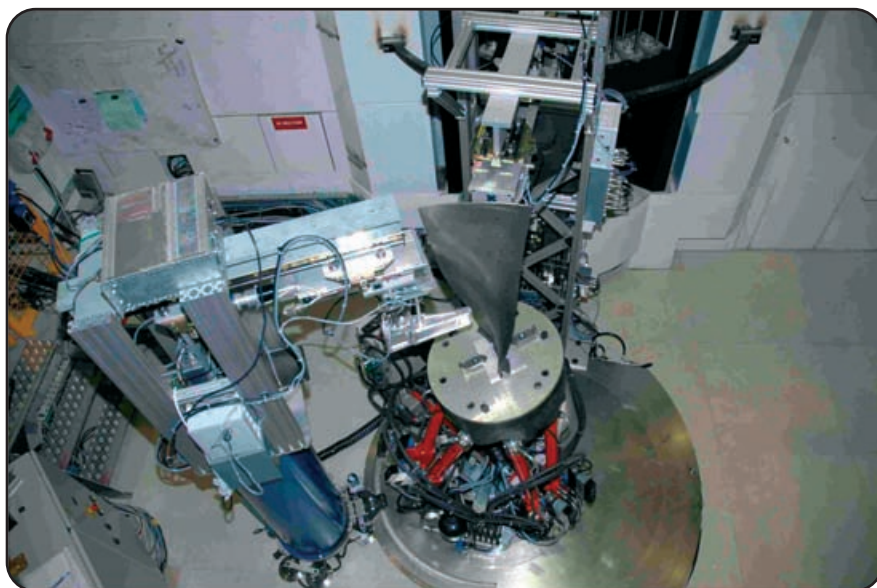
However, despite this attractive panorama, these materials have not yet been fully exploited from a technological point of view: Their use is still restricted to very specific applications. This is surprising considering the potential environmental benefits. Several reasons are usually put forward to explain this delay. Probably, the most important among them is the difficulty in applying the above mentioned metallurgical procedures, in particular secondary processes and finishing operations, on an industrial scale: Defects or flaws in the final components commonly appear.

Consequently, many products manufactured from these MMCs are still too expensive to be competitive in the market.

To solve these problems on a scientific level it is important to consider the new factors in the microstructure of these materials. A very important one is the generation of residual stress. During material processing, the presence of the hard, un-deformable ceramic particles obstruct the *natural* plastic flow of the metallic matrix: the aluminum phase must flow around them. As a result, residual stress is developed at the metal-ceramic interface. Residual stress also appears during the heating-cooling operations of these processes as a consequence of the different coefficient of thermal expansion, CTE, between the matrix and reinforcement (typically, a factor of six). This stress may be partial or totally relaxed by later treatments, but its presence is important not only for MMC processing, but also for the performance of the final component. Great efforts are now being directed at considering the magnitude and distribution of this stress in the performance of the components. For this purpose, finite element models and other mathematical and numerical methods, which also take into account materials properties, components dimensions, etc., are being employed in many laboratories. The only way to validate these models and, most importantly, to know the influence of the residual stress on material's properties is to obtain direct values for the magnitude and distribution of this stress.

A very outstanding method for determining the residual stress in structural materials and engineering components, and in particular in MMCs, is provided by neutrons.

Neutron diffraction, like laboratory x-ray diffraction, makes it possible to measure, with high resolution, the lattice spacing of crystalline materials



is used in the solid state, deleterious reactions linked to the metal-ceramic interface are avoided since the metallic phase never melts. Furthermore, the looseness of the homogeneity of the reinforcing particles is avoided and the properties in the welded regions can be similar to those of the base material. Furthermore, FSW is an energy efficient, environmental friendly and clean technique. For these reasons, FSW is a promising alternative procedure to conventional methods which involve melting in order to join parts manufactured from MMCs. During welding, a severe metallurgical transformation occurs to create the joint (severe plastic deformation). This transformation is absent in the surrounding material. As a consequence, the very inhomogeneous thermomechanical treatment that the whole component or structure undergoes is the origin of residual stress, whose influence may be crucial for the performance components or structures or during life service of an element. Knowledge of this stress is, therefore, needed to predict its behavior. Neutron diffraction is, again, the most appropriate method to *map* the complete residual stress state resulting from the welding process. The stress inside the nugget as well as around it can be completed by appropriate scanning these regions with the neutron beam.

Neutron beams from conventional stationary sources, such as nuclear reactors, have been the tools to conduct most of the work carried out in determining these stresses in MMCs, and other structural materials, up till now. At present, however, these achievements have resulted in substantial time consuming operations and long experiments, since the conventional neutron fluxes, even at the most powerful sources such as the

with the help of position sensitive detectors, PSDs. Diffracted peaks from known crystallographic planes shift from the un-stressed position upon loading (the crystalline lattice expands or contracts) and the magnitude of peak displacement is directly related to the stress which the lattice undergoes by means of equations of the elasticity theory. In other words, the crystalline structure is directly employed as a *gauge* in a similar way as an extensometer is used in mechanical testing. The advantage of neutrons over laboratory x-rays is that they penetrate matter to a great depth and can be used to calculate, in a non destructive manner, the magnitude of this stress at different parts inside materials. With an appropriate experimental set-up, stress gradients or distribution inside component can be “mapped”, and a complete description of the 3-dimensional residual stress state obtained. Because of the non-destructive characteristic of neutron diffraction, it can also be used, for example, to track the residual stress evolution in components as a function of specific heat treatments or life

service. Residual stress relaxation, usually a desirable state for optimal material’s performance, can be achieved after appropriate heat or thermo-mechanical treatments, having been calculated previously with the help of neutron diffraction. Hence, neutrons are a remarkably useful means for preventing failure in structures and constitute an essential tool for the safety of people in their daily lives.

With neutrons, a detailed description of the residual stress in each of the constituents of the composite can be also conducted separately. This permits the re-checking of the stress distribution with appropriate equations indicating specific equilibrium conditions.

An important metallurgical procedure, of great interest for MMCs, is the welding in the manufacture of final components or structures. Welding is, in fact, one relevant metallurgical process which has evolved tremendously in the last few decades. A promising, new method which is very appropriate for joining aluminum alloys and MMCs, is the so-called friction stir welding, FSW. With this method, which



reactor of the Institute Laue-Langevin, ILL, are not high enough to conduct rapid experiments. Matter is virtually transparent to neutrons and the diffraction process, unlike that with x-rays or electrons, is not a highly probable event. The detection of a sufficiently high signal of diffracted neutrons is thus a matter of data collection time.

Furthermore, the methodology to determine a complete residual stress map requires the measurement at many positions in the sample and rotations to obtain the full stress tensor. Finally, one diffracted peak, previously selected by an appropriate monochromator and set-up of the instrument, is typically used and the information "hidden" in other peaks lost. The possibility to pulse the source to detect and analyze various peaks by using the so called time of flight, TOF, spectrometers also exists, but the beam efficiency in this case is seriously affected. For these reasons,

the achievements in many cases are limited by the long experimental period.

The present possibility of investigating residual stress in MMCs with the new generation of spallation sources of neutrons opens new perspectives in the development and future applications of these materials. With these tools, very intense neutron fluxes in the form of very short but rapid pulses can be used to investigate inside materials and inside MMCs in order to understand the role of this stress on the microstructure and on the overall material and component performance. A much better understanding of the influence of this stress, how to control it, and even use it to the benefit of a given application, can be envisaged by the design of new experiments.

Besides detailed analysis of the residual stress state, distribution and evolution with appropriate treatments, neutron

diffraction also makes it possible to map the bulk texture of the different phases of composites. The texture of crystalline materials refers to the tendency of material grains or crystallites to be oriented in specific sample directions.

Texture determination is important since it also influences the macroscopic response of materials: the stronger the texture, the more anisotropic properties will result (properties depend on sample direction). In the case of MMCs, the possibility to record the texture of the reinforcing particles should be also possible. In many cases the reinforcing particles are not equiaxed but may be elongated (whiskers) or have a high aspect ratio.

In these cases, the possibility that the reinforcement is aligned with a given sample direction must be also considered. Texture determination requires measurement of the intensity of several diffracted peaks at different inclinations of the sample with respect to the neutron beam direction. So, texture determination in instruments located at stationary sources also results in long, time consuming operations. With spallation sources, however, these times can be significantly decreased due to their much higher neutron fluxes and to the possibility to acquire the signal of several peaks in one experiment. A new window of *in situ* experiments can, thus, be envisaged with the accessibility to high flux neutron sources such as the European Spallation Source, ESS.



FURTHER READING

- 1.- T.W. Clyne, P.J. Withers, An introduction to Metal Matrix Composites, Cambridge Univ. Press, Cambridge, MA, 1993.
- 2.- M.T. Hutchings, P.J. Withers, T.M. Holden, T. Lorentzen, Introduction to the characterization of residual stress by neutron diffraction. Taylor&Francis, London, 2005.
- 3.- M.E. Fitzpatrick, A.Lodini, eds. Analysis of residual stress by diffraction using neutron and synchrotron radiation. Taylor&Francis, London, 2003.

Neutron Reflectometry and Functionalized Surfaces and Interfaces

V. Lauter

Thin films are thin material layers ranging from fractions of a nanometer to several micrometers in thickness. *Electronic semiconductor devices* and *optical coatings* are examples of applications benefiting from thin film construction. *Ferromagnetic thin films* are used as *computer memory*. Thin films are applied to pharmaceuticals via thin *film drug delivery*. Thin films are used to produce thin-film batteries.

Most features of these thin film activities are represented by a relatively new research area, called surface *engineering*. Surface engineering has been one of the most expanding scientific areas during last 10 years and includes the design and processing of surface layers and their *characterization*. Novel experimental tools have enabled discoveries of a variety of new phenomena and enormous progress regarding fundamental understanding of physics and chemistry of thin films, their microstructural modifications and properties. Further effective development of thin film systems can be only realized if the fundamental process steps are well understood.

There is a rapid increase in the significance of *basic research* due to the need of a fundamental understanding of new properties of new materials. **Amongst the large body of complementary and competing techniques, neutron reflectometry plays the unique role in the analysis of new properties of thin film systems and their detailed characterization due to a number of advantages.** They can be summarized as follows:

- contrast variation between different elements or isotopes due to different cross section of different atoms and the interaction with nuclei rather than with diffuse electron cloud seen by e.g. X-rays,
- very high penetration and access to buried interfaces due to a very low absorption cross section,
- direct access to the layer magnetization distribution via the magnetic dipole interaction of the neutron spin with atomic magnetic moments,
- non-destructive even for delicate biological materials.

Since early 80-s conventional neutron specular reflectometry has been developed into a routinely used experimental technique for the investigation of thin films and multilayers. **Nowadays reflectometers are used for the investigation of magnetic systems, organic materials, polymers and biological films.** At present neutron specular reflectometry is used to investigate the structure of films or multilayers *perpendicular* to their surfaces with fields of application ranging from magnetic multilayers to biological films. Specular reflection delivers information about the depth profile of the mean scattering length density (SLD) averaged over the whole sample surface.

For example, neutron reflectometry was successfully applied to obtain a detailed structure of molecularly thin polyelectrolyte multilayer films. In this experiment the internal structure of self-assembled polyelectrolyte multilayer films was resolved to a high resolution. It determined that the surface of such films consists of stratified structures in which polycations and polyanions of individual layers interdigitate one another intimately.

Functional surfaces are surfaces of substrates that are modified or enhanced to provide a new or improved function to the substrate or composite. Coatings generally serve in a value-add situation, imparting useful characteristics to a substrate that is already performing its intended job. Examples of functional surfaces include hydrophobic or hydrophilic surfaces (for window glass, mirrors, plastics and many other substrates), anti-reflective surfaces (for applications like clear plastic wrapping materials), anti-microbial surfaces (used in, for example, food or medical packaging purposes), interfaces (to improve adhesion or interaction with

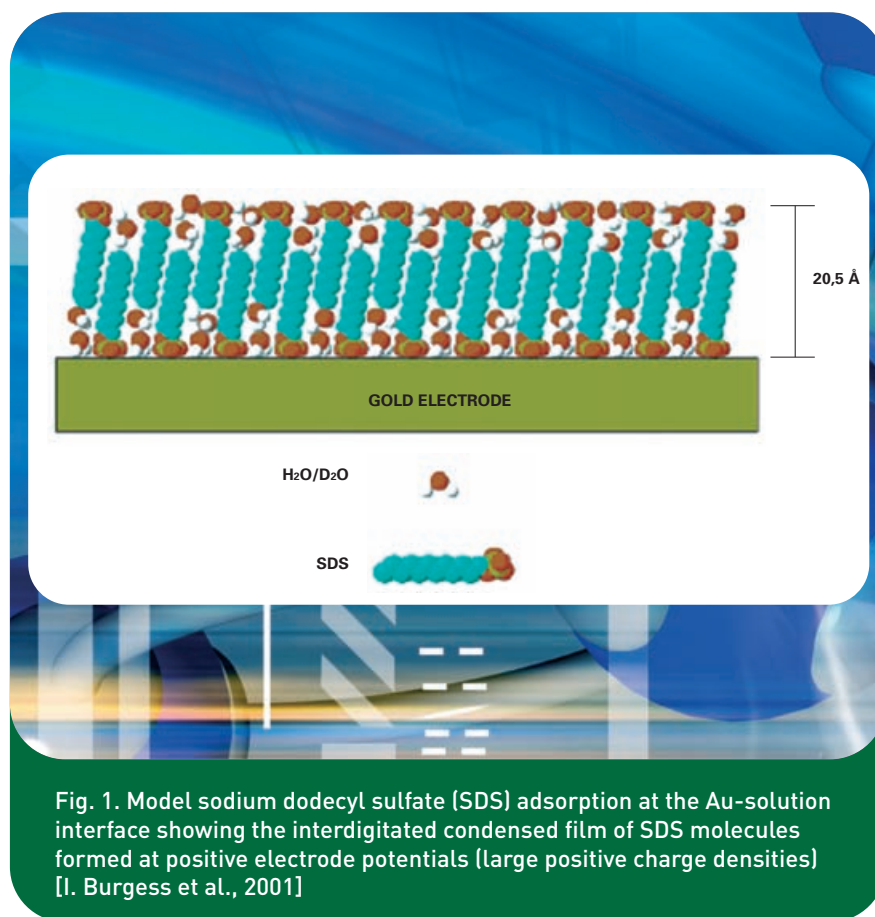


Fig. 1. Model sodium dodecyl sulfate (SDS) adsorption at the Au-solution interface showing the interdigitated condensed film of SDS molecules formed at positive electrode potentials [large positive charge densities] [I. Burgess et al., 2001]

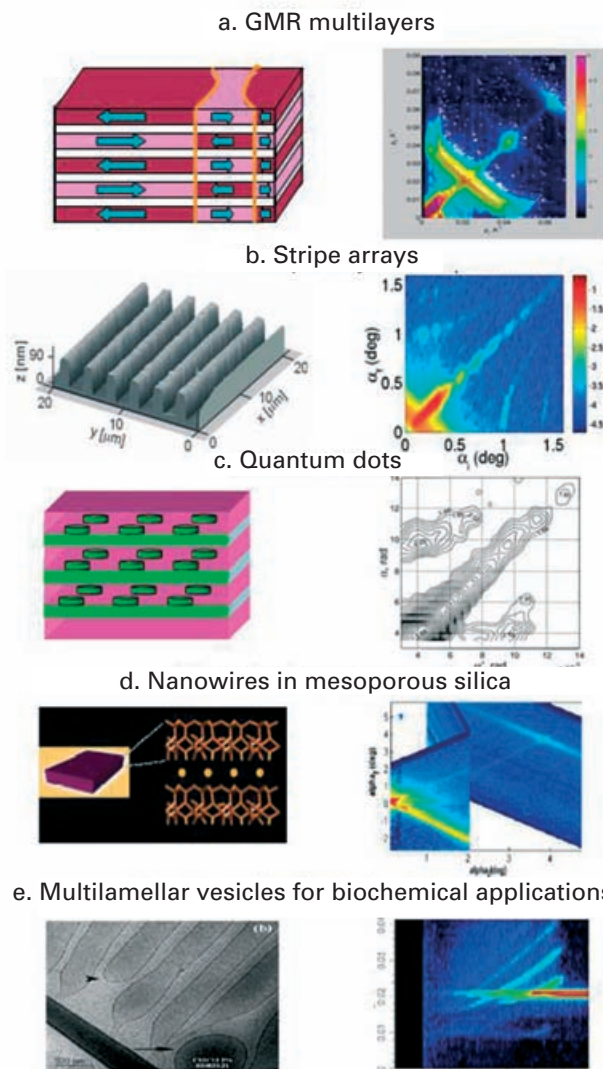
adjacent materials), and barriers (for protecting a substrate or making it more resistant to gas permeation). Adsorption and phase transitions in films of surfactants adsorbed at the surface-solution interface is another big area for neutron reflection experiments. A prominent example of a successful application of the neutron reflectometry is a characterization of sodium dodecyl sulfate (SDS) adsorption and aggregation at the gold-water interface. The results of this work offer a complete description of the structure and composition of the SDS films at the gold electrode surface (Fig. 1).

However, in reality *pure* specular reflection does not exist, because real surfaces or interfaces are not ideal and cannot be atomically flat. Therefore, specular reflection is *always*

accompanied by off-specular scattering.

The full range of off-specular scattered intensity became accessible mainly due to the use of multidetectors. Off-specular scattering probes the *lateral structure* (lateral form factor, structure factor or the roughness) at surfaces and interfaces in films or multilayers. Thus, the most exhaustive and detailed information on the 3-dimensional structure (transverse and lateral) of thin films and multilayers can be gained using a combination of grazing incidence neutron or x-ray scattering techniques, comprising reflectometry and off-specular scattering. Some examples of thin films with complicated surfaces and interfaces measured with neutron reflectometry with off-specular scattering are shown in Fig. 2.

Fig. 2



in multidomain ensemble. c) Lattice of Fe dots; scattered intensity is determined by the shape, size and distribution of dots and their magnetization. d) Nanocomposite film of metallic nanowires in mesoporous silica matrix; information about the size of the nanowires, monodispersity of their diameter and distribution and orientation within the matrix is encoded in the 2-D intensity map. e) Spherulites or multilamellar vesicles spontaneously formed in cationic surfactant with low concentration. Complex behavior, phase transition, size of multilamellar vesicles and the details of the transverse and lateral structure of the film can be extracted from the measured reflected and off-specular scattered neutron intensity.

A benchmark application on off-specular scattering to a self-assembled copolymer multilayers will be given below.

In view of the current interest in fundamental problems of polymer surface and interface formation, as well as due to technological importance, the structures of diblock polymer-multilayers were intensively studied by employing a number of different experimental techniques such as optical and atomic force microscopy, transmission electron microscopy, X-rays and neutron reflectometry. However, none of them gives detailed quantitative information simultaneously on both outer-layer lateral arrangement and the lateral structure of the inner interfaces. This information can be obtained from the experiments on off-specular neutron scattering, inasmuch as the different contributions to the measured pattern are discerned and modeled.

Symmetric diblock copolymers consisting of two chemically different polymer chains linked end to end are micro-phase separated into domains due to the immiscibility of the two polymers. The mixture of this diblock copolymer with a solvent is spin coated onto a flat substrate. During the following slow annealing to above the glass transition

Fig. 2. Panels on the left hand show nanostructures in real space, right hand panels represent the same nanostructures as seen by neutrons in experiments under grazing incidence. a) Fe/Cr multilayer (ML), consisting of magnetic layers (red and rose) with strong in-plane anisotropy and with lateral domains of alternating direction of

magnetization (marked with blue arrows) across the film due to exchange coupling via non-magnetic spacer layers (white); 2-dimensional map of intensity reflected and scattered by the Fe/Cr ML. b) Periodic magnetic stripe array with the easy axis along the stripes; 2-D intensity map is determined by the periodic lateral structure, ripple domains and correlations

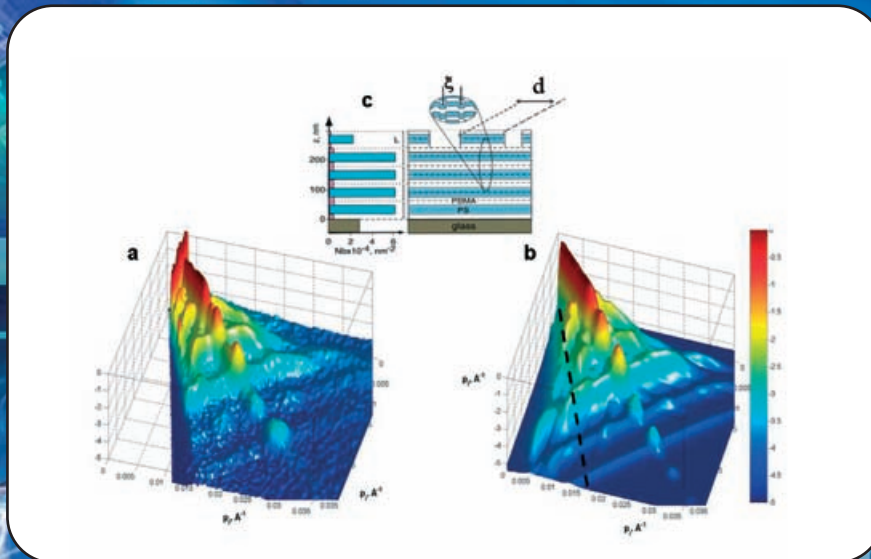


Fig. 2. Experimentally measured (a) and theoretically modeled (b) three-dimensional intensity maps of specular reflection and off-specular scattering from the annealed sample of P(d-S-b-BMA) multilayer film. (c) Neutron scattering length density profile of the transverse structure of the ML as function of the distance from the substrate extracted from the model fit to the data; lateral structure of the ML shows the lateral interfacial roughness fluctuations with the mean lateral distance ξ , as well as the surface island structure with the mean lateral dimension d .

temperature the micro-phase separation leads to a lamellar ordering parallel to the substrate.

An uncompleted top layer and rough interfaces are characteristic to most symmetric diblock-copolymer polymer films after annealing. The surface consisting of islands, holes or *labyrinth*-type structures, together with interfacial roughness buried inside the multilayer film, create off-specular scattering. Using a model based on the dynamical scattering theory for the analysis of the 2-dimensional map of the scattered intensity, we identified and modeled the different sources of off-specular

scattering and obtained rather complete information on the surface topology and the morphology of the interface roughness.

Another example of the application of neutron reflectometry with off-specular scattering to a multi-compositional material with a spatially defined order of different components is the determination of the distribution of nanoparticles inside the copolymer matrix. The nanocomposite was designed using a template matrix formed with symmetric diblock copolymers. These copolymers spontaneously self-assemble during annealing into a regular lamellar

structure. By coating the nanoparticles with one or another type of the polymer chains one provides a control on the nanoparticle distribution within one or another part of lamellar structure. Nanoparticles have a selective affinity to one of the blocks and self-assemble within this block during annealing. This leads to a spatially distributed ordered arrangement of the nanoparticles within the copolymer matrix. The application of neutron specular reflection with off-specular scattering accompanied by a two-dimensional data analysis allowed for a detailed description of the nanoparticles distribution in the multilayer (**Fig. 3**).

For the studies described above it is important to measure with a good statistics not only the specular reflection but also the off-specular scattering which has a one order of magnitude lower intensity. Reflectometry experiments will profit from orders of magnitude of increase in brilliance on a Spallation source.

For many problems of kinetics process *in-situ* studies are necessary. Spallation source gives an advantage to conduct such kind of studies due to a time-of-flight principle of reflectometry experiment. More developments are expected in the analysis of engineering products such as polymer electrolyte fuel cells. The potential of neutron reflectometry to quantify the cross-section profiles will help the improvement of adhesion, the control of diffusion. Finally there is promise that industrial applications of neutrons will be triggered by the implementation of new neutron sources like ESS.

The important role of reflectometers in the instrument park of a spallation source is highlighted in the report "Tailored instrumentation for long-pulse neutron spallation sources". However, only specular reflection is considered there; the application of off-specular scattering beyond the specular reflection adds the enormous progress to characterize the structure along the surface or interface as discussed above. **The high intensity combined with the adequate resolution in energy and reciprocal space of the future ESS is absolutely**

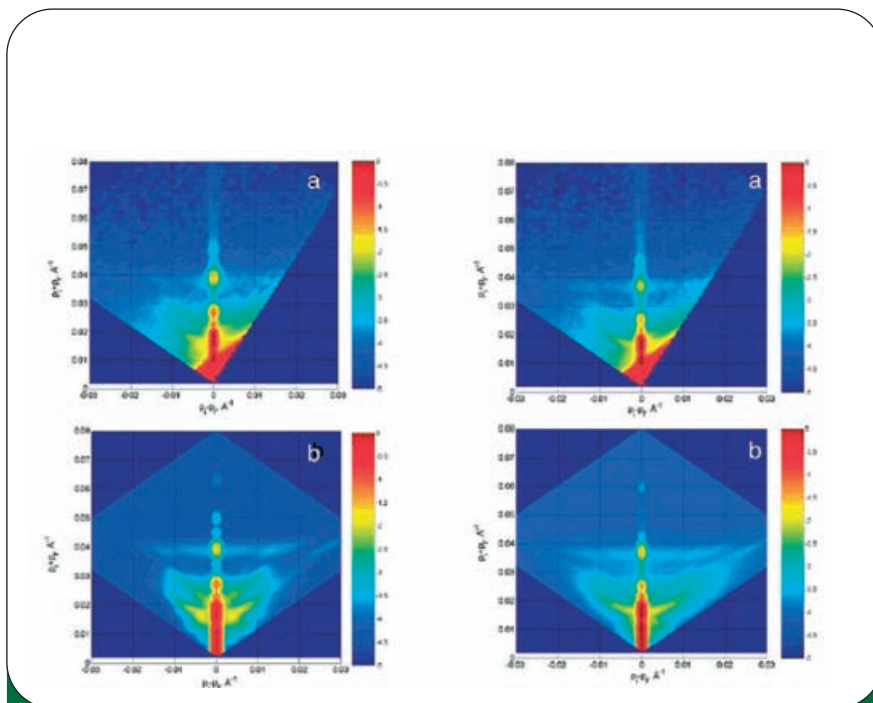


Fig. 3. Experimentally measured (a and a') and theoretically modeled (b and b') intensity maps of specular reflection and off-specular scattering from the block-copolymer multilayer films without (left-side panels) and with incorporated nanoparticles (right-side panels).

necessary to reveal the detailed film- or multilayer- structure given over a large area in reciprocal space. Grazing incidence small angle scattering (GISANS) should be added to reflectometry to extend the probed length scales towards nm-range and to three-dimensional reflectometry. Three-dimensional reflectometry means that not only the

structure perpendicular to the film and along one lateral direction is probed, but also the structure along the second lateral direction is investigated, including the dependence on the depth profile of the film. Three-dimensional reflectometry in high resolution will be a challenge even for the ESS, but the results will be unique.



FURTHER READING

J. Ankner, G. Felcher, JMMM 200 (1999) 741

M. Loesche et al. Macromolecules, 1998, 31 (25), pp 8893-8906

I. Burgess et al., Langmuir 2001, 17, 3355-3367

V. V. Lauter-Pasyuk, et al. Appl. Phys. A 74 [Suppl.], S528 (2002)

V. Lauter-Pasyuk, Journal de Physique, Collection SFN 7 (2007) 221-240

V. Lauter-Pasyuk et al., Langmuir 2003, 19, 7783-7788

H.Schober et.al. Nucl.Instr. and Meth. A 589 (2008) 34-46

V. Lauter-Pasyuk et al., ILL Annual Report 2004.

- Particle Physics, B. Martin, and C. P Shaw, 3rd Edition, Manchester Physics Series, 2008

- New Science and Technology for the 21st Century, The ESS Project, Volume II, Ed. D. Richter, 2002.

Health and Biotechnologies

2



2.1

Understanding Molecular and Cellular Processes using Neutron Scattering Experiments

S. Magazù

2.2

Neutrons: A Gentle Probe for Gentle Materials

A. De Francesco

2.3

Neutron Scattering as a Tool in the Development of Magnetic Bionanoparticles for Therapy and Diagnosis

A. Millan



Understanding Molecular and Cellular Processes using Neutron Scattering Experiments

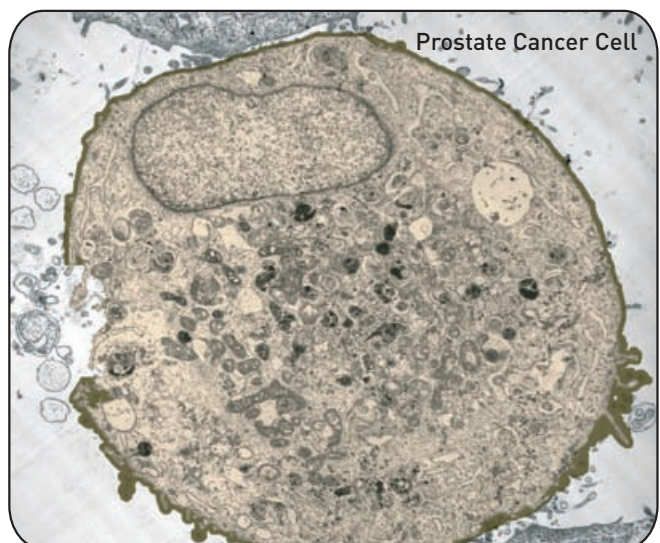
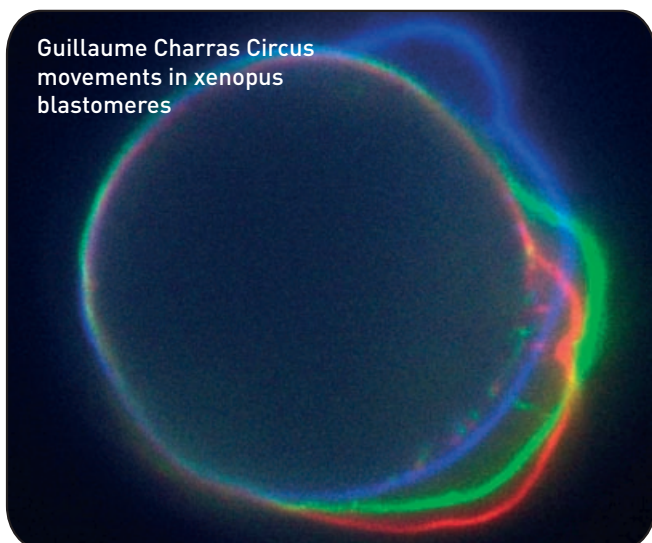
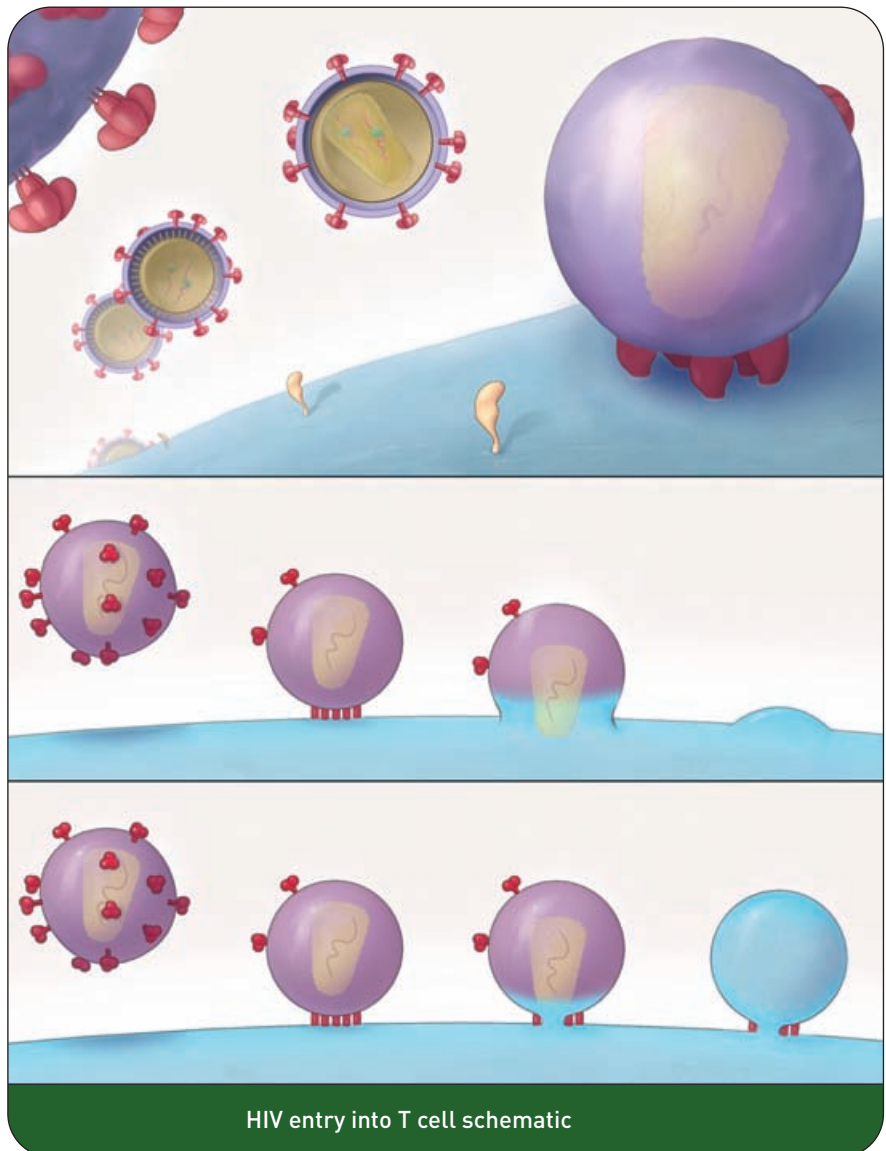
S. Magazù

Understanding molecular mechanisms underlying biological processes is one of the major goals in modern biophysics. Among the existing roadblocks in characterizing complex dynamics of biological processes, the existence of multiple kinetic paths and transient intermediate states makes these processes difficult to dissect by ensemble methods. Furthermore, although many experimental techniques can meet the necessary requirements, experimental difficulties, complexities in interpreting data and other drawbacks may limit their effectiveness, and so require the joint employment of different methodologies. Therefore, a fruitful trend to reach a fairly accurate physical picture requires the simultaneous application of complementary techniques.

With the development of neutron scattering within the last half century, neutrons have revealed themselves a powerful probe for the investigation of biological systems. In particular contrast variation in biomolecules by the strong discrimination of neutrons between hydrogen and deuterium allows distinct structure determination of hydrogen,

hydrogen bonds and water in proteins and enzymes, difficult to achieve with X-rays. Selective deuteration of proteins allows the localization of protein sub-units in protein complexes by small angle neutron scattering. Quasi elastic and inelastic neutron scattering can be employed to study various kinds of dynamics in bio-molecules ranging from collective motions in lipid membranes to the motions of water in hydrated proteins.

Thermal neutrons are adequate probes for three major features: (i) their typical wavelengths are of a few angstrom, which correspond to the typical interatomic distance, (ii) their typical energies are of the order of some meV, which correspond to the energy scale of the typical excitations in condensed matter, (iii) neutrons being particles without electrical charge, they can penetrate the sample and provide information about bulk properties, in contrast to charged particles like electrons, which mainly probe surface properties.



Achievements within the field of molecular and cellular processes related to neutrons

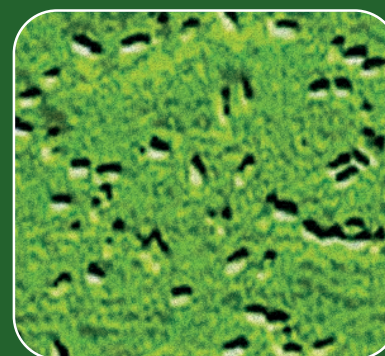
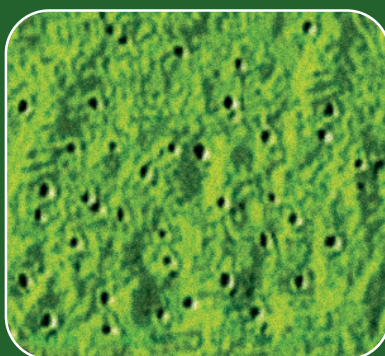
A theme of great interest nowadays in biophysics is that connected to the determination of the physical chemical mechanisms responsible for protein stability and denaturation.

From the applicative point of view this understanding is important for the development of various applications such as protein-based drugs stabilized by bioprotective host-matrices. In fact, the denaturation rate of biological agents is a determining factor for the shelf life of protein/enzyme based pharmaceuticals, and hence the protein dynamics determines in a direct way their shelf-life.

The presence of an environment made by a mixture of various components *in vivo* is connected to the function of the “biological machine”. Systematic studies on proteins in different solvents have shown how the morphology of the solute and the solvent, as much as the size of both components, are very important to understand the mechanism of protein stability. Recent experimental findings suggest that the characterization at different length and time scales of the protein-host medium system is essential not only for the understanding of the molecular mechanisms determining stability but also for the comprehension of protein and enzyme reactions at a molecular level.

Therefore **the coupling between the dynamics of the host medium with that of the protein is important in order to explain the bioprotectant function**. The topic of this contribution deals with the effects of some bioprotectant molecules on water and on protein dynamics and aims to provide a representative sampling of some experimental findings, which are nowadays object of scientific and applicative scrutiny.

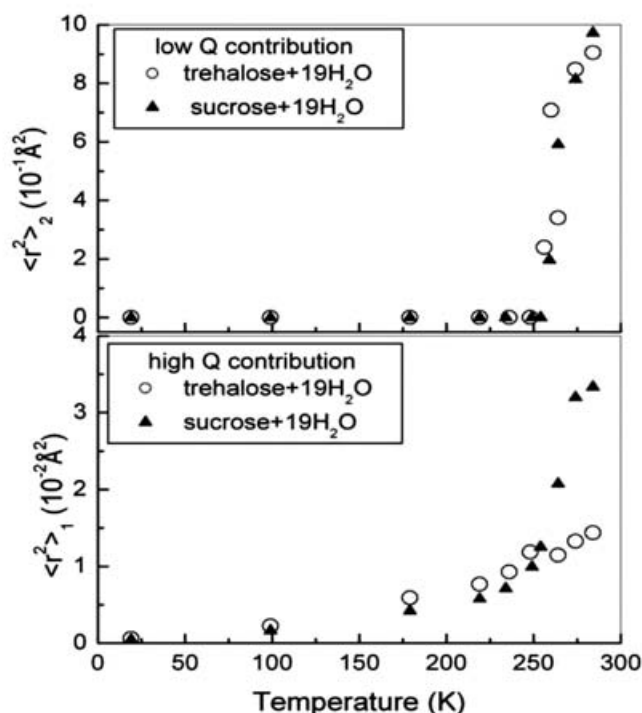
Fig. 1. Cryptobiontes (Phylum Tardigrada), plants (*Myrothamnus flabellifolia*) and bacteria (*Escherichia coli*) under stress and normal conditions



These are the homologous disaccharides trehalose and sucrose, which are cryptobiotic activating substances with different bioprotectant effectiveness, and which are directly comparable since they possess also the same number of hydroxyl groups. Such a research moves from the observation that many organisms, such as, for example, cryptobiontes (Phylum Tardigrada), plants (*Myrothamnus flabellifolia*) and bacteria (*Escherichia coli*), shown in **Fig. 1**, reveal extraordinary surviving capabilities to environmental stress conditions, such as dehydration and freezing, thanks to the synthesis of the disaccharide, which allows them to undergo in a cryptobiotic ("hidden life") state and to re-activate the vital functions when the external conditions come back favourable to the life. Although other disaccharides such as maltose and sucrose have shown similar properties, it clearly appears that trehalose is, with a great extent, the most effective.

Fig. 2 reports the mean square displacement as a function of temperature, as evaluated by the elastic intensity slope against Q^2 for trehalose and sucrose mixtures obtained by using the IN13 spectrometer at ILL (Grenoble, France). By **Fig. 2**, we observe that the high Q contribution for trehalose does not show an abrupt transition as in the case of sucrose. This indicates that the dynamical transition does not involve all the spatial scales but interests the range of lower Q values. The analysis of the mean square displacement for the three disaccharides clearly shows that the trehalose/ H_2O mixtures at various concentration values are characterized in respect to the maltose/ H_2O and sucrose/ H_2O mixtures by a lower fragility namely by a higher structural resistance to temperature changes. This correlation between fragility degree and bioprotection gives also an explanation for the better preservation provided by

Fig. 2. Mean square displacement as a function of temperature for trehalose and sucrose mixtures

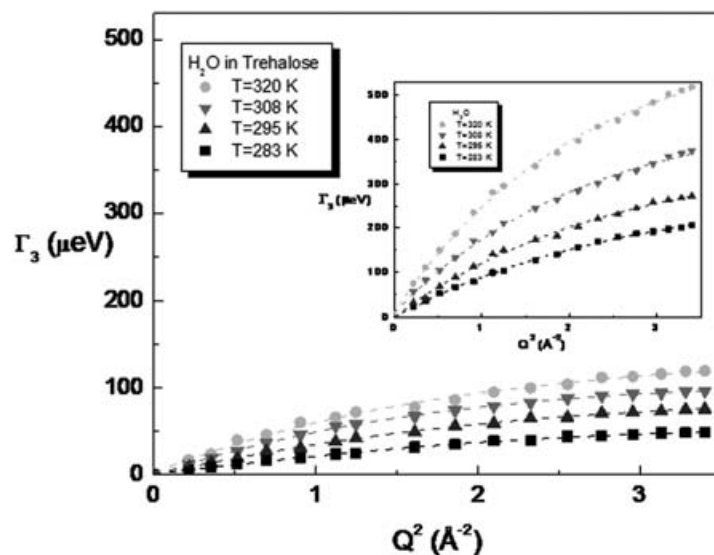


other bioprotectant systems: to exemplify, sucrose appears to be less fragile than raffinose, but, despite its lower T_g , offers a better preservation. On the other hand, the intramolecular OH stretching spectra of disaccharides in Inelastic Neutron Scattering (INS) reveals that the area of the tetrahedral contribution is smaller in the case of trehalose, so indicating that a more marked destructuring effect occurs. This result is backed up by Molecular Dynamics (MD) simulations with the behaviour of the orientational order parameter which reveals for trehalose a more marked downshift of the OH stretching mode and narrower widths

also for the bending modes so suggesting a "cryptocrystalline" character: the glassy protective shell hides a local crystalline coordination.

The higher kosmotrope character of trehalose is also reflected by dynamics. Starting from the Quasi Elastic Neutron Scattering data collected by IRIS at ISIS (Didcot, UK) and NEAT at BENSC (Berlin, Germany) spectrometers, shown in **Fig. 3**, the obtained values for the diffusion coefficients and of the residence times indicate that trehalose diffusion is constantly slower than the other disaccharides and that water in presence of trehalose suffers of a higher frozen effect.

Fig. 3 Translational linewidth as a function of Q^2 for trehalose/ H_2O mixtures. In the insert the water translational linewidth is reported as a function of Q^2



From a retrospective glance to these findings, it emerges that trehalose, besides significantly modifying the structural and dynamical properties of water, is able to encapsulate biostructures in a medium characterized by a lower fragility which justify its higher

bioprotective effectiveness.

Funnily enough, some of the cryptic secrets of trehalose lie just in the etymologic definition of its most appropriate adjective: *κρυπτος*, which contains the reference to the *hidden* life of cryptobiosis and to cover i. e. the

capability to encapsulate the biostructures to protect, creating a protecting shell characterized by *cryptocrystallinity*, i.e. the capability to give rise to a (hidden) nanoscopic crystalline structure which is responsible for the higher structural resistance [1-8].



Possibility of new ideas or experiments implemented with ESS

The promising applicability of neutron scattering to everwidening fields of biological studies is exciting. More than ever before, the neutron scattering community is interested on using the strengths and unique capabilities of different facilities and technologies to their best advantage and the large neutron fluxes produced in next-generation spallation facilities are likely to soon find expanded application in biology. Neutron scattering have been used by a wide range of scientists mainly from physical sciences for the last 30 years and more but the applications in the life sciences have been relatively

modest, involving only about 5% of the effort in neutron scattering centres. This is mainly due to some reasons: the majority of instruments have been flux-limited and some of the most interesting materials have usually been available only in very small quantities. **The construction of new neutron sources and the improvements in existing ones which make the accessible parameter ranges continuously expanding and performance restrictions less severe, are nowadays stimulating a flourishing activity of biological research using neutron scattering techniques, which**

reveals to be an important driving force in the field.

Problems at the interface between biology and physics offer unique opportunities for neutron scattering community to make quantitative contributions to biology. At present, an increasing number of physicists study, by new transdisciplinary approaches, systems of biological interest where complexity reigns. In the living world, complexity implies a degree of organizational hierarchy, defined by several length scales with an interplay between events at different levels. This interplay extends from the events that happen very slowly on a global scale right down to the most rapid events observed on a

microscopic scale. Neutron scattering will offer more and more important advantages in tackling biological complexity owing to the time-space scale to which it is sensitive, to the simplification brought about by the neutron-nucleus interaction and, above all, to the distinctive isotope character. The use of neutrons has already suggested a deep revision of some of the ideas concerning the molecular basis of a number of biologically-relevant processes. For this reason the importance of high neutron fluxes and of coordinating activities more closely than presently emerge.

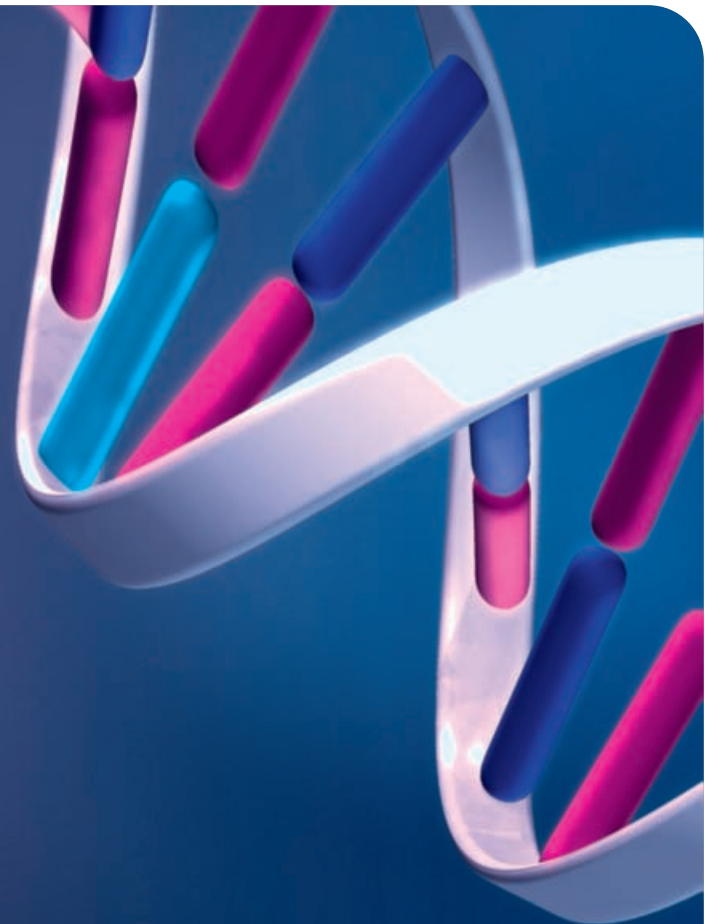
**FURTHER READING**

- B. Varga, F. Migliardo, E. Takacs, B. Vertessy, S. Magazù, C. Mondelli, *Chemical Physics*, 345, 250 (2008).
S. Magazù, F. Migliardo, M. T. F. Telling, *Food Chemistry*, 106, 1460 (2008).
D. Barreca, E. Bellocco, G. Laganà, U. Leuzzi, S. Magazù, F. Migliardo, A. Galtieri, *Food Chemistry*, 106, 1438 (2008).
D. Barreca, E. Bellocco, G. Laganà, U. Leuzzi, S. Magazù, F. Migliardo, A. Galtieri, *International Journal of Biological Macromolecules*, 43, 474 (2008).
S. Magazù, G. Maisano, F. Migliardo, A. Benedetto, *Journal of Molecular Structure*, 882, 140 (2008).
S. Magazù, G. Maisano, F. Migliardo, A. Benedetto, *Physical Review E*, 77, 061802 (2008).
S. Magazù, G. Maisano, F. Migliardo, A. Benedetto, *Journal of Physical Chemistry B*, 112, 8936 (2008).
S. Magazù, G. Maisano, F. Migliardo, G. Galli, A. Benedetto, D. Morineau, F. Affouard, M. Descamps, *Journal of Chemical Physics*, 129, 155103 (2008).

Neutrons: A Gentle Probe for Gentle Materials

A. De Francesco

Neutrons are an ideal and optimum probe to investigate biological matter. Proteins, nucleic acids, cellular membranes, cells and any biological system require gentle techniques to explore and study their properties. Despite their great power and efficiency and the enormous contribution they gave for structure determination of biological macromolecules, X-ray are indeed a quite invasive tool, and sophisticated expedients and solutions have to be found to exploit X-rays in Biological Science. On the contrary the specific properties of neutrons (i.e. low energies, neutral charge, interaction with the nuclei of matter) make these particles outstandingly respectful of these delicate systems and incredibly useful for understanding how they are built and how they move. A neutron beam is shot on a sample. Some of these neutrons interact with the nuclei living in the studied object, see what happen there inside and how the things are situated and move and then they come outside to tell us what they have seen (as long as we are able to understand and interpret their language and story).



Structure and dynamics of biological macromolecules is the key to understand how they work and, in a more general way, how they can accomplish the biological mission Nature has assigned them.

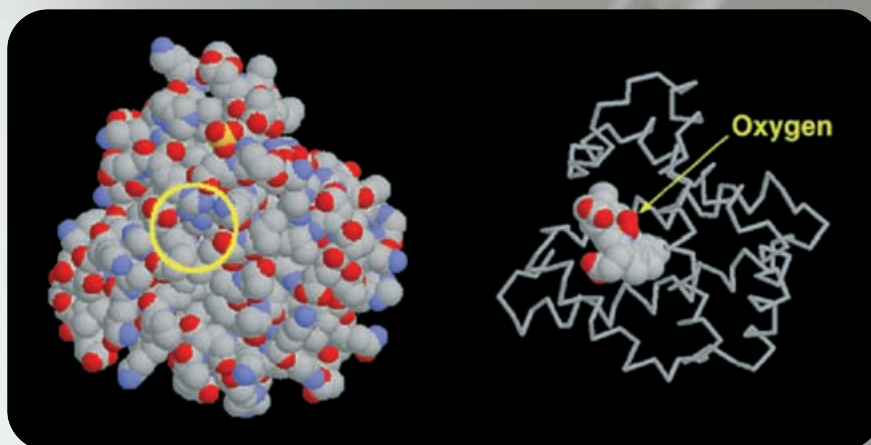


Fig.1: Myoglobin representation: the space occupied by atoms is shown. The yellow circle indicates the oxygen binding site (left side); the skeleton of Myoglobin is sketched showing only the active site where the oxygen finds its place.

Secondly, once some or, better, most of the basic principles about the physical properties of these systems are well acquainted we can even hope and try to build up our microscopic biological machineries to perform special activities we wish to implement. It is easy to imagine what consequences and impact can have a deep study on this subject and how many applications could be designed in the field of biotechnologies such as drug delivery, molecular and cellular recognition, cancer treatments, long storage of biological samples, design and production of biosensors, and many other biomedical applications.

To understand how structure and dynamics of a biological system are strictly and synergically correlated let's give an example. Proteins are polymers constituted by long chains of aminoacids. For the biological function of one specific protein it is important the precise sequence of these aminoacids and, roughly speaking, the three-dimensional structure of the protein itself. But for working properly this is not enough! The protein has to move. If we consider how the structure of a very common protein looks like, Myoglobin, we see something as in **Fig. 1**.

The Myoglobin is the protein responsible of the oxygen transport in our muscle tissue. However, looking at the structure of the protein (left side of **Fig. 1**) where the real space occupied by the atoms is indicated it is impossible even to guess where the atoms of oxygen can be bound by any site of the protein.

How do the oxygen atoms find the path to access the inside of the protein structure (since we know that the active site of the protein is not on the surface!)? Fortunately, things work otherwise and everything we see is, in fact, a dynamic object and plenty of different movements make the protein a living, breathing system. Very fast movements (billions times faster than a fleeting glimpse) allow the different parts of the macromolecule to move one with respect to the other and the necessary

space for the oxygen to penetrate inside the structure is continuously created. We can try to figure out even more clearly this scenario thinking of the two parts of an oyster shell opening and closing (much faster than that!) to allow the exchange of materials in and out the shellfish. **The physical characteristics and properties of neutrons allow for killing two birds with a stone getting simultaneously structure and dynamics of the biological sample. And most of all neutrons do this job**



for us without damaging the sample where this, besides to be very delicate, could be also very expensive.

Another magnificent property of neutrons permits extraordinary achievements in Biological Science. As above mentioned, neutrons interact with the nuclei of matter and particularly they interact in a very different way with Hydrogen and one of its isotopes, Deuterium. For the sake of simplicity, let's say that in one case the interaction is much stronger than in the other. Hydrogen is terribly abundant and uniformly distributed through all of biological matter. Exploiting as much as possible what is called the contrast matching technique, we can selectively deuterate different parts of a biological macromolecule or a complex system since from a chemical point of view we could say that Hydrogen and Deuterium behave in the same way. The result of this technique is to hush up a part of a system and emphasize the information and the signals coming out from another part of the system, making simpler the study of multi-component samples. It is like the spot light in the scene of a theatre

masterpiece where the attention is devoted first to one part of the stage and then to another.

The full comprehension of how a biological system is done and works is of invaluable importance in order to build artificial molecular devices capable to perform a huge amount of tasks and duties, especially in the medical field.

Bioengineering is the discipline devoted to the *creation* of artificial devices as, for example, bio-sensors. The bio-sensors are essentially constituted by a sensitive biological component and a physicochemical detector component. The first element produces a signal of some nature when interacting with an external agent and the second component, also called transducer, transforms this signal into another signal that can be more easily revealed and measured. The canary in the cage, as the one used by miners to warn them of possible gas leaks, can be considered as a folkloristic example of a bio-sensor. As soon as the canary *interacts* with the gas (there is a physical-chemical

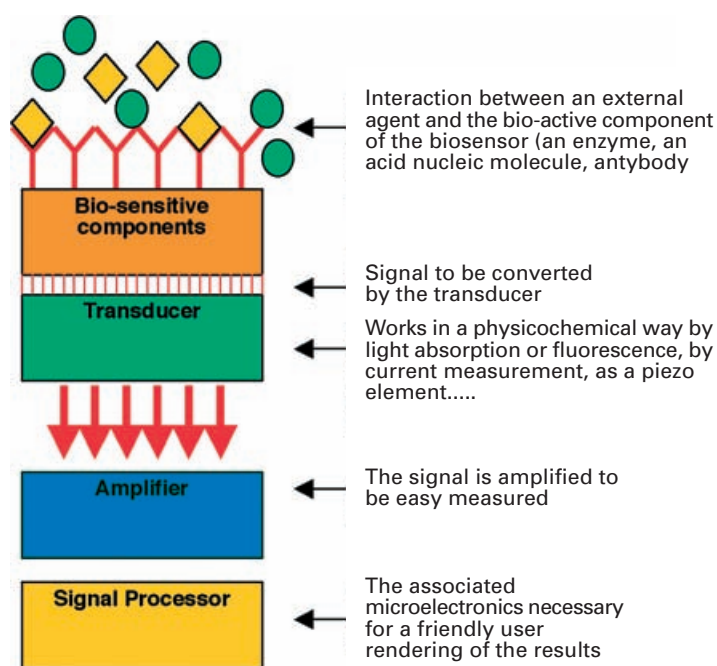


Fig. 2: Schematic representation of a biosensor

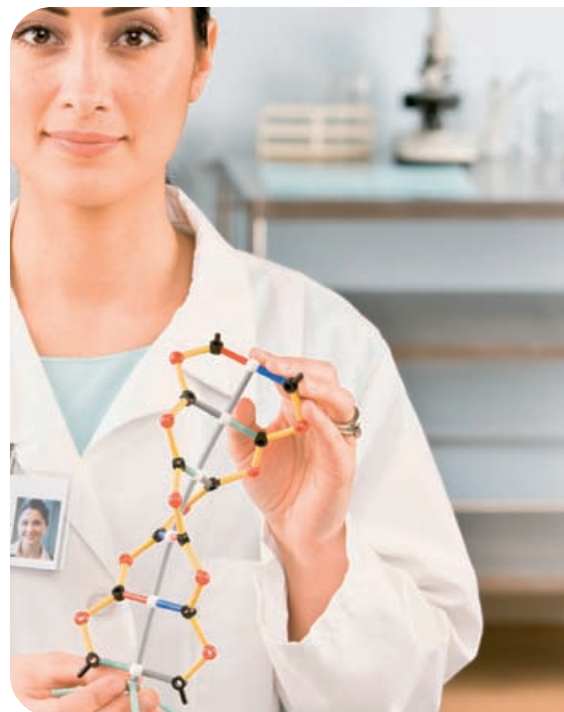
interaction between the gas and the canary's sense of smell) it *stops twittering* (this is obviously the easy signal to detect) warning the miners on time. Many bio-sensors on a molecular scale can be designed and produced to be used in medicine (glucose monitoring in diabetes patients), environmental science (detection of contaminants in water), food science (discovery of drugs and toxic compounds in food) and in many other fields. **The neutron scattering techniques can provide the necessary structural and dynamical details for a deep knowledge of the existent natural molecular systems and then promote the rational design (rather than problematic empirical searching) for new artificial molecular devices.**

That's because, once again, we can measure in a not invasive way how is the *shape* of our biological materials and which are the characteristic times involved in the dynamics and interactions of the observed system with other agents.

Most of the times, however, it is really complicated to directly study the biological systems as they are in their native state since they are constituted by an enormous amount of atoms and different chemical groups behaving differently, for example, as for their affinity with water. That is why it is generally very helpful to tackle in advance a systematic study of simpler biological model systems able to mimic some essential chemical-physical properties of native samples, whether we deal with proteins or cellular membranes. The interaction with water is indeed really important for biological function. If not sufficiently hydrated, biological macromolecules are not able to accomplish their commitments properly. On this ground, a very promising research about model systems is nowadays undertaken for example on polymer functionalized gold nano-particles (GNP) which can be produced in a flexible way and with interfacial properties more homogeneous with respect to more complicated native systems and that can be modulated in a controlled way.

These particles are constituted by a gold core of microscopic dimensions coated by tentacles of hydrophilic polymer chains. The use of neutrons on these more controlled samples provides a variety of informations about dynamics of the polymer chains, interfacial water molecules (hydration water), inter-particle dynamics and so on, providing an indirect source of information which can be essential in the understanding of more *real* systems like cellular membranes. Besides the interest on these GNP as *puppets* able to reproduce some basic properties of native biological matter, a growing interest on suitably functionalized GNP is spreading through the scientific community for some peculiar characteristics and potentialities of these nano-systems: the biocompatibility, the high surface area (large amount of drugs can be loaded on GNP), the ease of characterization and surface controlled modification (any kind of organic compounds as drugs, peptides, antibodies, can be attached to the GNP) makes these objects ideal candidates for drug delivery and cancer therapy. The idea is to render these systems selective killers of cancer cells both via chemical interaction and physical attacks. In fact, other studies in progress suggest the possibility to link GNP to cancer cells or amyloid fibrils (thought to be responsible of disease such the Alzheimer disease) and destroy them by selective and not invasive irradiation.

Fig. 3. Sketch of a functionalized PEG-Au nano



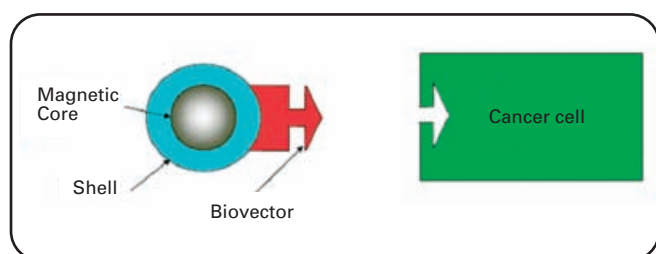
These appealing and fascinating subjects related to biological Science could receive an incredible push by the new European Spallation Source and the high performance instruments which will be designed for neutron scattering. Although neutrons are an ideal tool to investigate matter and particularly biological matter for the outlined characteristics, neutron techniques suffer of an intrinsic limitation due to source brilliance. In fact low intensity and, consequently, the need for large amounts of sample (which could be really expensive, especially in the case of deuterated samples) for maximizing the information provided by neutron scattering still represents the major limitation to the progress of research in this field. **The promise for large gain factors, up to three orders of magnitude above the present available sources, will open new horizons in the study of structure and dynamics of biomaterials.** A high flux, together with a sensible improvement in time and space resolution, will increase considerably the data acquisition rate and quality and will enhance the chance for time resolved experiments with second to milli-second resolution, that is to say, the possibility to follow the kinetics of important biological processes.

Neutron Scattering as a Tool in the Development of Magnetic Bionanoparticles for Therapy and Diagnosis

A. Millan

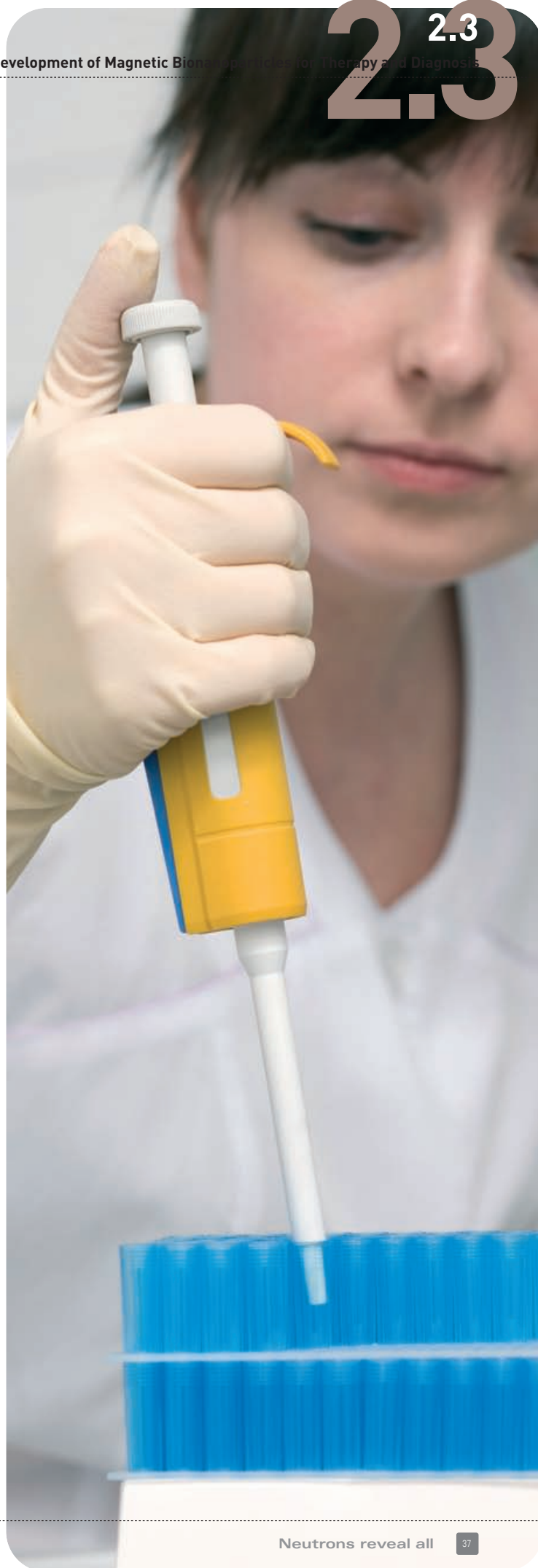
One of the most important factors in life quality is health, and one of the biggest threats for health is cancer. In spite of the increasing success in cancer treatment it is still a leading cause of death worldwide (around 13% of all deaths in 2007, according to WHO), and most of us have experienced the terrible effects of cancer treatment in some friend or relative. High incidence, high mortality, and traumatic treatments are three aspects closely associated to cancer. A key factor to reduce mortality is early diagnosis. Thus, it is important to decrease the smallest size for tumour imaging detection to a minimum, down to a single cancer cell if possible. **To avoid the trauma caused by secondary effects, treatment should be more specific and only localized in tumour cells, excluding the rest of the body. A promising tool that may play both roles, even simultaneously, is the use of magnetic nanoparticles.** Being magnetic they change the response of water hydrogen atoms in a tissue in a magnetic resonance scan, and therefore they generate a contrast in magnetic resonance imaging (MRI). That is, the area (i.e. a tumour) containing the magnetic nanoparticles (MNPs) will appear darker than the surroundings in an MRI image. The advantages of MNPs with respect to other contrast agents are high sensitivity and low toxicity. This is still under investigation but expectations are to achieve the ultimate goal: single cell detection.

Another interesting phenomenon associated to magnetic nanoparticles is that they warm-up when irradiated with radiofrequencies, which at moderate frequencies and intensities are harmless to the body. This phenomenon can be used to heat tissue (i.e. a tumour) at a distance, if it is previously loaded with MNPs. Heat kills cells above 43°C. Therefore, if we introduce MNPs in a tumour we can visualize it by MRI at an early stage of development and, at the same time, destroy it with radiofrequency radiation. The question now is how to place the particles into the tumour and only there. A smart way to get that would be to provide the particles with a linker (biovector) that can only attach to cancer cells as a key fits in its lock. We can also provide the particles with a biopolymer shell to enhance their stability in biological fluids. Then, we can inject a suspension of these particles into the blood so they will travel to the tumour and stick to it. A scheme of this system is shown below.

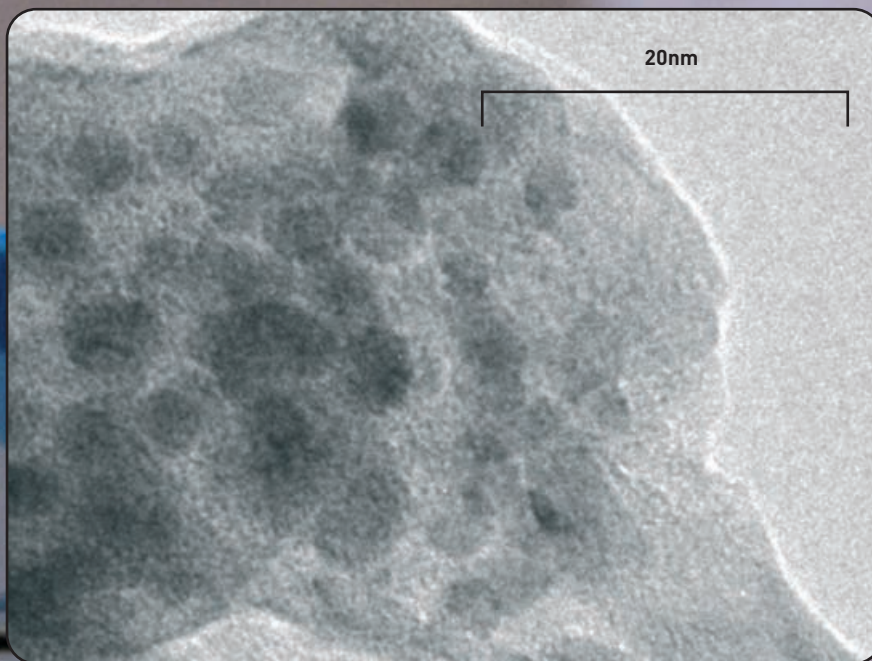


Some preparations of this kind are already commercially available and they have been used in clinical practice, mainly as contrast agents, but also in hyperthermia therapy. However, they are still in development, and far from reaching an optimal performance. In order to exploit all their potential it is necessary to obtain a fine control of their structure and to optimize their magnetic properties for a maximum performance in MRI diagnosis and hyperthermia therapy. **None of these goals can be achieved without an appropriate characterization of the size, shape, and disposition of all the bionanoparticle components (core, shell and biovector), and a determination of the particle arrangement in the biological fluid. It is at this point where neutrons can play a fundamental role.**

The first thing to consider when looking for a characterization technique for bionanoparticles is their small size. The dimensions of each part of these objects are usually in the range from 1 to 200 nm. Of course, we can observe them by electron microscopy, and below we show an example of a multicore particle in a polymer shell. However, to obtain this image we

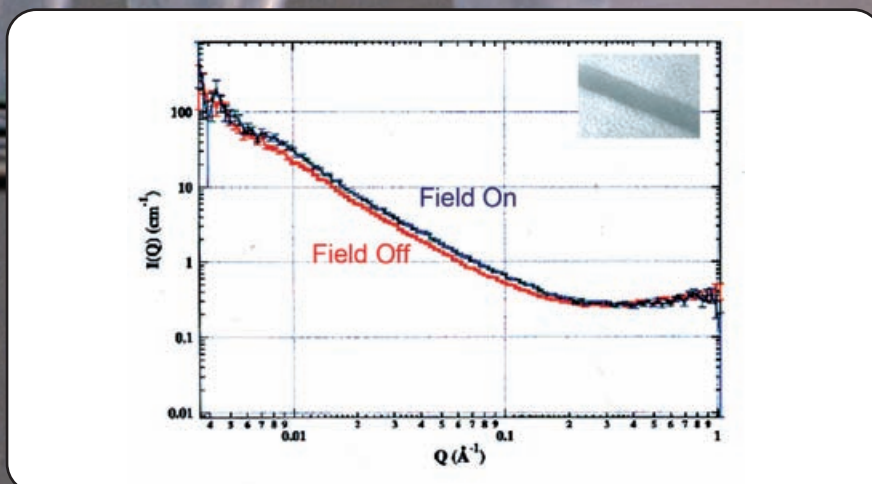


have to manipulate the sample, dry it onto a surface, and place it in vacuum. In this process, and especially concerning the organic components, we are changing the particle size and shape, and we lose any information about how the particles arrange in the fluid. If we want to avoid any manipulation of the sample, we must resort to techniques based on radiating the sample with a beam, and analysing the beam after interaction with the objects. Light, X-ray and neutron radiation can give us some information about the dimensions of objects in the range we need, and about how they arrange in the fluid. However, only neutrons can give us the whole package. Even further, it will tell us about the magnetic state of the particle magnetic core. Moreover, the size of bionanoparticle components fits very well in the observable size range in small angle neutron scattering that is 1-300 nm.



Why neutron scattering is so useful for the observation of magnetic bionanoparticles? Let's explain first a few concepts. These nanoparticles are tiny magnets that contrary to the big ones, that have their poles in a fixed position, change their sense of polarization constantly from the heat of the environment. However, we can fix their polarization by cooling or approaching a magnet. Neutrons are like

magnets themselves so they are sensitive to magnetic fields and they will deviate when passing across the nanoparticles if they are magnetized. In this way their deviation is giving us information about the magnetic state of the particles. Below we show a plot of the scattered neutron intensity of a sample that contains rod-like iron oxide particles (see the inset) before and after the switching of a magnetic field.



Neutrons have also a mass so they will deviate when they collide with the nuclei of atoms in the nanoparticles. And that give us structural information such as particle size and shape and particle ordering in the fluid. There are two facts that make them especially useful for bionanoparticles, with respect to other types of radiation: 1) neutrons interact

strongly with light atoms
such as hydrogen,
carbon and
nitrogen; and
2) hydrogen
(H) and

deuterium (D) have opposite scattering signs. As a consequence of the first point, the organic matter that is mainly composed of these three elements, and it is "obscure" for X-ray radiation, becomes very "visible" for neutron radiation. The second point allows us to enhance or cancel the intensity scattered by an organic component of the bionanoparticle by substituting, totally or partially, H by D in the component. In these two ways, neutrons allow us to determine the structure of this organic shell and that of the antibodies (or any other kind of biovector) anchored to this shell. This is extremely important when designing bionanoparticles because the ability to reach a target will depend on this structure.

There are examples of the usefulness of neutron scattering for the analysis of magnetic core-shell nanoparticles dispersed in fluids. It has been proven that this technique can reveal the size of core and shell, the linking of organic components to the core, the ordering of the particles in the fluid and the magnetic state of the core, all together

The production of bionanoparticles and their use in biomedicine is one of the hottest topics in this field. However, neutrons are hardly used by this community, probably because there are not many facilities available for this kind of experiments, and mainly because an appropriate use of this technique needs a high skill and extensive training. The ESS project could fill the gap and that would have a high impact on the development of bionanoparticles for diagnosis and therapy of diseases such as cancer.

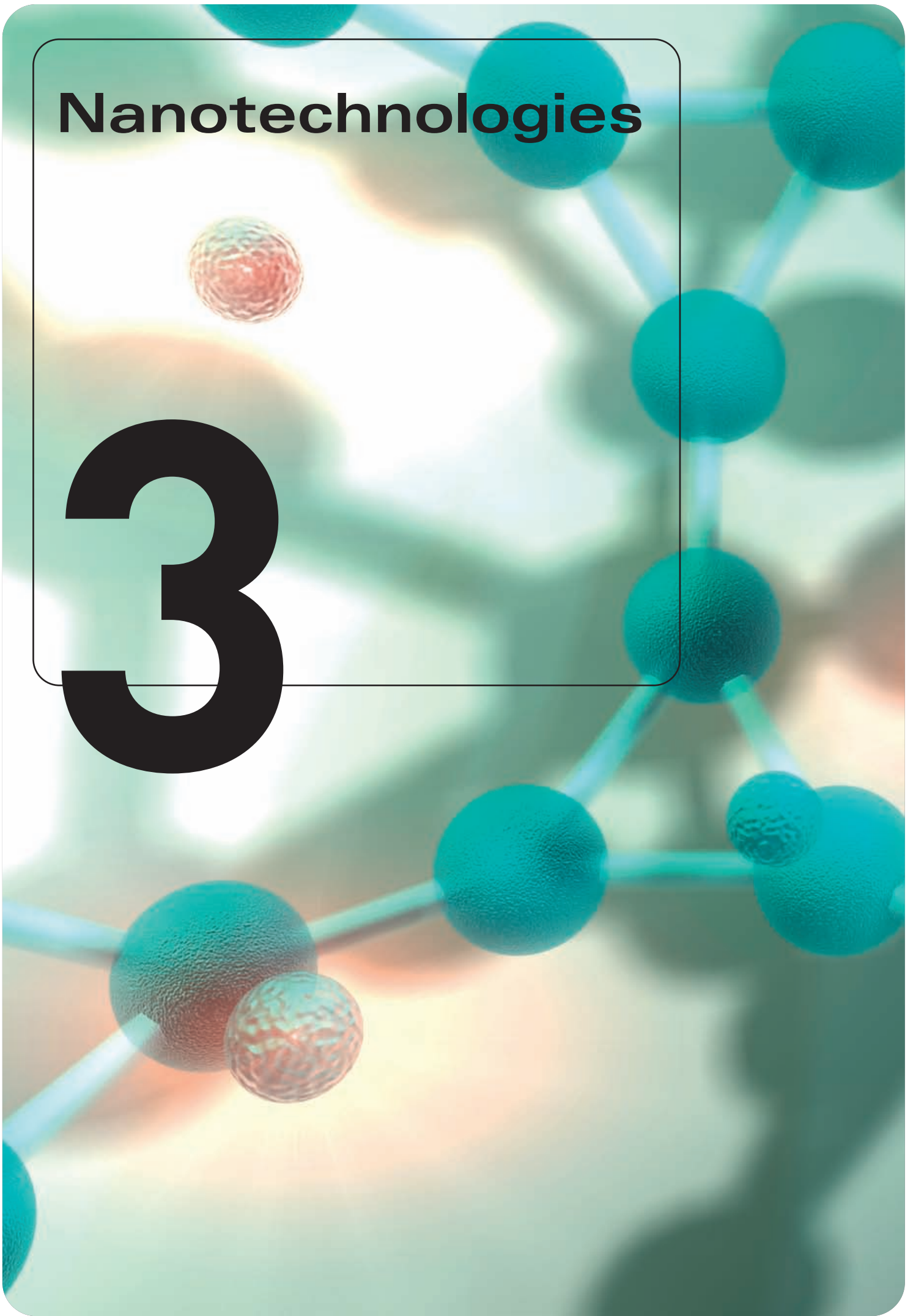


FURTHER READING

R. Weissleder et al Nature Med. 2000, 6, 351
A Wiedenmann et al J. Phys.: Condens. Matter 18
(2006) S2713.

Nanotechnologies

3





3.1

**Research on Nanoparticules
using Neutron Scattering**

L. Fernández Barquín

3.2

**Neutron Spectroscopy of
Isolated Magnetic Molecules**

G. Chaboussant

3.3

**Nanocomposites for
Structured Light Materials:
the Input of SANS**

F. Boué

3.4

**Nanomagnets for Quantum
Computation**

F. Luis Vitalla

Research on Nanoparticles using Neutron Scattering

L. Fernández Barquín

Research on Nanoparticles

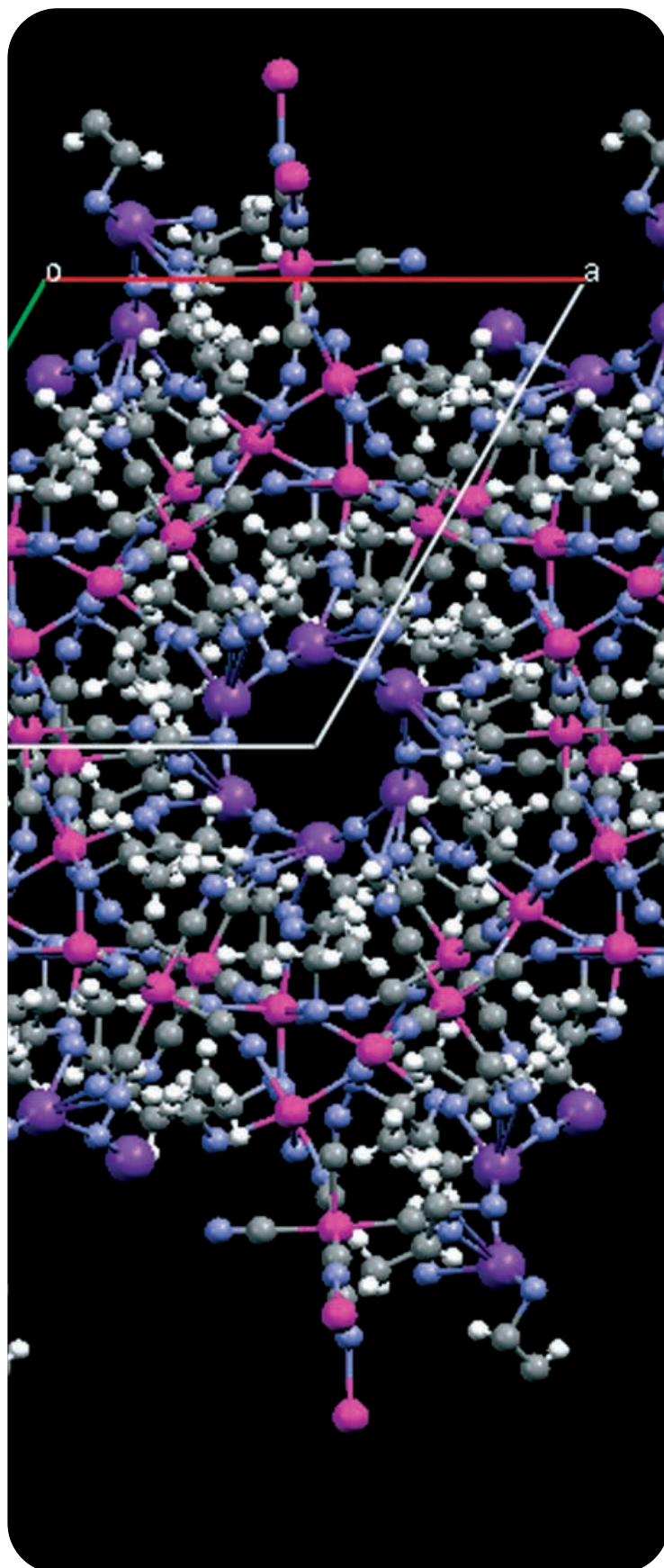
It is more than 40 years since Nobel Laureate P Feynman pronounced one of his famous sentences during a seminar at Caltech: “there’s plenty of room at the bottom” implicitly triggering the interest in small structures. The prefix nano (one thousand times smaller than a micron) is presently attracting considerable scientific, technological and public attention. **This basically stems from the fact that some physical properties may vary with the reduction of size of the material and the number of devices can be increased as a consequence of the reduced size of every unit.** If we are able to understand and produce in a controlled manner those nanostructures, there will be obvious benefits for society. Thus, we have at hand a new variable to control (size), which becomes a handy and powerful tool as it is also occurring with the application of high pressure to materials over the last decade. Another implication is the multidisciplinary character of nanosize and nanotechnology and thus on how science should deal with new challenges as occurs specifically with the application of, for instance, magnetic nanoparticles in biomedicine. Other subjects can involve physicists, chemists, archeologists or geologists working all together.

We had to wait some time until some results were achievable in practice; this waiting period was due to the lack of instruments to produce quality nanostructured samples and to observe them clearly. An opinion commonly accepted is that only at the time when G. Binnig and H. Rohrer in Zurich developed the scanning tunneling microscope in 1982 that period was totally over, a huge milestone for nanoscience and nanotechnology was laid down. With such a delicate instrument it was not only possible to observe atoms but also to control their positions. Unfortunately, this technique required somewhat sophisticated nanostructures which were only available in the best laboratories. The discovery and its development was granted a Noble prize (1986) for both scientists together with E. Ruska, for his electron microscope, another hit in the observation of small scale structures, already in 1936. The latter is a complementary tool and can be used in other less-perfect materials, reaching also atomic resolution in relatively standard microscopes nowadays.

The nanostructures can be fabricated in different forms but in many cases the research has been focused on structures comprising an ensemble of nanoparticles embedded in a matrix. These have

been performed by different production processes (solid state, chemical reactions or deposition techniques such as Molecular Beam Epitaxy, Pulsed Laser Deposition, etc.) The deposition techniques provide very good samples: particles at defined distances, layers of a few defined atomic stacks but with the inconvenient of a reduced quantity (barring their technological potential). By contrast, the first process tends to produce nanoparticles with a broader distribution of sizes but the quantities which are gathered are massive in comparison to the deposited samples. The chemical routes are somewhat in the middle of the other two, providing relatively large quantities of materials, sometimes with a precise arrangement of the nanoparticles. Just note here that another complementary classification scheme regarding the synthesis is the one based on the *top-bottom* or *bottom-up* philosophies, that is to say there can be nanometric entities (particles) formed either with unit blocks assembled together or procedures to divide bulk materials into smaller units reaching ultimately the nanometer scale.

In this context, there are several basic questions to solve: the first one is to unveil the real structure of the nanoparticle system, that is, the average size and dispersion of the particles. A simultaneous issue deserving attention is obviously to extract the composition of the particles and, thirdly, to ascertain whether the particles are formed by a core surrounded by a shell, that is to say, the intraparticle structure. This last issue has become very important and challenging as commonly, after the production process, there could be an unexpected shell layer with phenomenal physical/chemical consequences. As a matter of fact, a great deal of attention has been devoted to nanoparticles showing magnetic properties, with research and development activity finding solutions for the three mentioned demands. This cannot be considered too surprising since, already in the 50s, Louis Néel (Nobel prize award in 1970) anticipated that the reduction of size of the magnetic particle would lead to a coherent rotation of the ensemble of magnetic moments the particles. **Technological possibilities of the magnetic nanoparticles are a hot topic nowadays, but with their roots already reviewed in 1980, in the curious colloids named as ferrofluids, as an example.**



Neutron Scattering Research

It has been described that neutrons are ideal probes to scrutinize the structure of materials. Suffering elastic scattering with the nucleus, they can provide information of the nature and the degree of arrangement or order within the material. Additionally, inelastic scattering can be equally performed with neutrons with great flexibility, providing amazing evidence of movements and diffusion in the compounds. Another relevant ingredient inherent to the neutron nature is the interaction of the magnetic moment of the neutrons with the magnetic nanoparticles, providing information about their characteristics. Therefore, nanoparticles can be studied with different instruments and under

different thermal, magnetic and pressure states, allowing for the discrimination among magnetism and structure. In the following, we will comment on some possibilities constituting a small bunch of attractive examples in a vast field.

From the beginning of the neutron scattering research, diffraction analyses are in the very core of these techniques. Let us then initiate a simplified review of some studies of the magnetic nanoparticles commenting a recent diffraction result. A study was recently carried out using diffraction spectra at several temperatures below room temperature, from a couple of diffraction instruments which were combined with spectra from in-house X-ray diffractometers. Through crystallographic calculations, the data for the size, stress and nature of the nanoparticles were compared to electron microscopy evidence providing a full structural landscape of the alloys. It was also observed that the particles, even with small sizes retained their internal ferromagnetic (magnet) nature.

It is more frequent to find nanoparticles in neutron experiments in which small-angle instruments are used. This

instruments combine specific wavelength neutrons with detectors situated at very far distance from the sample and at a very small angle. Recent technological applications include magnesium hydrides for the hydrogen storage, witnessing the presence of bimodal nanoparticle distributions, or a more traditional interest such as precipitates in steel. Often, models of interacting hard sphere models are applied, as in 5-40 nm SiO_2 nanoparticles in a polymer matrix. If the sample is magnetic, the nuclear (structure) scattering is additional to the magnetic structure and a global study can be performed. In such cases, polarization analyses can be included, that is, the outstanding possibility to polarise neutron beams into one orientation (and concomitantly to detect them after passing through the sample). **SANS in magnetic materials have been used to detect the core/shell nanoparticle structure in ferrofluids, also providing a scattering length profile.** Other nanostructured ferromagnets have been analysed starting with the pure Fe, Co and Ni or Rare Earth elements or analyzing alloys for which it is important to explain the coercivity of the magnetic

materials and the existence of spontaneous magnetic correlations and variation with the external field. It is also possible to analyse materials which are in bulk but present nanoscopic clusters (ie.: small nanoparticles) which may resemble nanoparticulate magnets; enormous efforts have been carried out with magnetoresistive oxides. In consequence, research with neutrons using magnetic particles is a remarkable and promising field.

Regarding the analysis of inelastic spectra, this kind of neutron experiments is slowly producing fine results with difficulties mostly related to the flux limit of the normally low quantity of available nanoparticle sample. Experiments are yet relatively scarce though there exists several excellent reports, for example, complete theoretical and experimental evaluations have been recently carried out in rutile TiO_2 , with a special interest on the acoustical phonons. It is also possible to study the variations produced in the propagation of magnetic waves (spin waves) due to the increase of temperature and the reversal of spins. Another wonderful possibility is to study the Arrhenius magnetic relaxation of

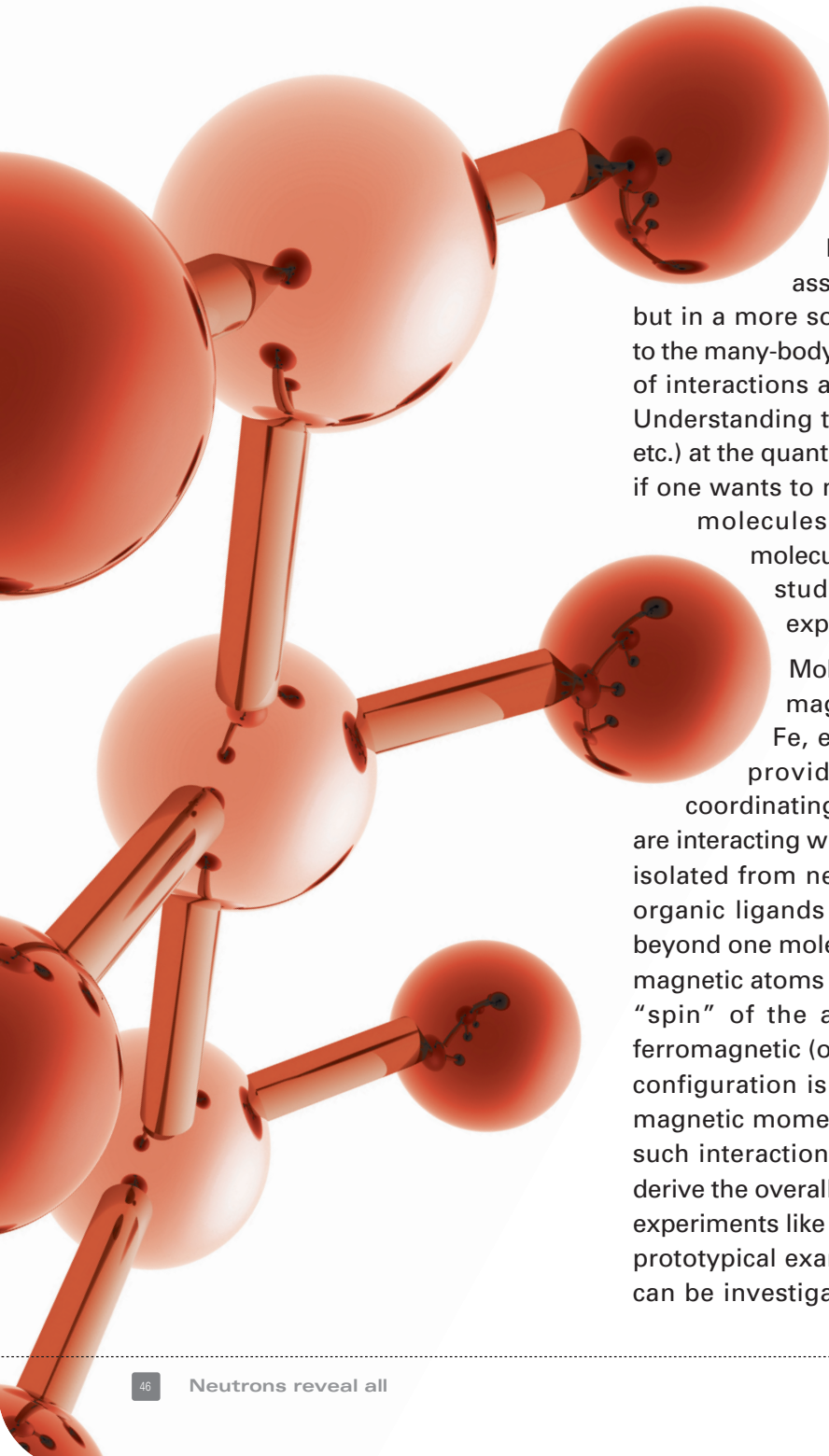
spins, this was studied in antiferromagnetic 15 nm hematite particles. A field where more and more results are expected is the study of the magnetic moment relaxation with the aid of a very precise and fast techniques for dynamics based of the correlations between magnetic moments (neutron spin echo). With the aid we can access a very fast time window where we can “photograph” the relaxing magnetic moments at various temperatures. An example of this was recently evidenced in archetypal 20 nm Fe particles in an alumina matrix.

Layered structures can be fabricated as a number of thin nanometric strata. Occasionally, the layers may contain nanoparticles embedded in a certain matrix. The neutron reflectometry is a technique which has gained interest in the last decade. With this technique one can obtain a depth profile and the sharpness of an interface on, simply, the distance between planar interfaces. Some recent results include the study of granular multilayers and their domain structure, the structure of metallic gold nanoparticle or the control the nanoparticle dispersion in polymeric films.

The long awaited construction of the ESS will not only assure the research on neutron scattering for decades to come but will also allow to perform experiments in materials where now there are some limitations in the expected two orders of magnitude in flux. This is the case for nanoparticle samples which are in many cases obtained in low quantities. It is necessary to improve the results directed towards the distinction between the core and the surface layer (in some materials). Equally the extraction of the magnetic structure is not an easy task yet, usually the evidence of a spin canting found on the surface of the particles is highly dependent on the flux at low scattering angles. In this sense, the inelastic neutron scattering experiments with nanoparticles are even more dependent of the flux. Finally, if we attempt to run samples formed by nanoparticles on a regular basis in reflectometers or neutron spin echo devices, the increase of flux provided by ESS is of paramount importance and many scientists will turn immediately to this sophisticated techniques.

Neutron Spectroscopy of Isolated Magnetic Molecules

G. Chaboussant



Often unnoticed, quantum effects are part of our daily life, and most technologies – such as electronics, medical imaging, or “smart materials” devices - are now operating at levels where quantum physics plays a dominant role over classical physics. Molecules, from water to large molecular assemblies like DNA, do obey quantum physics, but in a more sophisticated way as single atoms. This is due to the many-body nature of molecules and to the intricate pattern of interactions and topologies that make up their properties. Understanding their properties (magnetic, electronic, optical, etc.) at the quantum level is therefore of paramount importance if one wants to manipulate or transform them. In this regard, molecules with magnetic properties and especially molecular magnetic clusters are now intensively being studied because they provide a perfect field to explore quantum effects at a molecular level.

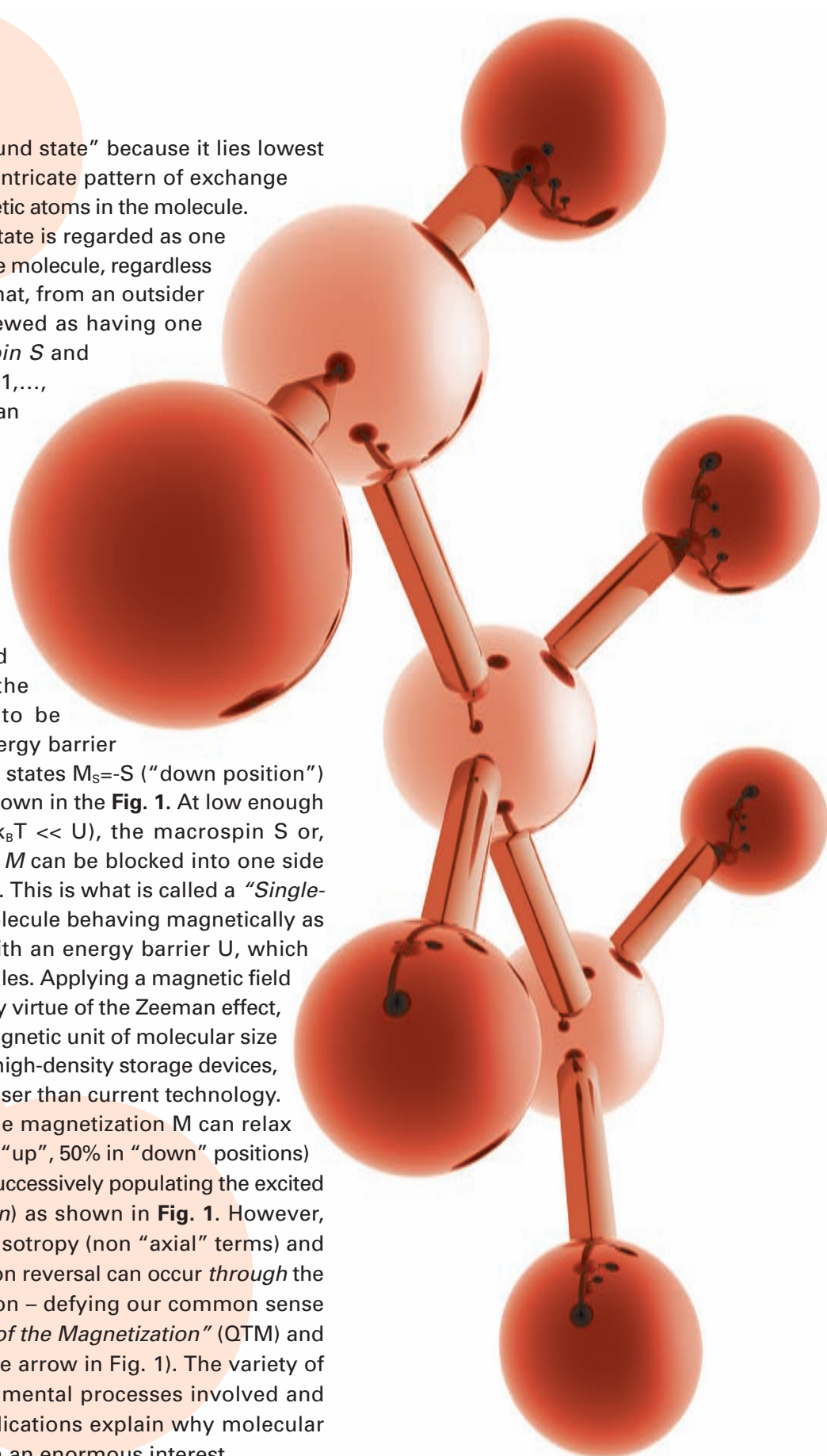
Molecular magnetic clusters are made up of several magnetic ions, usually transition metal (Cu, Mn, Fe, etc.) ions, linked together by chemical bonds provided by organic ligands or other forms or coordinating molecules. The magnetic ions in one cluster are interacting within each cluster, but are virtually magnetically isolated from neighboring clusters due to the encapsulating organic ligands preventing magnetic interactions to extend beyond one molecule. The *exchange interaction* J between two magnetic atoms involves the magnetic moment (related to the “spin” of the atom) of these atoms and it is said to be ferromagnetic (or antiferromagnetic) when the most favorable configuration is a parallel (or anti-parallel) alignment of the magnetic moments. In magnetic clusters, there are several of such interactions and - using quantum mechanics – one can derive the overall magnetic properties of one single cluster from experiments like neutron scattering. Such clusters are therefore prototypical examples where collective magnetic phenomena can be investigated right down to the core. The most stable

configuration is called the “ground state” because it lies lowest in energy. It is the result of the intricate pattern of exchange interactions J between the magnetic atoms in the molecule.

In some instances, the ground state is regarded as one single collective state of the whole molecule, regardless of the atomic details. It means that, from an outsider view, each molecule can be viewed as having one single “macro-spin” of *total spin* S and quantum number $M_S = -S, -S+1, \dots, S-1, S$. Of course, the situation can be much more complicated.

Because magnetic ions are embedded in a crystalline environment they are subject to so-called “magnetic anisotropy” D which tends to favor some very specific directions for the preferred orientation of the spin S . If the magnetic anisotropy is said to be “negative axial”, there is an energy barrier

$U = |D|S^2$ between the quantum states $M_S = -S$ (“down position”) and $M_S = +S$ (“up position”) as shown in the **Fig. 1**. At low enough temperature compared to U ($k_B T \ll U$), the macrospin S or, equivalently, the *magnetization* M can be blocked into one side of the barrier almost indefinitely. This is what is called a “*Single-Molecule Magnet*” (SMM), a molecule behaving magnetically as one large magnetic moment with an energy barrier U , which can be up to 85K in some molecules. Applying a magnetic field can reverse the magnetization, by virtue of the Zeeman effect, creating a bistable (up/down) magnetic unit of molecular size that could open the way to ultra-high-density storage devices, several orders of magnitude denser than current technology. With increasing temperature, the magnetization M can relax back to equilibrium ($M=0$, 50% in “up”, 50% in “down” positions) by “climbing up” the barrier by successively populating the excited states (*called thermal relaxation*) as shown in **Fig. 1**. However, under the right conditions of anisotropy (non “axial” terms) and magnetic fields, the magnetization reversal can occur *through* the energy barrier. This phenomenon – defying our common sense – is called “*Quantum Tunneling of the Magnetization*” (QTM) and is of purely quantum origin (blue arrow in **Fig. 1**). The variety of molecular structures, the fundamental processes involved and the potential technological applications explain why molecular magnetic clusters attracted such an enormous interest.



What neutron scattering do for molecular magnetic clusters

The field of molecular magnetism, and particularly SMM's, has greatly profited from neutron scattering investigations.

From low-dimensional magnetism (spin chains, spin ladders, spin liquid-like systems, etc.), competing interaction systems to spin clusters with SMM behavior or spin clusters with ring geometry, neutron scattering has been implemental in the understanding of the basic physical properties of such molecular systems.

More specifically, Inelastic Neutron Scattering (INS), both from continuous and pulsed neutron sources, plays a key role in understanding the inner mechanisms leading to large energy barriers U , thus to high temperature permanent magnets of molecular size, and to an observable QTM effect. INS experiments enable not only to determine the anisotropy parameters driving the QTM, but also to understand the effects of the chemical environment, external pressure or magnetic field, and to determine with great accuracy the exchange interaction parameters J in very complicated molecules. As shown in the **Fig. 2** in the case of Mn_{12} -acetate (a molecular complex containing 8 Mn^{3+} and 4 Mn^{4+} , with a spin ground state $S=10$ and an energy barrier $U=65K$), INS spectra are characterized by peaks at finite energies, which correspond to an energy exchange between the incoming neutron and the macrospin S resulting in quantum state changes in the cluster ("transition" from an *initial state* M_S with energy E_i to a *final state* $M_{S'}$ with energy E_f for instance). Quantum physics tells us that only transitions obeying some specific selection rules are allowed (all transitions shown in **Fig. 2** have $\Delta M = M_{S'} - M_S = \pm 1$). Each inelastic peak in the figure corresponds to one such transition. From the knowledge of their energies and intensities, it is possible to obtain information on the exchange interaction terms controlling the formation of the ground state and the small anisotropy

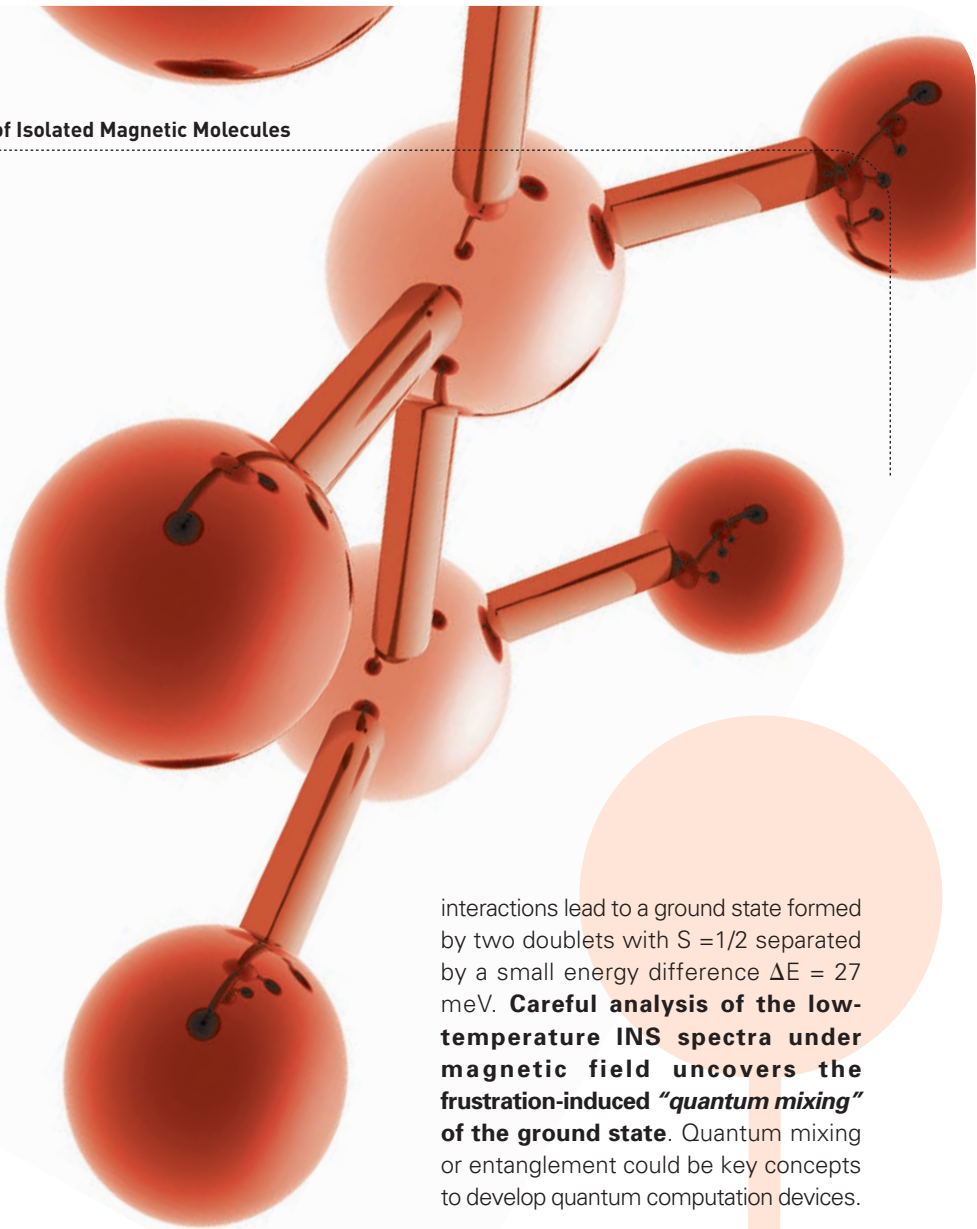
terms controlling the QTM. Often, in order to obtain significant results, high-resolution instruments (in the range of 1-10 μeV) are required at the expense of neutron flux; this is why **a new source like ESS with a manifold increase in flux will enable scientists to reach new limits in the exploration of subtle quantum effects.**

In some instances, magnetic clusters are considered "*magnetically frustrated*" in the sense that not all couplings can be satisfied simultaneously. The ground state and the excited states, located at higher energies, reflect such frustration. The effect of such frustration can be directly studied by INS where the observed transitions help to map out the cascade of energy levels above the ground state. Each transition brings information on the initial state and final state. This is best shown in the polyoxovanadate V_{15} , which contains 15 $S=1/2$ V^{4+} ions. In this molecule the frustrated antiferromagnetic

interactions lead to a ground state formed by two doublets with $S = 1/2$ separated by a small energy difference $\Delta E = 27$ meV. **Careful analysis of the low-temperature INS spectra under magnetic field uncovers the frustration-induced "quantum mixing" of the ground state.** Quantum mixing or entanglement could be key concepts to develop quantum computation devices.

Another example of the power of neutron scattering is the determination of exchange couplings in Mn_{12} . This could not have been achieved using standard magnetic measurements due to the magnitude of the couplings and to the interplay of at least 4 competing antiferromagnetic and ferromagnetic exchange interactions within the Mn_{12} cluster. A combination of low (0-2 meV) and high-energy (2-50 meV) INS studies confronted with numerical calculations made possible to derive a coherent set of exchange coupling parameters which could satisfy the known experimental data.

Recently, thanks to the combination of high flux and high resolution, time-resolved studies permitted to measure directly the magnetization decay in magnetic molecular clusters in real time by fine-tuning an external magnetic field. **A giant leap in performance will make it possible to process real-time experiments with much finer details and with much smaller samples.**



New horizons with ESS

Recent advances in neutron instrumentation (better flux, better energy resolution, better sample environment like pressure cells or magnetic field inserts) now permits the use of smaller samples and to perform more complex experiments. For instance, applying pressure on SMM's like Mn_{12} and Mn_4 enabled to get an insight into the mechanism leading to large negative axial anisotropy. Pressure cells above a few kilo-bars are only

available for relatively small samples so, for pressure studies, much larger flux will be most welcomed.

ESS will fill up the remaining gap between the neutronician's needs and the chemist's capacity to synthesize small single crystals in order to perform cutting edge experiments with high-resolution, high flux and complex sample environment. ESS will certainly open up new challenges in the field; especially towards kinetic measurements (real time experiment, relaxation measurements),

spin density maps (diffraction experiments) with extremely fine details and high-energy/high resolution INS experiments. In fact, in the energy range between 100 meV and 1eV, neutron scattering stands alone, as no other technique can match its unique abilities to probe such a large range of energy and wave-vector transfer. **For all these reasons, ESS will be a state-of-the-art neutron facility for magnetism, in particular molecular magnets, both for magnetic structures and magnetic spectroscopy.**

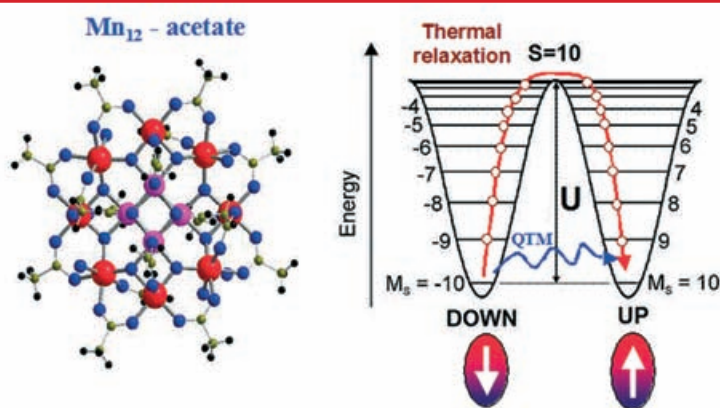


Fig. 1. Structure of Mn_{12} -acetate with 12 Mn ions (red ions are Mn^{3+} , purple ions are Mn^{4+}) forming an $S=10$ macro-spin at low temperatures. Right: Energy levels of the $S=10$ ground state of Mn_{12} -acetate. The two wells are separated by an energy barrier $U = |D|S^2$. The M_S energy levels are split in energy according to the equation $E(M_S) \approx -|D|M_S^2$. The red and blue arrows indicate schematically the "thermal relaxation", over the barrier, back to equilibrium and the Quantum Tunneling pathway through the barrier, respectively.

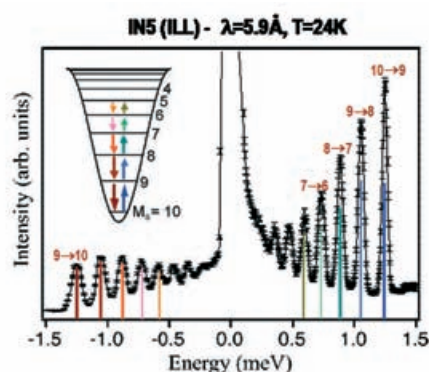


Fig. 2. Inelastic Neutron Scattering spectrum of Mn_{12} -acetate. The $\Delta M = \pm 1$ transitions are characteristics of the $S=10$ ground state whose levels are split - to first order - by the magneto-crystalline anisotropy term D : $E(M_S) \approx -|D|M_S^2$ (see inset). Energy positions and peak intensities are controlled by the anisotropy parameters.



FURTHER READING

R. Bircher, G. Chaboussant, C. Dobe, H.-U. Güdel, S.T. Ochsnein, A. Sieber and O. Waldmann "Single-Molecule Magnets under Pressure", *Advanced Functional Materials* **16**, 209 (2006).

S. Carretta, P. Santini, G. Amoretti, T. Guidi, J. R. D. Copley, Y. Qiu, R. Caciuffo, G. Timco and R. E. P. Winpenny, "Quantum Oscillations of the Total Spin in a Heterometallic Antiferromagnetic Ring: Evidence from Neutron

Spectroscopy", *Physical Review Letters* **98**, 167401 (2007).

G. Chaboussant, S. T. Ochsnein, A. Sieber, H.-U. Güdel, H. Mutka, A. Müller and B. Barbara "Mechanism of ground-state selection in the frustrated molecular spin cluster V_{15} "

Europhysics Letters **66**, 423 (2004).

G. Chaboussant, A. Sieber, S.T. Ochsnein, H.-U. Güdel,

M. Murrie, A. Honecker, N. Fukushima and B. Normand, "Exchange Interactions and High-Energy Spin States in Mn_{12} -acetate", *Physical Review B*, **70**, 104422 (2004)

O. Waldmann, G. Carver, C. Dobe, D. Biner, A. Sieber, H. U. Güdel, H. Mutka, J. Ollivier and N. E. Chakov, "Magnetic relaxation studies on a single-molecule magnet by time-resolved inelastic neutron scattering", *Applied Physics Letters* **88**, 042507 (2006).

Nanocomposites for Structured Light Materials: the Input of SANS

F. Boué

First of all, the author wishes to acknowledge all the work on the presented topics done by Y. Rharbi presently at Laboratoire de Rhéologie, Grenoble, J. Oberdisse, presently LCVN, Montpellier I, A. El Harrak, presently at ISIS, Strasbourg, and at LLB J. Jestin, G. Carrot, F. Cousin, and our Ph. D students, C. Chevigny, N. Jouault, and A.S. Robbes.

Introduction: nanocomposites and what brings neutron scattering

Light materials, often called also « soft materials », have many advantages. Certainly they require less energy to be created as well as less energy to function but they often need more « structuring » in order to match the same properties of « heavy » materials. Here *we will focus on how light materials can be used in mechanical improvement, although examples of materials used in electromagnetic or in conductivity properties are on the spot.* A simple way to achieve mechanical improvement is to create some kind of alloys by adding a small amount of some « harder » material. It appears that the best solution is to create some sort of harder paths in the soft material, the most efficient ones are ramified structures at the nanometer scale. From these building blocks larger scale structures can be built.

No doubt, these structures are often *complex*. Even when it is possible to visualize them with the naked eye, or with more sophisticated means such as optical or electronic microscope, it is often very difficult to describe and understand them. *Neutron scattering is very useful to study these systems, because it covers scales ranging from the nanometer to the micron in the same experiment.* Importantly, we can take advantage of the use of markers (such as nanoparticles attached to a given molecule or

array) or isotopic substitution (deuterium replacing hydrogen) to retrieve the different species. A very well known technique is contrast matching that takes advantage of the different scattering factors of the different species to enhance one with respect to the others.

The very good accuracy of the measurements comes in connection with these possibilities. They can be given in absolute units; the parasite signals can be removed properly, there is no multiple scattering, and the contrast can often be calculated accurately... thus the result can be directly compared with models and even numerical simulation. This, again, is very powerful for material science at the nanoscale. Furthermore, in some cases, one can even observe the real materials in a R&D approach. Deuteriation will be seldom in real material since it is costly, but some simple components can be introduced such a deuterated solvent to label some part of the sample.

Finally, owing to its high penetrability neutron allows to study samples under complex environments: temperature (hot or cool), shear cell, pressure cell, dielectric, electrostatic field, magnetic field, confinement...all this often used in materials studies.

Looking at the hard phase: dispersion for controlled connectivity

One way of introducing a nanostructure in a light material is to introduce nanoparticles, and let them assemble in a structure at the relevant nm scales. The formation of large aggregates (e.g. micrometric) should be avoided and to this end several ways exist to prevent it.

The “lucky” direct dispersion

Though the usual result of direct dispersion (without any additive) is a rather large aggregation, a satisfactory dispersion of 10 nm diameter silica in polystyrene has been achieved in a very simple way. The scattering curves (**Fig. 1.a**) can be interpreted as due to a quasi-fractal aggregate structure, with a correlation peak appearing at large volume fraction ϕ and varying with ϕ , following a percolation law. Transmission Electronic Microscopy experiments (**Fig. 1.b**) confirm their homogeneity at larger scale (e.g. > 300 nm), so the structure is nicely well known and can be used as a starting point for further investigation using intrinsic neutron properties, as described below.

Nanolatex, nanoferrolatex

Aqueous mixtures of polymer nanolatex and colloidal nanosilica have allowed us to produce a large dispersion.. After drying the mixture a latex film containing silica particles with dispersion depending on the pH of the preparation (from large branched aggregates at acidic pH to individual particles at low pH) is produced. Magnetic nanoparticles enable us to orient the so-formed aggregates (**Fig. 2**) and to obtain anisotropic mechanical modulus. In this case neutron scattering gives us the displacement of the aggregates and their deformation.

Grafted nanoparticles

One sophisticated way is to grow chains from the surface after grafting of a polymerization initiator. Here is an example of using **contrast matching**. The solvent of synthesis is added with a fraction of deuterated solvent, which matches either the polymer, in which case we can check extremely accurately the very good

stability (no change with respect to the initial sol), or the silica. In this latter case we can fit the scattering of the individual objects by a core (= silica)-shell (= the chains around) model. The principle is illustrated in **Fig. 3**, in which both cases of silica grafted by normal and deuterated polymer (which can be used in further experiments) are displayed.

Looking at the soft phase: more neutron methods based on contrast

After characterizing the various hard phase structures we can proceed to the study of what occurs inside the soft phase, in our case the polymer matrix.

A special matrix has been synthesized in such proportions that it matches the scattering of grafted silica nanoparticles (**Fig. 3**). We can thus follow both the silica and the corona scattering inside the matrix, and understand how it is interspersed with the matrix chains, which is a key point for dispersion! Moreover we can stretch our polystyrene films, and follow the anisotropic scattering and measure how deformed the corona is!

The direct dispersion system

is convenient for another typical neutron scattering trick, the so called Zero Average contrast method, which cancels the inter-chain scattering and enables us to observe the **single polymer chain conformation** inside the filled sample. This allows us to discuss the controversial studies on the influence of confinement by fillers. Furthermore, to better understand reinforcement, the chain deformation inside the composite has been followed.

Magnetic nanoparticles,

after dispersion in a polymer matrix, can benefit from these different methods while inducing magnetic orientation during composite preparation.

Softer hard phase.

We would like to quote another study on samples where the hard phase can also

become “soft”. For that some nanobeads of latex synthesized from deuterated styrene were incorporated inside a soft “latex film”. Thus, these beads inside the latex film, in particular after applying a compression to the matrix film, can be “seen”. The latex is a strong elastomer. The d-PS nanobeads deform only if the temperature of stretching is above the *glass transition*, which permits to follow the influence of the *confinement* in the beads of variable size on the inner glass transition. This is a very active and controversial subject – linked to glass transition in *thin films*, and it could also be very useful for designing self hardening paints, without any “Volatile Organic Components”, as required by European Union for coatings of the future.

Other neutron techniques: inelastic scattering for the dynamics

We have just evoked the influence of confinement on the glass transition in polymers. For a long time this has led physicists to look for a sort of “glassy layer” induced by the confinement at the surface of the hard particles, or in between in the “directly dispersed” system. We have observed characteristic mechanical times much longer than the pure matrix one, although SANS plus TEM gave us inter-aggregate distances larger than 50 nm. This may be due to long glassy paths. This can give us the **dynamics** of chains, at a convenient scale of a few nanometers (times $\sim 10^{-8}$ to 7 seconds), and here also we can count on the difference between normal and deuterated chains to study specifically the chain motion. The large time range brought by the ESS would be very useful for these systems.

Numerical simulations

As said in Introduction, the good reliability of neutrons for translating, rather faithfully, what exists in real space into reciprocal space makes the comparison with computer simulations very sensible. Although the system is a bit complex, first attempts were made, where the paths of the nanoparticles inside the deformed film are simulated.

Other light matrices

As said in Introduction, these methods can be applied, beyond polymers, to many other soft phase hosting hard particles. The latter can be, for example, microemulsion of micelles (spheres or cylinders) connected by a telechelic polymer, or an aqueous tribloc polymer gel.

Applications to industry and further prospective

From an industrial point of view, the list of materials concerned by this type of studies seems potentially infinite. In the following we just outline some examples.

Certainly tires industry (cars, trucks and planes), where the rubber contain fractal-like aggregates of carbon black (with elementary beads ~ 1 nm), and other elastomer needing reinforcement, will certainly benefit from forthcoming studies at the future ESS.

Studies of rheological changes can be fruitful in soft systems through nanoparticles. This studies have (and certainly will have) a strong impact in, for example, personal care industry or pharmaceuticals.

Properties other than mechanical may be sought, as well. Presently, carbon nanotubes embedded in polymer are developed for conductivity properties. In order to prevent the permeability of packaging (e.g. of food) to different gases, platelet-like fillers like clays are often used. This points out the interest of using different shapes and mineral nature of nanoparticles, synthetic or natural.

At the sight of all these different systems, a large access to user teams from many areas would be a determining opportunity; it is certain that ESS offers a huge step forward for these kinds of materials of high potential in very near future.

Fig. 1: SANS from nanosilica directly dispersed into polystyrene, compared with TEM. Middle: scattering for different filler concentration. The curves are normalized by the volume fraction of silica. Insert: $I.Q^3$ versus Q plot for the same data. This highlights the oscillation around $4.10 \cdot 10^{-2} \text{ \AA}^{-1}$, due to initial particles at contact. Left and right: Transmission Electronic Microscopy on the nanocomposite filled with 6.6% v/v (left) and with 15.7% v/v (right) of particles (black is silica, grey is polymer). Medium magnification showing both the maximum size of aggregates and the good homogeneity at larger scale.

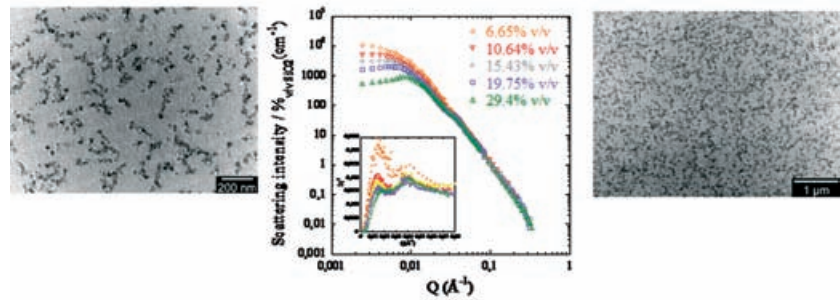


Fig. 2: Right hand: anisotropic scattering of magnetic nanoparticles in polymer films formed by latex-beads, and orientated by constant field. Left hand: application: obtaining a anisotropic mechanical reinforcement.

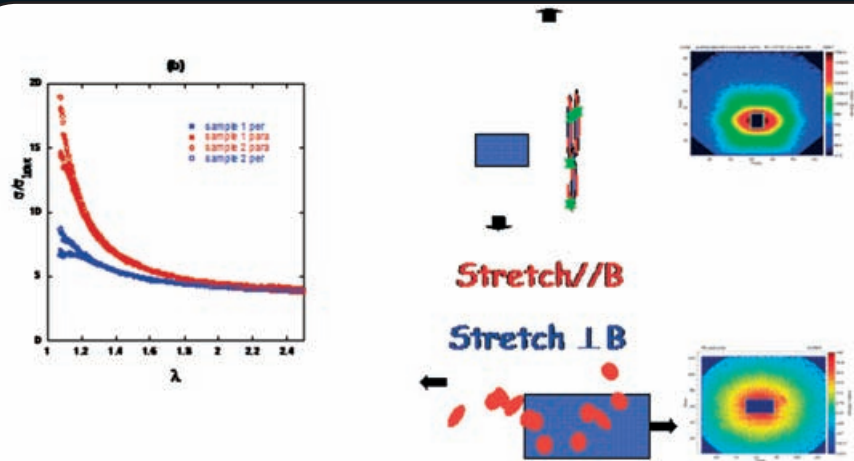


Fig. 3 : Contrast matching : principle and application to a core-shell particle (with normal (below) or deuterated (above) shell) enabling to see either the particles or the corona inside a matrix (either a solvent or a matching matrix[®]).

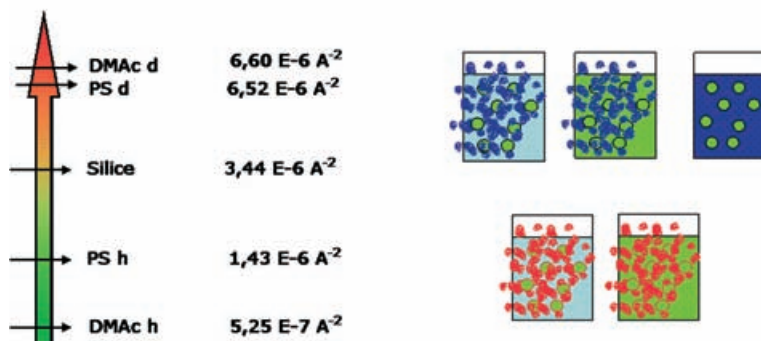
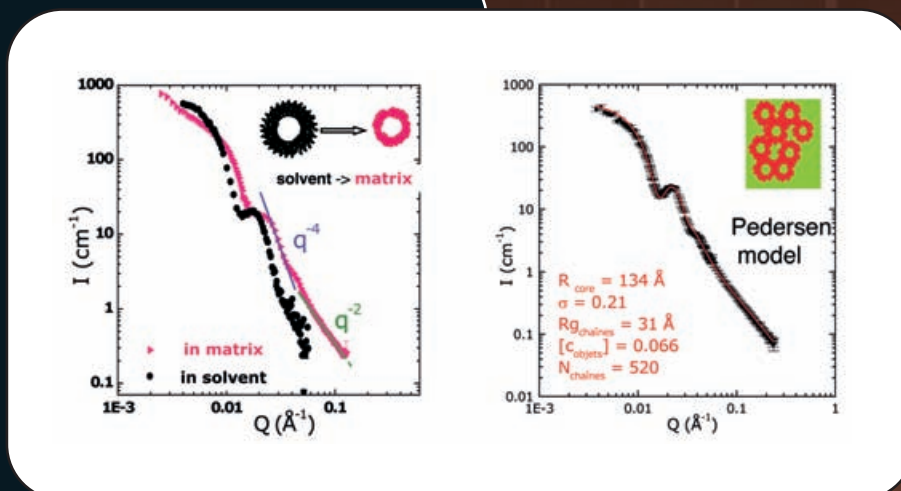


Fig. 4. Grafted silica: scattering and modeling. Left: comparison between the scattering from the corona of the same particles in matching solvent (dark diamonds) and in a matching polymer matrix (light triangles), showing that the shell is retracted in the latter case (shift to large q equals shift to shorter scales). We showed recently that this influences the interaction and the dispersion with the matrix. Right: fit of the scattering by a core-Gaussian chain shell model (Pedersen) of core radius 13 nm and chain radius of gyration 3 nm.



FURTHER READING

A. Bansal, H. Yang, C. Li, K. Cho, B. C. Benicewicz, S. K. Kumar, L. S. Schadler, *Nature materials*, **2005**, 4, 693.

S. Sen, Y. Xie, A. Bansal, H. Yang, K. Cho, L. S. Schadler, S. K. Kumar, *Eur. Phys. J. Special Topics*, **2007**, 141, 161-165.

Study of deformation in a soft/hard composite, Y. Rharbi, B. Cabane, M. Joanicot, F. Boué, *EuroPhys. Lett.*, **46** (4), 472-478 (1999).

Structure of Latex_Silica Nanocomposite Films: A Small-Angle Neutron Scattering Study J. Oberdisse, B. Demé, *Macromolecules*, 2002, 35 (11), pp 4397-4405

Anisotropic reinforcement of nanocomposites tuned by magnetic orientation of the filler network, Jacques Jestin, Fabrice Cousin, Isabelle Dubois, Christine Ménager, Ralf Schweins, Julian Oberdisse, François Boué, *Advanced Materials* 2008, 20 (13), 2533 – 2540.

Polymer grafting Chemistry on 10 nm individual particles: proving control by Neutron Scattering, G. Carrot, A. El Harrak, J. Oberdisse, J. Jestin, F. Boué, *Soft Matter*, 2006, 2, 1043 – 1047.

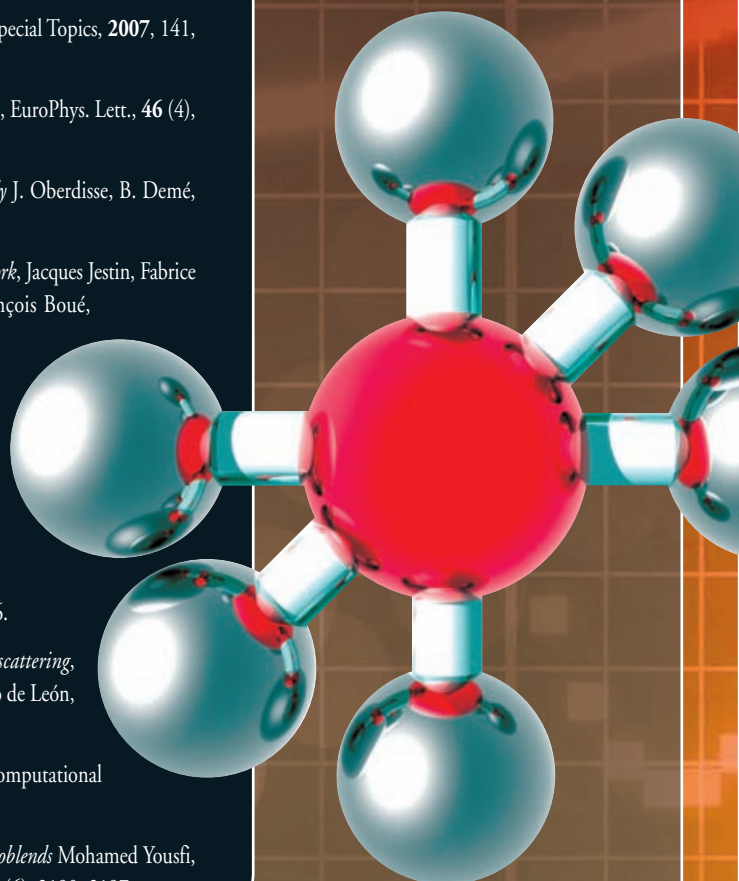
Chain Conformations and Bound-Layer Correlations in Polymer Nanocomposites S. Sen, Y. Xie, S. K. Kumar, H. Yang, A. Bansal, D. L. Ho, L. Hall, J. B. Hooper, K. S. Schweizer, *Phys. Rev. Lett.* 98, 128302 (2007)

J. Berriot, H. Montes, F. Lequeux, D. Long, P. Sotta, *Eur. Phys. Lett.*, **2003**, 644, 50-56.

Effect of stretching on the sub-Tg phenylene-ring dynamics of polycarbonate by neutron scattering, Arrese-Igor, Silvia ; Mitxelena, Olatz ; Arbe, Arantxa; Alegría Loinaz, Ángel; Colmenero de León, Juan; Frick, Bernhard *Phys. Rev. E* 78, 021801 (2008).

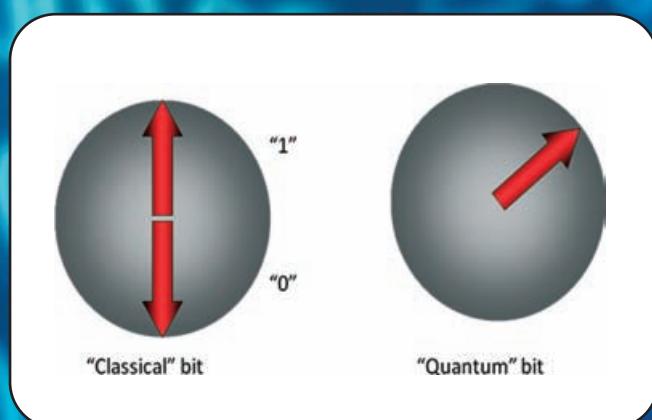
Numerical simulations... in soft/hard nanocomposites J. Oberdisse, Y. Rharbi, F. Boué, *Computational and Theoretical Polymer Science*, 10, 207-217 (2000).

A Novel Method for Studying the Dynamics of Confined Polymers in Nanoparticles in Nanoblends Mohamed Yousfi, Lionel Porcar, Peter Lindner, François Boué, Yahya Rharbi, *Macromolecules*, 2009, 42 (6), 2190-2197.



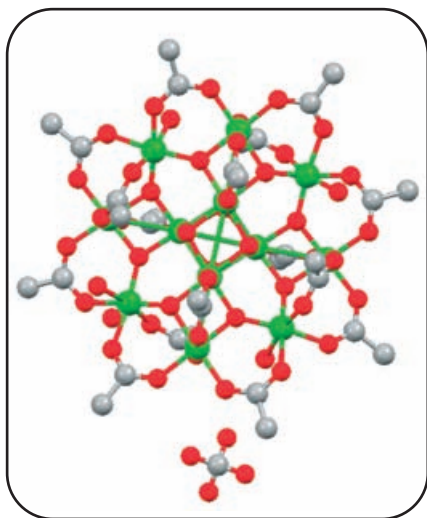
Nanomagnets for Quantum Computation

F. Luis Vitalla



A computer can be seen as a machine that manipulates the state of a string of information units, or bits. In conventional, or “classical”, computers the bits can be either “1” or “0”. A quantum computer, when it exists, would be a machine that operates the bits according to the laws of quantum mechanics. *The units of quantum information, or q-bits, are then allowed to stay in states that are neither fully “1” nor fully “0”. These states are called quantum superpositions.* Thanks to the possibility of manipulating such superpositions, quantum computers are able to reduce the complexity of some tough computational tasks. The application of quantum computers would speed up searching for information in large databases, open the way to codification of secret information, unreachable to any external party, and enable the simulation and optimization of new complex materials and medicals before actually fabricating them.

A major challenge for this field is finding reliable candidates to form the hardware of future quantum computers, i.e. the q-bits themselves. Q-bits based on nuclear spins present in molecules in solution or single ions trapped in optical lattices, have enabled the realization of simple quantum algorithms. However, the need for scaling up towards realistic computers, able to carry out more complex calculations, justifies the search of solid state devices. Nanoscopic magnetic materials, or nanomagnets, represent a rather attractive choice, since these materials are already used as the bits of today’s hard disks. The two information states, “1” and “0”, can be codified simply by two opposite orientations of the spin (“spin-up” and “spin-down”), and superpositions of these can in principle be generated and manipulated by the application of resonance techniques.



Recent achievements: molecular q-bits

The basic requirement of a magnetic q-bit is that any operation performed on it must be entirely governed by the laws of quantum mechanics. External perturbations have to be avoided or at least minimized, since they introduce unpredictable errors in the calculations. This requirement turns out to be extremely difficult to achieve for magnetic materials with sizes above that of individual atoms. The reason is the extreme fragility of any quantum phenomenon to “observation”, which explains why our everyday’s world appears to obey Newton’s “classical” laws despite the fact that all objects are made of quantum atoms.

Fortunately, molecular chemistry has provided ways to synthesize large amounts of identical nanomagnets, made of a few or even individual atoms. These molecules are termed “single-molecule magnets” or molecular bits because they are able to store magnetic information at temperatures below $-270\text{ }^{\circ}\text{C}$. In 1996, it was found that the molecular spins can flip via a phenomenon known as “quantum tunneling”. Although this phenomenon was known to occur in, e.g., electrons travelling across semiconducting devices or alpha particles emitted by radioactive nuclei, this was the first uncontroversial evidence of its existence in mesoscopic-size materials. The fact that tunneling is directly linked to the existence of quantum superpositions made these nanomagnets good candidates for solid-state q-bits.

The phenomenon of tunneling is, to a large extent, determined by the energy level structure of the molecular bits. For a number of molecules, neutron techniques (inelastic scattering) have provided access to directly measuring the energy level structure, in this way unveiling the origin of their quantum magnetic dynamics. In addition, the interaction of the neutron’s spin (it also behaves as a tiny nanomagnet) with the spins of the molecular bit enables to directly determine the magnetic state of

the latter. Via the application of external magnetic fields, the molecular bit can be manipulated from being either “1” or “0” to a quantum superposition. By adequately engineering the magnetic properties at the molecular scale, the lifetime of the quantum superpositions and the ensuing quantum dynamics against the external “noise” (usually known as decoherence) has been made sufficiently long to carry out a large number of computations, making these materials competitive with other solid-state q-bits.

As it happens in the case of conventional computers, carrying out logical operations requires the use of logical gates, in which more than one bit intervene. A quantum computation can be performed via a sequence of operations carried out on single q-bits and the operation of quantum gates involving just two q-bits (CNOT gates). In the course of the latter, the states of the two q-bits can become correlated in a unique way, with no analogue in Classical Physics. The possibility of manipulating these quantum “entangled” states of two or more q-bits in the course of the computation is a crucial ingredient for the performance of quantum computers when confronted with complex problems. **A realistic quantum computer would consist of an ordered network of mutually interacting q-bits. Understanding the entangled quantum dynamics of these networks is one of the most fascinating challenges of this research field.**

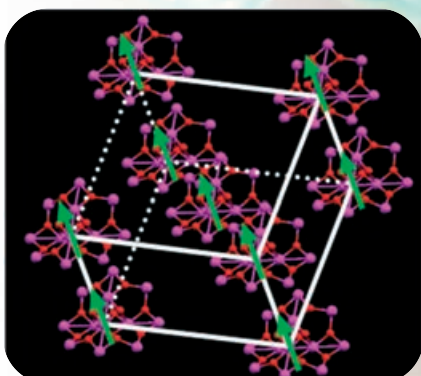
The wavelike character of neutrons and their spin makes them suitable probes to directly measure magnetic correlations. It has been possible, for instance, to evidence the existence of quantum collective states in ordered crystals of Mn_{12} molecular bits. Neutron inelastic scattering has also been employed to determine the length scales over which quantum entanglement extends in inorganic crystals containing Ho atomic nanomagnets, and to discover that entanglement can be strongly limited even by the very weak interaction between these atoms and the spin of their nuclei.

New chances offered by ESS

The application of neutron techniques to investigate entanglement in crystals of molecular bits is usually limited by the small size of the samples. The signals to be measured are then often too small to extract the full information sought.

Therefore, access to a more powerful neutron source, such as promised by ESS, could help to properly design the architecture of tomorrow's quantum computers. Other applications can also be envisaged. For instance, an ordered crystal of q-bits can store entanglement and transfer it to neutrons travelling through it, in this way acting as a kind of repeater for communication of quantum information.

Another advantage of molecular materials is their high degree of processability. Each molecule being a completely independent entity, they can be dissolved and then deposited onto solid substrates. The ability of making truly ordered two-dimensional arrays appears to be a key step towards the access and manipulation of the information stored in individual molecular bits. Although there has been an extraordinary progress in the last years, there are still many technical and also scientific problems to solve. A crucial question is how the quantum molecular properties will change as the molecules stand on a solid substrate. Again, the use of novel neutron sources as well as the design of environmental conditions (*in situ* preparation of single molecular layers, magnetic fields orientable along the three directions of space, and others), could help the scientists to find the most promising materials to the future quantum computers.



FURTHER READING

M. A. Nielsen and I. L. Chuang, *Quantum computation and quantum information processing*, Cambridge University Press, 2000.

D. Gatteschi, R. Sessoli and J. Villain, *Molecular Nanomagnets*, Oxford University Press, Oxford, 2006.

M. N. Leuenberger and D. Loss, *Nature* **410**, 789, 2001;

R. Caciuffo, et al., *Phys. Rev. Lett.* **81**, 4744, 1998;

I. Mirebeau, et al., *Phys. Rev. Lett.* **83**, 628, 1999;

F. Troiani et al., *Phys. Rev. Lett.* **94**, 207208, 2005;

S. Bertaina et al., *Nature* **453**, 203, 2008;

V. Vedral, *Nature* **453**, 1004, 2008.

F. Luis et al., *Phys. Rev. Lett.* **95**, 227202, 2005.

H. M. Ronnow et al., *Science* **308**, 389, 2005.

Cultural Heritage and Archeometry

4



4.1

**Neutrons in Archaeometry
and Conservation Science:
the Contribution of Neutron
Scattering to Cultural
Heritage**

G. Artioli

4.2

**Neutron Study of Ancient
Paper: an Example of Early
Biomaterials**

C. Mondelli

4.3

**Neutron Scattering
Applications to Cultural
Heritage Materials and
Artefacts**

R. Rinaldi



Neutrons in Archaeometry and Conservation Science: The Contribution of Neutron Scattering to Cultural Heritage

G. Artioli

Archaeometry, originally started as the application of scientific methods in archaeology and essentially confined in the early times to dating methods, is now joining efforts with the more focused **conservation science** within the broader context of applying a vast array of scientific methods to the understanding and the preservation of our cultural heritage.

There is a broad, challenging and very stimulating research area, having poorly defined and strongly interdisciplinary boundaries, which is the application of the concepts and methods of scientific research to cultural heritage problems. The general aims are: (1) to characterize and understand the **physico-chemical nature** of the objects (i.e. phase identification, chemical quantification, assessment of the distribution and heterogeneity of materials, etc.); (2) to insert the object in the appropriate **space and time context** (i.e. absolute and relative dating,

relationship with the surrounding, history of the object, authenticity, provenancing, etc.); and (3) to propose protocols for the interpretation of the object and of the **processes** acting upon it (i.e. assessment of alteration and degradation, preservation and conservation techniques, materials compatibility, interpretation of the origin and use of the object, etc.).

Within this perspective, present trends concerning the application and practice of scientific methods to cultural heritage problems are quite well defined: modern ion and X-ray sources are mostly devoted to analysing materials at the submicron scale, **whereas neutron beams, thanks to their penetrating nature, are leading the way in the analysis of large absorbing objects and real-size 3D imaging and characterization of the materials.** Recent achievements, the present state of the research, and future developments are briefly discussed.

Past achievements of neutron beams applied to cultural heritage

Neutrons can be profitably used in all areas of materials characterization, including *imaging* (2D imaging, 3D tomography), *crystallography* (phase identification and quantification, strain and texture analysis, microstructural characterization), and *chemical analysis* (elemental and isotopic quantification) (**Fig. 1**).

Despite the large number of technical applications, the single most used technique in the past is neutron activation analysis (NAA), that is the use of neutron beam to irradiate the sample and activate all possible nuclear decays within the material. The use of NAA dates back to the early days of neutron beams and it has been especially applied to the chemical analysis of ancient ceramics, glass, and stone artifacts. As a matter of fact most of early systematic investigation of ancient silica-based materials have been performed using neutron techniques. These analyses still stand as a reference for modern research.

Of course **neutron radiography** has also been very popular, because of the ease to insert large objects into penetrating neutron beams, and obtaining real-size images of the interior of objects. A very specific technique widely used in conservation and art history of paintings is the combination of radiography and neutron activation and it is called **autoradiography**. It is performed using the neutron beam as the irradiation sources for activation of secondary processes within the whole painting. The nucleus captures a neutron and turns into a metastable

radioactive isotope that will decay with its characteristic half life emitting an energy quantum in the range of γ -rays. The probability of capture depends on the activation cross-section specific for every isotope. During the irradiation, the painting is fixed on a support in front of the opening of the neutron guide under a small angle ($< 5^\circ$) to the neutrons direction, so that their main free path within the paint layer is maximised. The support is then scanned with a velocity of a few cm/s allowing for a uniform activation of the total area of the panel. Due to the short irradiation time, on average only about 0.4% of the atoms became radioactive and the the method is considered non-invasive. Induced radioactivity commonly falls below safety levels within days. These secondary γ -emissions are detected at different times and form in the 2-D detector images corresponding to the distribution of the specific radioactive isotopes. Since each pigment has a specific chemistry, the elemental distribution corresponds to the use of specific colours in the picture. **Neutron autoradiography is capable of revealing different paint layers buried during the creation of the painting.** In many cases, the individual brushstroke applied by the artist is made visible as well as changes and corrections introduced during the painting process (**Fig. 2**). The technique is very complementary to X-ray radiography and long-wavelength (UV-Vis-IR) reflectography of paintings.

Fig. 1. Different aspects of the use of neutrons in the analysis of cultural heritage materials and objects.

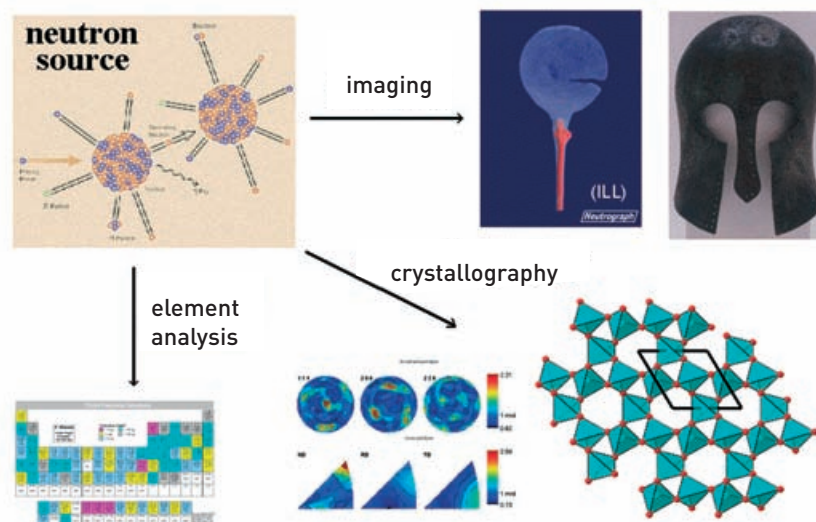




Fig. 2. Autoradiograph (right) of the "Girl with a Platter of Fruits" (c. 1555) by Titian (left). Measurements performed at the Berlin BENSCC reactor (Laurenze-Landsberg et al. 2003).



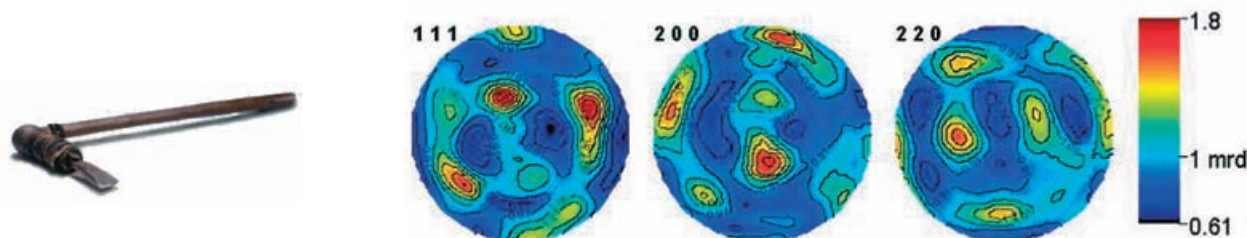
Recently developed methods and applications

In recent years, a number of techniques developed in materials science have also been applied to the cultural heritage problems and materials. The two areas that are most rapidly increasing the quality and range of applications are tomography and crystallography.

Neutron tomography is the natural development of neutron radiography. The stacks of radiographs measured during the rotation of the object in front of the neutron beam are analysed by fairly complex mathematical techniques and a 3D virtual image is reconstructed from the process. The penetration of neutron beams into thick objects and the different absorption processes with respect to X-rays make modern neutron tomography an invaluable tool for art and archaeological research. **Neutron tomography is rapidly becoming a fundamental technique for the preliminary analysis of valuable art objects before and during the planning of conservation strategies.**

Furthermore, many techniques routinely used in the **crystallographic characterization** of materials are now being introduced in cultural heritage studies. Heading the list are the common techniques used in powder diffraction to identify and quantify crystalline phase in complex and composite materials. However, an increasing number of investigation apply more sophisticated full-profile analysis to neutron diffraction data, so to extract valuable information on the microstructure and orientation texture of polycrystalline materials. The neutron texture analysis has been specifically successful in the reconstruction and interpretation of metal manufacturing techniques in ancient metals, so that it may be proposed as a totally non invasive alternative for the metallographic investigation of archaeological metal objects. This is an absolute requirement for unique and precious objects, which can not, of course, be sampled (**Fig. 3**).

Fig. 3. The prehistoric Iceman axe is the only Copper Age axe ever found with original wooden handle and leather ropes (http://www.archaeologiemuseum.it/f01_ice_uk.html). Neutron texture analysis of this unique object and other coeval copper axes greatly helped in the interpretation of prehistoric metallurgical techniques (Artioli 2007).



Possible developments with ESS

Neutrons are becoming an invaluable tool in archaeometry and conservation science.

The pursuing of the European ESS project will undoubtedly bring cultural heritage application even further. Not only the recent development in neutron tomography and in crystallography of cultural heritage materials will become routine analytical tools, but novel, integrated research will be possible thanks to the increased neutron flux and energy resolution. It is now conceivable to propose novel experiments that will integrate imaging, diffraction, and chemical spectroscopy into combined measurements, thus yielding a far greater density of complementary information and at the same time limiting the neutron dose on art and museum objects and the subsequent induced radioactivity. Recent combination of imaging and diffraction, or diffraction and prompt gamma activation analysis are showing the path to be followed.



FURTHER READING

Speakman R. J., Glascock M.D. (eds) (2007) Special issue: Acknowledging fifty years of neutron activation analysis in archeology. *Archaeometry*, 49, 179-420

Laurenze-Landsberg C., Schmidt C., Mertens L.A., Schröder-Smeibidl B. (2003). Neutron autoradiography of the painting "Armida abducts the sleeping Rinaldo (aprox.1637) by Nicolas Poussin. Annual Report 2003 Hahn Meitner Institut, Berlin pp36-37

Ainsworth M.W., Brealey J., Haverkamp-Begemann E., Meyers P., Groen K., Cotter M.J., Van Zelst L., Sayre E.V. (1982) Art and autoradiography: insights into the genesis of paintings by Rembrandt, Van Dyck and Vermeer. *he Metropolitan Museum of Art, New York.*

Artioli G. (2007) Crystallographic texture analysis of archaeological metals: interpretation of manufacturing techniques. *Appl. Physics A*, 89, 899-908.

Artioli G., Kockelmann W., Magerl A., Mezei F., Rinaldi R., Schaefer W., Schofield P.F., Zoppi M. (2002) 6.5 Cultural Heritage: Artefacts and Materials. In: *The ESS Project, Volume II. New Science and Technology for the 21st Century. ESS Council*, 6-47/6-54.

Casali F. (2006) X-ray and neutron digital radiography and computed tomography for cultural heritage. In: Bradley D., Creagh D. (eds.) *Physical techniques in the study of art, archaeology and cultural heritage. Vol. 1. Elsevier, Amsterdam. Pp. 41-124.*

Janssens K., Van Grieken R. (ed.) (2004) Non destructive microanalysis of cultural heritage materials. *Comprehensive analytical chemistry series. Vol. XLII. Elsevier, Amsterdam.*

Leonardi R. (2005) Nuclear physics and painting. *Nucl. Phys. A*, 752, 659c-674c.

Lehmann E.H., Vontobel P., Frei G. (2007) The non-destructive study of museum objects by means of neutron imaging methods and results of investigations. *Nuovo Cimento*, 30, 93-104.

Neutron Study of Ancient Paper: an Example of Early Biomaterials

C. Mondelli

Paper is the most diffuse writing support in the world. The process to produce paper was invented in China in the year 105 by Ts'ai Lun. Before the invention of paper, humans used different supports for writing like stones, clay palimpsest, wax tablets up to papyrus 5000 years ago in Egypt, Rome and Greece and parchments all around Europe in the II century B.C. They are both very light and easy to find. In particular parchment remains very popular in Europe for books up to the XII century when in Spain and in Italy the industrial production of paper started. Only in the 7th Century paper became diffused outside China, firstly in Korea then in Japan and finally in central Asia, where the Arabs learned directly from the Chinese in order to introduce this art in the Middle East and in the Mediterranean. (Fig. 1).

Fig.1 Paper invented in China in 105 A.C. reached Europe in the Middle Age



At the beginning, the Arabs transmitted the know-how of paper production to people in Egypt and Morocco. In 1150, the first European paper mill was installed in Xativa (Spain, Valencia's region), where paper was produced following Arab traditional technique. Paper then made its way to Italy and to Fabriano, where in 1278 the Paper-makers Corporation was born officially. There, the talents of the first papermakers favoured a rapid growth of both quality and quantity of paper production. Probably following the tradition of using hammers operated by water wheels used in the manufacturing of wool - very flourishing in the region at this time - the papermakers in Fabriano started to use multiple hammer hydraulic mill to pound the rag cloths, making the sludge for paper paste, instead of the

stone mortar and the wooden piston operated by hand used by Arabs. This innovation allowed to make better quality paper: very light and thin. Furthermore they reduced the inconveniency of easy deterioration of the paper sheets due to the wheat-starch sizing used by Arabs to condition writing paper. The Fabriano paper-makers substituted the starch substances with gelatine or other animal sizing extracted from discarded meat of the local tanners. The third innovation was the use of watermarks; these are signs used as trademarks of the different paper-makers and that are observable against light, (Fig. 2). Their prototypes were deposited in the appropriated corporation register. The use of watermarks permits today the identification of the production mill of ancient paper and often its date.

Fig. 2 a) Ancient watermark of Fabriano's mills used in the period from 1529 and 1629. b) Watermark of a French mill of XV century



a



b

From Fabriano the paper manufacturing diffused in North of Italy (Bologna, Milan etc.), in France, Germany and in the rest of Europe.

Certainly the Arabs were the original teachers of the Fabrianese papermakers and linen and hemp were the same raw materials used in Fabriano to manufacture paper. But the innovative techniques introduced by them definitely perfected its resistance to time, pathogenic agents and its quality, so that, slowly, it became the most diffused writing material available and the more convenient as it was cheaper than parchment and other materials used prior to its invention. With the new technique of printing on paper, in the

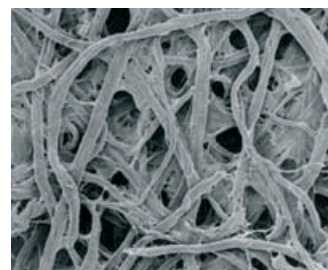
second half of the 15th Century, paper takes on the responsibility as instrument and irreplaceable medium for the diffusion of culture and information.

At the present time, an important part of the prevention of cultural heritage consists on limiting as much as possible the deterioration of hand-made paper artefacts such as books, documents or artistic drawings present in numerous libraries, archives and museums all over the world. In order to develop the appropriate conservation methods, an advanced knowledge of the state of conservation of the artworks and of the degradation processes, which affect them, is necessary.

Fig. 3

a) A microscopic image of paper

b) Layout of structure of paper where it is possible to distinguish the ordered zone in yellow



a



b

From a microscopically point of view paper is like a spaghetti plate composed by polymeric chains of cellulose and it is a quite complex material. It is possible to distinguish two different kind of organization of the fibers: a part completely disordered (amorphous) and a part ordered, where the fibers are quasi-parallel (crystalline) (Fig. 3). In spite of the efforts done to understand the process of degradation up to now we do not know exactly how to define in an objective way the degree of degradation; this fact indicates that we do not know completely the processes of degradation. We know that the atoms of iron present in the ancient inks, reacting with air oxygen favour the decomposition of paper in a process called "slow-fire" responsible of mechanical wakening and discoloration of the substratum. Another killer is the

acidity of paper itself. This acidity depends on different factor, principally on the raw materials used to manufacture the paper. It is responsible of the deterioration of the mechanical properties of sheets, shortening the cellulose polymeric chains.

Neutrons scattering is a powerful technique in order to study materials and it is a fantastic way to study a complex material like paper. Because it is a non-destructive technique we can use it on ancient samples without destroying them.

Depending on the energy of the neutrons used and on the geometry of the instrument, we can investigate 'where the atoms are and what the atoms do'. Technically we can study the structure (the organization of atoms) and the dynamic of the materials (the movement of the atoms). Furthermore neutrons are very sensitive to light atoms as hydrogen, carbon and oxygen that are the main component of organic materials like cellulose. In particular the use of neutrons made possible to discover that only the disordered regions of cellulose are accessible to water and this phenomenon is part of the degradation process. In fact the amorphous regions degrade more rapidly than the crystalline ones.

Several ancient samples were studied with different neutron techniques. They consisted of pieces of dated and identified paper produced from the XV to the XVI centuries in Europe, showing various levels of degradation and discoloration. All of them are sized with gelatine as it was current in the past and they are not printed in order to avoid using samples with degradation coming from the iron present in inks with the associated degradation process of slow firing. The samples are coming from end sheets of ancient books, i.e. the sheets of paper used by the bookbinder at the beginning and the end of a book in order to protect the main text block. This is very helpful in order to determine precisely the age of the paper. Additionally they often present directly a watermark (Fig. 2 b), which allows for a precise identification of the mill where the paper was produced. The results on ancient paper are controlled measuring at the same time modern handcraft pure cellulose with and without gelatine, native or artificially aged. Neutron investigation allows demonstrating that the permeability of water and other external agents are the main cause of cellulose degradation in paper and that solvents are trapped locally in small cavities in between cellulose fibrils. The radius of this cavities (determined by neutrons) increases with artificial and natural aging up to a limit corresponding to the radius of the fibril itself. Such detailed knowledge of cellulose fibers sheds light on the intimate structure of cellulose and will provide a boost to the effort to prevent degradation of important historical paper handcrafts.

Neutrons help to better know the structure, but not only. Neutrons are a very good probe for the dynamics of systems like cellulose. This dynamic can be directly related (under certain conditions) to the concept of fragility like in glass, which is a completely amorphous system. This study shows that gelatine play a fundamental role in the preservation of paper and modify the fragility of cellulose.

Neutrons are a fantastic probe for materials in cultural heritage because they are a non-destructive technique, they are penetrating and

they can be used for imaging and tomography and they are perfect for ancient organic materials like paper, wood, parchment, papyrus and so on. The only limits are imposed from the advance in the neutron technique itself. A new neutron source with higher flux and a wider energy range should not just be suitable but necessary in order to push the studies of ancient and modern systems.

For that reason the new source ESS may allows a strong advancement in the field of cultural heritage, which is a field of research bridging different disciplines, touching a general public.



Neutron Scattering Applications to Cultural Heritage Materials and Artefacts

R. Rinaldi

The recent vast expansion of neutron scattering techniques to scientific and technological applications has involved all areas of the wide field of materials, including organic and inorganic, natural and man-made, modern and ancient. This last aspect has recently proven to be particularly attractive when considering the peculiar neutron properties and the interactions neutrons have with matter as compared with other penetrating radiation. Furthermore, such a wide expansion has inevitably created new needs for instrumentation developments in order to answer specific questions raised by the various fields of application.

An earlier and still valid application of neutrons in archaeology is that of instrumental neutron activation analysis for the detection of trace elements and isotopes in the materials under investigation. However, while such technique can still be applied to full advantage in archaeological research, especially in its more recent variety of the prompt gamma activation, it does not represent the main focus of present and future research in archaeology and archaeometry with present day and future neutron sources where scattering and absorption processes are usefully employed to widen the scope of material research analysis to include ancient materials. The aim is that of gathering otherwise unobtainable information on the nature and origin of the raw materials used in the manufacture of ancient artefacts, reconstructing technological development and trade paths of the artefacts and evaluating the state of preservation of the finds in a totally non-destructive, non-invasive mode. **When compared with other physical methods of material analysis, neutrons can provide complementary and unique answers to all of these questions on relatively large, intact and potentially precious archaeological objects.**

Such capabilities stem from the interactions of neutrons with the atomic nuclei rather than with the electrons of the atoms, hence on a length scale which is five orders of magnitude smaller when compared with X-rays. The result is a much deeper penetration (low attenuation) into most materials and independent of atomic number (and isotope). The inevitable draw back of such weak interaction consists of a correspondingly weak signal. This however, can be overcome, to a great extent, with the advent of higher brilliance sources such as the ESS.

4.3

Achievements of neutron scattering in archaeometry and conservation issues

Neutron scattering, especially at spallation sources in the Time of Flight mode, is particularly suited to non-destructively investigate ancient materials and artefacts for the following reasons:

I Neutrons provide a signal from the bulk of the sample, hence independent from surface alteration or corrosion layers. These, in turn, can effectively be detected as distinct signals, providing useful information for conservation issues. In the case of polycrystalline materials such as metals, alloys, ceramics, stone, etc., phase compositions can be derived by Rietveld analysis of diffraction patterns which neutrons provide at very high resolution. In alloys such as bronze, the element composition can be derived from accurate measurements of the unit cell expansion due to the incorporation of Sn into the copper fcc lattice. Accurate profile analysis yields information on strain and micro-strain produced during manufacture.

II In polycrystalline materials, the large volume investigated is representative of the whole object (even for coarse-grained materials) and offers good statistics for mapping crystal orientation distributions for texture analysis as well as for coarser textural properties such as grain/voids in porosity measurements and mixing/mingling properties of poly-phased materials. This can provide fingerprint information, e.g. on working treatments for metals and alloys, on geologic history and physical properties for stones, aggregates, and materials in general.

III Minor phases can be determined within the bulk as well as on the surface of the object (corrosion, alteration layers, precipitates, etc.) at the level of a few tenths of a wt% or at much lower detection levels with the advent of more powerful neutron sources, such as the ESS.

IV Neutron scattering is rather insensitive to geometry and shape of the objects under examination, hence no sample preparation is needed. The object is left undisturbed and the analysis is totally non-destructive. In the time of flight mode, none or very little movement of the sample is needed to acquire a complete pattern up to high scattering angle. Multi-detector set ups can considerably reduce exposure times by increasing count rate and count statistics of data collection.

V Activation decay is very fast for ceramic and stone and relatively fast for metals and alloys (generally within minutes/hours in the former and hours/days in the latter) for the few hours of exposure needed for data collection.

Phase identification and quantification, microstructure, strain and texture analysis of archaeological objects by neutron diffraction has only recently been undertaken, but **the potential applications of such in-depth investigations span many fields of interest within archaeometry, conservation, archaeological and natural history research**, ranging from routine fingerprinting to complex conservation problems. The standard diagnostic tools used today for stone, minerals, ceramics, plasters, paintings, glass and metals, are not suitable for the characterisation of inhomogeneities at both the microscopic and macroscopic scale, that would provide information on material properties such as: element distribution, crystalline structure, mixing and mechanical properties, thermal treatment profiles, etc., developed during manufacture. For instance, hydration, segregation, alteration, chemical and physical inhomogeneities, twinning, crystallinity, texture, strain, etc., all represent fundamental aspects required for the determination of the historical and cultural background of archaeological findings, to correctly reconstruct their history, provenance, manufacturing technology, trade paths, and to evaluate material deterioration.

The examples reported in the following paragraphs provide just a taste of the achievements and future prospects in only a few of the many fields of application to ancient materials and artefacts which may be envisaged.

Ancient bronze alloys

One of the many recent examples of time of flight neutron scattering applications to ancient bronze at a spallation neutron source (ISIS, UK), dealt with the ancient metal technology during the Bronze Age in the Po valley region, Northern Italy. Pieces pertaining to three different classes of materials as to use and manufacture (tools, arms and ornaments), dating from the Middle to Late Bronze Age, were investigated. Different workmanships were involved in the production of such diverse pieces; evidence for manufacturing signatures could be detected. The objects exhibit a wide range of Sn contents and different degrees of alloy homogeneity; higher Sn contents are associated with the presence of two bronze phases (α and δ), also coexisting with some unalloyed pure Cu. These results provide fundamental information on casting and production methods. The identification of oxidation and alteration products such as cuprite and nantokite is crucial for conservation issues. **(Fig. 1)** provides a quick review of some of the results obtained. Many are the neutron-based techniques that can be applied to ancient metal research especially when non destructiveness is a must.

Ceramics

During firing of ceramics the starting materials undergo solid state reactions and phase transitions depending on the firing temperature, duration and atmosphere. Ancient or pre-historic ceramics fired at moderate temperatures often exhibit very complex diffraction patterns due to a wide variety of mineral phases, among them clay minerals and sheet silicates which need high intensity and resolution for identification and quantification. Many such studies have appeared recently and the need for high intensity and high resolution is strongly felt also in order to speed-up the measurements and increase sample through-put.



Stone materials (surface reactivity, water content, texture, etc.)

The specific problem of stone degradation in historical buildings needs the detailed characterisation of the constituent materials and textures, including porosity and fluid contents. The methods and techniques are identical to those used in the investigation of modern building materials such as cements and concretes, or in geological materials (rocks) of various origin and technical properties. Water, carbon dioxide and sulphate ions are largely responsible for the degradation of natural building stones even when present in very low concentrations; the detailed study of such systems on a micro- and nano-scale can solely be addressed by the unique capabilities of modern neutron facilities. A detailed study of the kind of reactions involved in stone degradation and depth reached within the material, carried out also by neutron scattering investigations, is guiding the recent interventions undertaken for the restoration of the stones on the exterior of the Cathedral in Vienna (Fig. 2).

Direct imaging, radiography, tomography

Neutron penetration can be advantageously exploited for imaging applications in order to determine the inner features of bulk, opaque materials and artefacts. The morphology, composition, density and phase distribution beyond the reach of less penetrating probes can be addressed also in view of specific applications in archaeology and preservation. An example of such applications is given in Fig. 3.

The neutron flux supplied by the ESS will enhance the quality of artwork imaging through the use of energy-tuned narrow (but still intense) neutron beams, and the use of fine collimators and high resolution detectors for phase enhanced contrast.

Conclusions and future prospects

Neutrons, as opposed to electromagnetic radiation (such as X-rays), are the best probe for examining the intimate bulk properties of thick, undisturbed samples as in the case of unique cultural heritage materials and artefacts. Neutron analysis, which is intrinsically non-invasive, is both unique and complementary to more conventional techniques. When sampling is not possible, neutron methods provide chemical, phase specific, microstructural and textural information from undisturbed large volumes.

The many-fold increment in signal and resolution afforded by the most modern sources and instruments planned for the ESS, will allow element sensitive small volume phase identification and quantification, accurate determinations of manufacturing signatures, detailed crystal structure analysis of the constituent phases, and direct imaging in two- and three-dimensions by digital imaging and tomography techniques also enhanced by phase contrast, energy-tuning and polarized neutron techniques (the last for magnetic contrast).

These methods can certainly provide a clearer picture of the technological, commercial and, more generally, historical and archaeological features of the finds and also help in solving authenticity problems. With a view to preservation, they can provide invaluable information towards the choice of restoration and conservation procedures.

As with the natural materials and mineral sciences, the potential of neutron scattering is only recently being realised in the fields of archaeometry and preservation of cultural heritage materials and artefacts. With the availability of modern and future neutron sources such as the ESS, there is much to look forward to with the opening of new avenues in this field of study.



Fig 1. Example of a Bronze Age axe (courtesy of Museo Civico Archeologico Etnologico, Modena, Italy) with the (111), (200) and (220) pole figures from data collected on the cutting edge showing moderate texture due to working procedures. The (111) reflection profiles from three of the samples reveal very different Cu/Sn contents responsible for d-spacing peak shifts. The highly structured profile (in red) reveals the presence of a wide

range of compositions within the same sample, including a considerable proportion of unalloyed Cu. The bronze alloy with the highest tin content contains some delta phase. Background; the reconstruction of typical Bronze Age "Terramare" dwellings in the archaeological park of Montale, Modena, Italy. [Ref.: J. Phys.: Condens. Matter 20 (2008), 8pp, DOI:10.1088/0953-8984/20/10/104253].

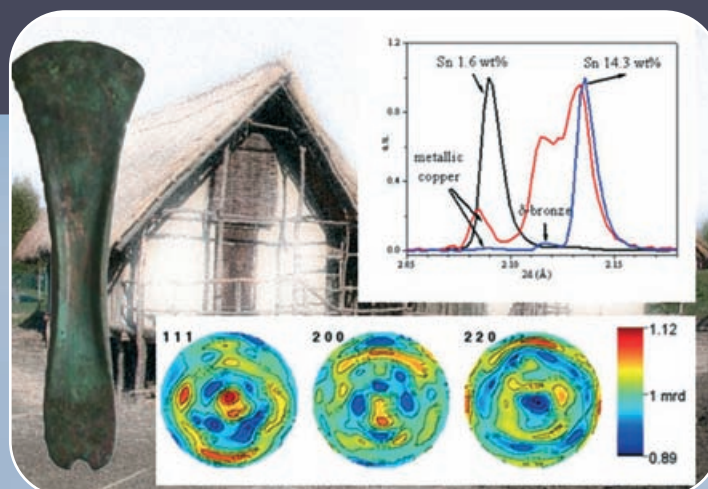


Fig. 2. Restoration interventions on the limestone of St. Stephan Cathedral, Vienna, are based on the accurate determination of the depth reached by the surface degradation of the carbonate into sulphate (which neutrons can easily detect), in order to induce the chemical reversal of the reaction throughout the whole alteration layer. Left: work has begun on the main spire in 2008. Centre and right: the black alteration patina and crust is a sure sign of the dangerous alteration into the water-sensitive Ca-sulphate which would eventually cause the total loss of the stone carvings in a relatively short time.



Fig. 3. Neutron tomography of Renaissance bronze statuette "The Sun" (courtesy of Rijksmuseum, Amsterdam) manufactured in Nuremberg (ca. 1575). Left: outer contours, right: tomographic slice through the middle. Total height: ~46 cm. The outer and inner properties of the cast are revealed showing manufacturing details. (E. Lehmann, RICH Workshop, Trieste, Dec. 2005).



Transport Technologies

5



5.1

**Residual Stresses with Neutrons
in Automotive, Aeronautic and
Railway Industries**

J. Ruiz Hervias

5.2

**Neutron Radiography and
Tomography in Engines and
Rockets**

M. Ceretti

5.3

**The Importance of Neutrons
to assess the Quality of
Welds**

G. Bruno

5.4

**The use of Neutron for
the Study of Composite
Materials used for Engines**

G. Garcés



Residual Stresses with Neutrons in Automotive, Aeronautic and Railway Industries

J. Ruiz Hervias

Residual stresses are those that remain inside the material after their original cause (i.e. external forces or temperature gradients) has been removed. They are generated by the different thermal and mechanical treatments employed in the fabrication of a component and they can be modified by applied loads during its service life. Residual stresses may cause dimensional changes and distortions in the components which render them useless for engineering applications. As an example, during welding, the temperature of the welding zone is higher than the temperature of the base metal. When the finished weldment cools down, contraction of molten metal during solidification is resisted by colder surrounding metal, leaving residual stresses.

Residual stresses are dangerous because, unlike applied stresses, they are concealed. Consequently, engineers do not take them into account in design, and this may cause unexpected failures. If residual stresses are high enough, cracks will develop in the material with the risk of catastrophic failure. This is particularly important in the case of high-risk components for the transportation industry (automotive, aeronautics and railways), where residual stresses are essential in making reliable estimates of life times.

There are several methods to measure residual stresses, including destructive and non-destructive techniques. From the non-destructive techniques, diffraction methods (X-rays and neutrons) are the most widely used for a quantitative assessment of residual stresses. X-rays are very useful for surface and subsurface measurements (with material removal, up to approximately 0.5 mm depth). However, if a bulk measurement is needed, **neutrons are the best choice. They penetrate easily into engineering materials (i.e. steel and aluminium alloys) and can provide truly non-destructive residual stress measurements inside large components.**

In the following sections, some examples of the importance of residual stress determination in the automotive, aeronautic and railway industries will be presented.



Automotive industry

One of the main issues driving innovation in the automotive industry is the reduction of fuel consumption. This is very important both from the economic and environmental perspectives. One way to achieve this goal is to reduce automobile mass, by using new materials.

A very important element in automotive engines is the crankshaft, which translates the linear piston motion into rotation. A great potential exists in decreasing its mass and increasing its lifetime by replacing the currently used material, cast iron, by steel. When the engine is running, the crankshaft is subjected to mechanical fatigue. This can be particularly damaging at locations of stress concentration, such as holes or sharp edges, as shown in the broken crankshaft of **Fig. 1**. In this case, the failure was initiated at a fillet (stress concentration) and was propagated by fatigue. Surface treatments are used to improve the durability by generating beneficial residual stresses in the near-surface layer of the component. In order to quantify and optimize the particular surface treatment employed, residual stresses have to be measured deep inside the crankshaft at the most critical locations. This can only be achieved by neutrons, due to its high penetration in steel.



Fig. 1. Original and broken crankshaft. Failure was initiated at a fillet and propagated by fatigue

Residual stresses have been measured by neutron diffraction in the fillets of crankshafts up to approximately 5 mm depth. Although the measurements are

very time-consuming, the obtained results served for an optimisation of the process parameters and to calibrate routine quality control procedures.



Aeronautic industry

The design and construction of aircrafts is nowadays influenced by several factors, i.e. safety, cost reduction, weight saving and reduction of CO₂ emission. Consequently, materials with improved performance and optimized production processes are needed. However, the introduction of new materials and techniques in aircraft production processes is slow because of safety issues.

There are two areas where residual stress control is particularly important: high-energy efficient turbine disks and advanced joining techniques for airframe structures.

Residual stresses in turbine disks

Nickel-based superalloys are used in turbine engines. The manufacturing process involves thermomechanical treatments which induce considerable residual stresses inside the disks. As a consequence, unacceptable geometrical distortions are produced during machining of a disk to its final shape. It is then mandatory to accurately characterize the through-thickness residual stress profile, in order to adjust the fabrication process to minimize distortion.

The size of a typical turbine disk is relatively large (320 mm diameter, thickness up to 25 mm). Neutron diffraction has been applied to study residual stresses inside the disks. However, experimental measurements in real components are limited. Thinner samples are used instead because much less measurement time is required.

Residual stress control in advanced welding techniques

The different components of an aircraft's frame are joined to each other by means of rivets. Each rivet is a potential source of cracking (as can be seen in **Fig. 2**) and adds considerable weight and cost to the structure. Existing fusion welding techniques are particularly difficult to apply to high strength aluminium alloys used for aircraft frame. Advanced welding techniques, such as laser beam or friction stir welding, are considered as candidates to substitute riveted airframe structures, due to the potential weight and cost reduction involved. However, a number of issues have to be solved before. In aluminium alloys, the mechanical

behaviour of the weld material is worse than that of the base material. In addition, there is limited information about the generation of residual stresses with advanced welding techniques.

In the future, we can envisage fully rivet-free aircraft frames. For this purpose, skin-skin joints will be needed, joining larger aluminium panels. **However, the structural integrity and durability of these large welded panels will have to be thoroughly assessed, and a detailed evaluation of the residual stress state in various sheet thickness and heat conditions is essential. This can only be achieved by neutron diffraction.**



Fig. 2. Failure of a riveted aluminium skin panel which has penetrated the fuselage.



Railway industry

Residual stresses are important in railway industries due to safety concerns. Recent railway disasters were caused by failure of wheels and rails.

In the case of rails, the manufacturing process involves bending/unbending operations to straighten the rail. This leaves residual stresses inside the rails which are later modified by the high contact stresses between the wheels and the rails. During service, cracks are initiated below the rail surface. They remain undetected while they propagate inside the rail under tensile stresses, as shown in **Fig. 3**. Sudden failure occurs when the cracks become critical. The interaction between the residual stress state inside the rail and the crack propagation process is not precisely known yet. Experimental techniques to study residual stresses in bulk pieces of rail would be needed.

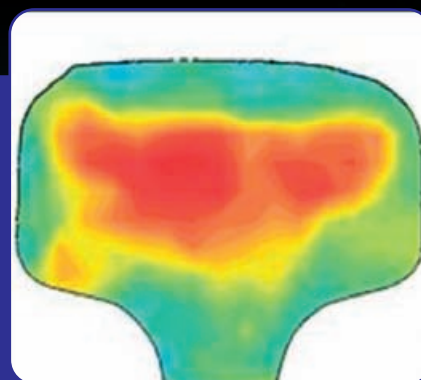
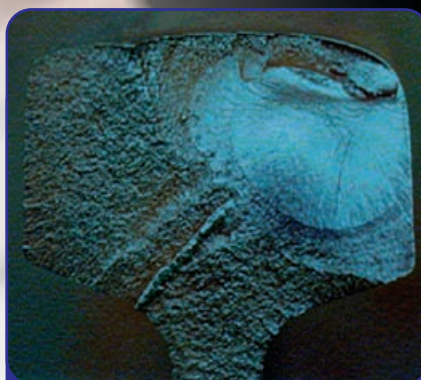


Fig. 3. Example of a failure from and internal defect in a rail, and neutron residual stress map (courtesy of NCCR, NIST) of a rail slice (red is tensile stress)

In all of the examples presented there is a need to measure residual stresses deeper inside real engineering components and structures. In addition, the spatial resolution and the sensitivity should be increased while the measurement time should be decreased. It is believed that ESS will contribute to improve the above-mentioned issues just

because of the increased neutron flux. Dedicated high-resolution instruments will allow us to measure real size components in more realistic conditions. An improved understanding of residual stresses will lead to a surer foundation for structural integrity assessments in the transportation industries.

Neutron Radiography and Tomography in Engines and Rockets

M. Ceretti

In recent decades, the transport sector has grown tremendously, with far-reaching implications for citizens and environment. The development of innovative technologies is nowadays a key issue of transport research in order to meet important challenges:

- Reducing the environmental impact of transport, including harmful emissions and noise.
- Increasing the efficiency of combustion of e.g. fossil fuels.
- Improving safety and security of transport operations and services.
- Increasing mobility of people and goods.
- Improving competitiveness.

In this context, the development of new and improved materials as well as new processes is a key issue to mastering many of these challenges.

Among the different experimental techniques used to characterize these materials, neutron scattering is a valuable tool for a variety of applications. Neutrons can deeply penetrate into most engineering materials, thus delivering integral, bulk information; e.g. aluminum or commonly used steel are nearly transparent to neutrons. Neutrons are also sensitive to lighter elements, in particular to hydrogen or lithium. The characterization of matter using neutron

scattering techniques provides much more complementary information compared to that obtained from X-rays. Even if the flux offered today by the most intense neutron sources is several orders of magnitude behind the brilliance of the 3rd generation synchrotron source, **the specific properties of neutrons yield unique possibilities for the non destructive characterisation of components, either fabricated or under service condition, as engine parts.**

Among the different scattering techniques, neutron radiography and tomography are particularly well suited for the imaging of inner features of engineering units, inaccessible by any other techniques.

Neutronography is a neutron imaging technique which provides “snapshots” of the internal organization and positioning of a heterogeneous object. The principle is quite simple (**fig. 1**): a collimated neutron beam of a given neutron source impinges the object to analyze. The transmitted beam, which is attenuated by different absorption and diffusion mechanisms, is then recorded by a detector. As different materials have different attenuation behaviours, the neutron beam passing through a sample gives information about the composition and structure of the sample, giving a two dimensional image which is the projection of the object in the detector plane [1-2].

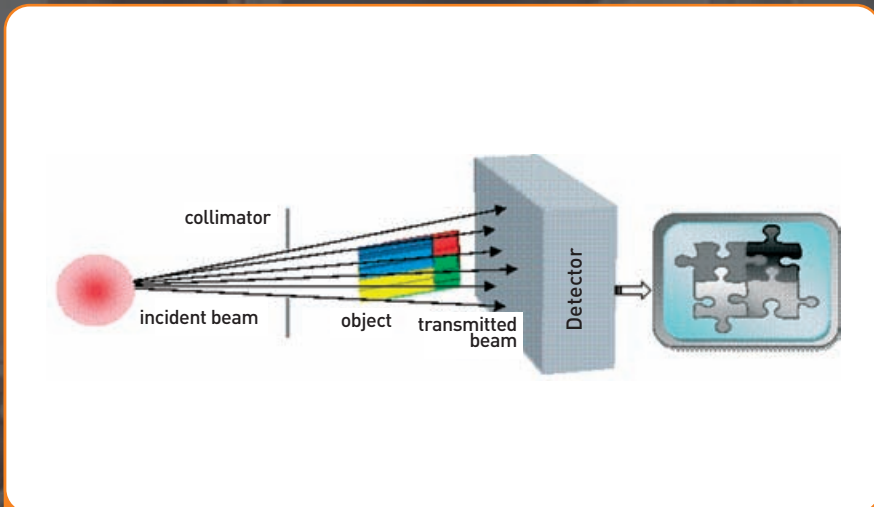


Fig. 1: Scheme of a neutron imaging experiment: a neutron beam of a neutron moderator is collimated, passing through the sample and finally registered by a 2D neutron detector (film, image plate, CDD...)

One example is shown in figure 2, all the inner parts and all the rubber toric joints of some pyrotechnic cutters used in ARIANE 4 space programme are clear.

In the nuclear sector, neutron radiography is used to control the nuclear fuel rods before or after irradiation (quality of the filling, changes in shape and dimensions of the pellets induced by the irradiation), or of the control rods containing neutron absorbing elements.

Another fundamental feature of neutron imaging is the possibility to have a direct examination of dynamic events. The resulting information helps in understanding the dynamical behaviour of complex systems. Most of the applications known so far consist in visualisation of fluids moving through metallic containers, as the hydrogen atoms included in such fluids (generally hydrocarbons) are detected by neutrons. At today's neutron sources the exposure time for neutron radiography is typically of the order of seconds. For imaging fast-moving objects, exposure times are required below one millisecond, which today is only possible by using stroboscopic imaging [3].

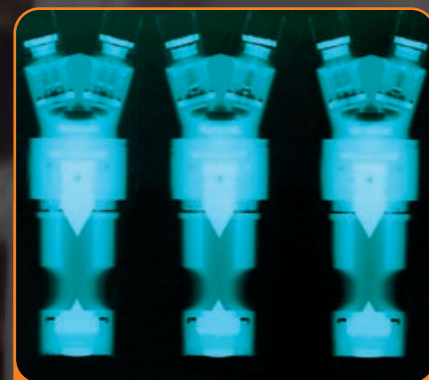


Fig. 2 : Neutron radiography images (Orphée/CEA) of pyrotechnic cutters (Dassault-Aviation) used in ARIANE programme. About 400 pyrotechnic cutters as well as all the pyrotechnic elements for ARIANE 5 have been checked by neutron radiography.

By combining images from measurements at different angles, tomography reconstruction may be carried out, giving a three dimensional image of the internal structure of an object.

Applications of neutron imaging techniques in engineering transport sector

The early days of neutron radiography date back for more than 50 years and today it is one of the principal tools for industrial non-destructive testing. Many neutron sources around the world are equipped with neutronography facilities. This technique provides very high quality images, comparable to those obtained by X-ray radiography, and adds specific contrasts, too. Indisputably, a certain number of critical defects could not be detected without neutron radiography. **Unlike any other imaging technique, it is the only tool visualizing even quantitatively components containing hydrogen inside metal envelopes of several centimetres thick.** To state some applications providing useful expertise in the transport sector, we can emphasize:

- Corrosion control in aluminium aeronautics components (hydroxide formation, detected already at 30 microns depth);
- Control of welded joints homogeneity and quality;
- Control of the spatial distribution of precipitates in composites materials;
- Control of seals, coatings and joints containing hydrogen;
- Inspection of the quality of a filling (by a powder or a resin), for examples in explosives.

At present, **Neutron Radiography is one of the main Non Destructive techniques, able to satisfy the quality-control requirements of explosive devices used in space programmes.** One of the first applications in this field was to check the continuity of explosives in the detonator fuses, used in space pyrotechnic. In recent years, most of the space launchers in the ARIANE space programme have been systematically controlled by neutron radiography (Orphée/CEA Saclay, France). The aim was to exclude eventual critical defects in the explosive after its fabrication and to check the coolant system of engines for permeability prior to each launch in order to prevent any fatal overheating.

The main fields where dynamic neutron imaging has proven to have enormous potential are:

- Oil lubrication (engines, gear boxes...)
- Fuel behaviours (carburettors, injectors...)
- Two-phase flow phenomena (heat exchangers, condensers, steam generator tubes, fuel cells...)
- Transfer and migration of fluids into porous media (wetting of soils, pollution migration, plant growth...)

Of particular importance for such investigations is the neutron's unique ability to see liquids, with high precision, even in heavy and complex environments. This is particularly important to study lubrication processes. In fact, it is known that ineffective lubrication leads to permanent wear and failure of mechanical parts, which causes relevant damage. **Fig. 3** shows a neutron radiography of a car engine. With stroboscopic neutron imaging technique it was possible to study the oil flux in a running engine [3].

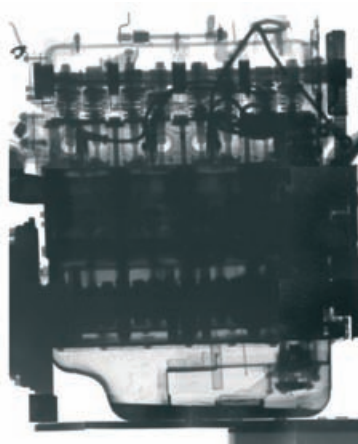


Fig. 3: A FIAT 4 stroke engine rendered semi transparent by neutron radiography.

<http://www.physik.tu-muenchen.de/antares/>

In the search of new and clean energy sources, fuel cells promise to generate electricity and heat, replacing internal combustion engines in the transportation sector. Effective control of water distribution in fuel cells is a key factor to maximize their performance. Neutron radiography, performed *in situ* within an operating fuel cell, is a powerful tool [4]. In particular, the ability to simultaneously correlate water distribution with cell operating conditions and cell performance provides a degree of understanding of water management that is not available with any other existing technique.

Neutron tomography provides accurate three dimensional images of objects by a mathematical reconstruction of a big number of projections taken in different sample orientations. It is thus understandable that, once the introduction of highly efficient and high resolution two dimensional neutron detectors takes place, neutron tomography will be introduced as non destructive industrial testing technique [5].

Fig. 4 shows a neutron tomography of an aviation turbine blade, with a detailed reconstruction of the inner structure. The internal void structure as well as the small holes for the cooling air flow of the blade are clearly visible. Examination of turbine blades with X-rays is not possible due to the high attenuation coefficient of titanium alloy.



Fig. 4: Neutron tomographic reconstruction of a section of a coated Ni superalloy single crystal jet turbine blade.

<http://neutra.web.psi.ch>

New ideas for experiments in this field potentially relevant for ESS

All these applications in transport sector have a common object: to improve safety by checking whether engines, cars, aircraft or rocket components are functioning reliably, regarding any possible features to avoid any fatal damage. However, relatively little industrial neutron radiography/tomography has been undertaken at present because it is too time consuming and space resolution is quite lower comparatively to X-rays.

The new European Spallation Source ESS will provide an unprecedented high neutron flux: gain factors exceeding three orders of magnitude are expected. **The increased flux and intrinsic time structure of the neutron beam will allow new investigations with innovative instrumentation inconceivable on existing neutron sources** [6]. These improvements will have a huge impact on neutron radiography/tomography: ESS will add a new dimension to real scale tomography and radiography. The new source will enable large field (200x200mm) sub-millimetre resolution images to be obtained in seconds and thus tomography of large industrial component experiments will become routinely feasible. Furthermore, the pulsed nature of the beam will allow the development of a new area of science, such as structural mapping neutron tomography. In this context, the time of flight method will allow the use of the Bragg edge cut-off techniques to identify different components and phases within engineering components.

The high neutron flux will enable real-time studies of time dependent processes and the routine operation of neutron tomography. The readily understandable results and the clearly visible complementarity to X-ray radiography will guarantee industrial interest in this kind of technique.



In short, the scientific goal for research investigations at the new generation neutron source will be the study of time dependent processes (also real time operation of components) in real components and in real environment. To state only few of the possible application relevant in the transportation sector, we can think of the neutron tomography of machine parts under working conditions in real time, and with structural sensitivity, with a real scale monitoring the performance of lubricants or cooling fluids within engines. In the field of fuel cell development, ESS will allow a strong contribution to improve their performances.

Acknowledgement: Dr. G. Bayon (Orphée/CEA Saclay) and H. Lehmann (SINQ, PSI, NEUTRA) are gratefully acknowledged for providing pictures.



FURTHER READING

- [1] G. Bayon, "Neutronographie et radiographie aux neutrons", in « Neutrons et Matériaux », EDP Journal de physique IV, Vol. 103 (2003)
- [2] E. H. Lehmann, "Neutron Imaging Methods and Applications" in Neutron Applications in Earth, Energy and Environmental Sciences, Chapter 11, Springer Science (2009)
- [3] B. Schillinger, J. Brunner, E. Calzada, "A study of oil lubrication in a rotating engine using stroboscopic neutron Imaging", TUM Institute for Experimental Physics E21, Annual Report 2005, 26-31
- [4] D. Kramer, E. Lehmann, G. Frei, P. Vontobel, A. Wokaun, G.G. Scherer, Nuclear Instruments and Methods in Physics Research A 542 52-60 (2005)
- [5] B. Schillinger, R. Gebhard, B. Haas, W. Ludwig, C. Rausch, U. Wagner "3D Computer tomography in Material Testing and Archaeology", 5th World Conference on Neutron Radiography Berlin, Germany, June 17-20, 1996
- [6] M. Ceretti, R. Cowley, M. Daymond, T. Lorentzen, A. Magerl, P. J. Withers, H. Zabel "Materials Science and Engineering at the ESS" in New Science and Technology for the 21st Century, the ESS Project Vol. II (2002)

The Importance of Neutrons to assess the Quality of Welds

G. Bruno

A friend of mine wanted to change the bearings of his car and I objected to him that he needed a press (**Fig.1**) to do it properly. However, he replied that he could build one himself. Indeed, he said, he just wanted a couple of metal beams, since he had a welding kit available.

Yes, welds are present in everyday life at all level of complexity, and basically all (metal?) components you may encounter with a non-trivial shape are welded together. Cars, airplanes, pipes, nuclear reactor vessels are usually welded.

Most probably, if my friend's press fails, he will not be able to mount the bearings, but you may want a higher level of safety if we speak about the frame of a car and you want to be more than sure that your nuclear reactor vessel will not fail at the weld. Moreover, my friend's press is only subject to the forces applied by its use, high-tech components are subject to much more severe conditions. An airplane is subject to shocks and impulsive loads during landing, a reactor vessel is exposed to corrosive environment (hot steam or pressurised water) and thermal gradients, in addition to the usual operating loads (e.g. the internal pressure for a vessel).

This complicates the assessment of the component's life and increases the level of confidence with which one wants to qualify those materials and parts.

For this reason, very sophisticated models are being developed by means of the most state-of-the-art software packages (e.g. Finite Elements Modelling), statistical treatments and computers. Those models need the most reliable input experimental data to be safely validated. Those data need to be obtained in conditions as near as possible to the real



Fig.1. A commercially available bearing press

operating conditions and anyway on real parts (i.e. with the actual component geometry).

It is evident that laboratory characterization equipments can only give partial answers to this request. They certainly yield very useful information on the materials behaviour and properties, but very rarely they can qualify the parts as a whole. Indeed, the information is often averaged (think of the detection of cracks by means of ultrasounds) or extracted from surface layers (like in the case of X-ray inspection of pipes or railways).

The key word is non-destructive

While in many of other articles of this booklet you may read that the keyword is Neutron, here it will not be the case. When it gets to life assessment of keystone components, the most important criterion for their characterization is non-destructive. Once we can provide the modellers with data taken in a *non-destructive* manner, many of the main requirements are fulfilled for the most realistic and reliable characterisation and subsequent predictions. We can, in fact, keep the geometry of the real part, we can investigate a component, which has undergone real operating conditions, we can observe the cross-correlation of all parameters affecting the life duration. This complicates the analysis, but discloses unexpected correlations

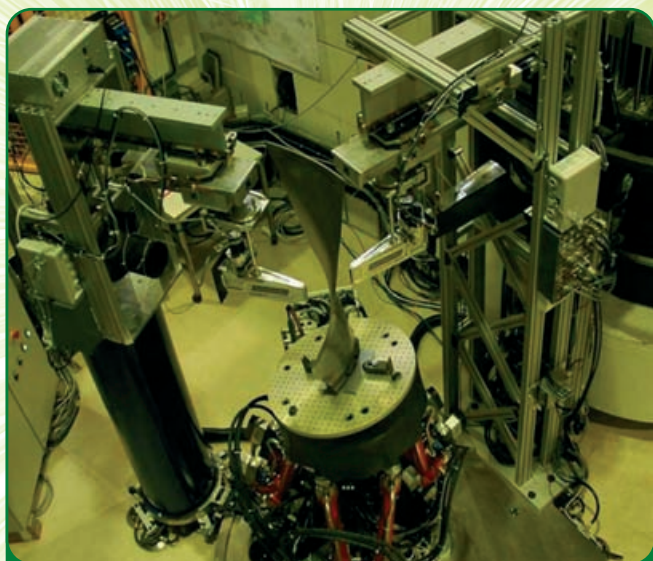


Fig. 2. An airplane turbine blade can be mounted on the Hexapod of SALSA, the strain imager at the ILL, Grenoble, France. Taken from [2]

It is natural, then, that the word Neutron comes into mind when talking non-destructive. Indeed, Neutrons have such a large penetration in matter (apart some very special elements or isotopes) that they can probe the interior of very thick components (metallic or not) without any problem. To clarify this, even the hard X-rays and the number of photons available at a synchrotron would be almost useless if your gear wheel is covered by molybdenum [1].

One of the most successful applications of Neutrons is the determination of Residual Stresses in real components (and of course in ideal specimens). Non-destructive, for sure.

Well, residual stresses are locked in components because of inhomogeneities in their shape, their properties or the operating conditions they have been submitted. They have nothing to do with what you can measure by pulling or pushing a bar (what is called a tensile test, supposed to give the material's

behaviour under uniaxial stress), for the simple reason that if we permanently deform a metal bar, while pulling it, creating what is called 'necking', we do not induce residual stresses! Residual stresses are (and must be) considered as a part of the material's microstructure, but they are not visible under a microscope. You can imagine how difficult it must be to detect them. Well, someone (actually many, see e.g. [2]), long time ago, found a way: using diffraction. **The idea is to use the crystal lattice planes of a grain as the "gauge length" from which we detect the deformation of our part.** If we use a probe, which goes straight to the point where we want to detect the information and yields information averaged over a statistically significant number of grains, then we can safely say that the small region investigated has such and such amount of stress. This probe is the neutron. **This is why several instruments have been built at neutron sources all around the world, to exploit this fact (see Fig.2)**

Another problem, which may come on the way is the following: if we know the response of the grains probed by neutrons at a particular location in our component, how can we be sure that those grains represent that location? More technically, we must bear in mind that diffraction probes only those grains oriented in the good way with respect to the incident neutrons. This is not much. One way to increase this number is to use a 'white' beam, i.e. neutrons of several energies (wavelengths). This is done at the 'spallation sources'. In this way we access the whole diffraction pattern, i.e. all (well, many of) the peaks and can properly average the strain over differently oriented grains. It is this average strain and stress, which is to be considered as the nearest to the macroscopic, ultimately engineering relevant.

Why Neutrons for Welds?

Welds have sometimes very complicated microstructures and carry high residual stresses, due to the very different thermal histories of even adjacent points.



Fig. 3. Macrograph of a TIG weld. Very differently oriented and shaped grains are present together with cavities. Courtesy of O.Fraboulet (Corning SAS, CETC, Avon, France).

In fact, the temperature gradients can reach several hundred °C/cm during welding. Those mismatches can create situations where even the reference material (ideally unstrained) can change. Imagine what happens in a classical weld (e.g. tungsten

inert gas, TIG): the materials melt at their joint and re-crystallise under very different conditions. Heat and matter flow occurs in very short times, thus creating the typical dendritic structures or elongated grains (**Fig. 3**), actually very nice to observe. Moreover, the flow direction depends on the shape of the weld: for a V-weld, it will roughly follow the inclination of the bead. It can be expected that also the stress field changes its orientation with the microstructure.

The reader may have understood that tackling those problems non-destructively is a real challenge. But Neutrons can do that. Mapping the residual stress throughout the weld has now been done several times, see **Fig. 4** for some examples [3,4], and we now know a great deal about, for instance, the difference between the heat affected zone (HAZ) right near the weld seam and the strain affected zone (SAZ), which may extend several mm from the seam.

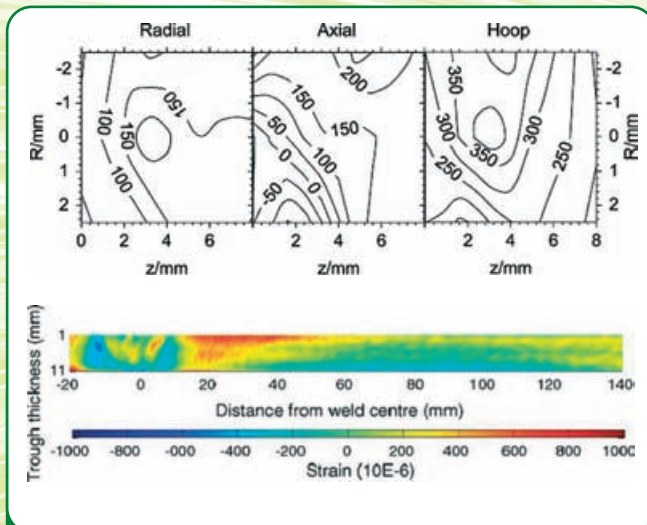


Fig. 4. Two examples of strain/stress maps in an inertia weld [taken from [3]], i.e. cylindrical component and in a metal inert gas (MIG) weld [see [4]], i.e. on a steel plate

In this respect, as mentioned above, the use of pulsed sources adds the crystallographic average to the grain statistics and therefore permits a direct comparison between the strains determined by diffraction and those measured by destructive macroscopic techniques, like the contour method. Another interesting aspect of the use of pulsed sources is the possibility of mapping the reference lattice parameter (to which the measured lattice parameters need to be compared in order to calculate strains). The technique of Neutron Transmission Diffraction [5] is particularly suitable to this end. By tilting a slice cut through the weld, one can map the reference variation and directly compare with non-destructive mapping on the real component (like exemplified in **Fig. 5**). Although one may argue that this becomes no longer non-destructive, it is clear that the insight that neutrons (and in particular pulsed neutrons) can bring to the assessment of the microstructural variations

and those of the stress state in real components is unrivalled and in fact unique: the modellers start having reliable and suitable data for their calculation and predictions of component life duration, the materials scientists deepen their understanding of the phenomena in such complex situations. Finally, the society benefits of this increased level of confidence and safety.

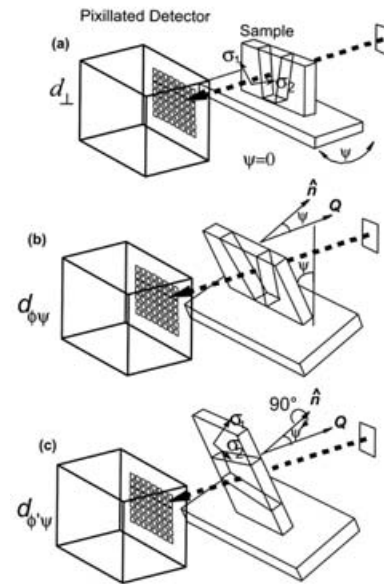


Fig. 5. The three orientations necessary to determine the reference lattice parameter map in a weld, by means of neutron transmission diffraction [taken from [6]].



FURTHER READING

- [1] G. Bruno, C. Fanara, F. Guglielmetti, B. Malard- *Characterization and residual stress analysis of wear resistant Mo thermal spray-coated steel gear wheels*-Surf. Coat. Tech. 200 (2006) 4266-4276
- [2] DJ Hughes, G Bruno, T Pirling, PJ Withers, First impressions on SALSA, the new engineering instrument at the ILL- *Neutron News* 17 (2006) 28
- [3] R Glocker- *Materialprüfung mit Röntgenstrahlen unter besonderer Berücksichtigung der Röntgenmetallkunde*- Springer (1958)
- [4] M Preuss, PJ Withers, JWL Pang, GJ Baxter- *Inertia welding nickel-based superalloy: Part II. Residual stress characterization*- Met. Mater. Trans. A33 (2002) 3227-3234
- [5] MN James, PJ Webster, DJ Hughes, Z Chen, N Ratel, SP Ting, G Bruno, A Steuwer- *Correlating weld process conditions, residual strain and stress, microstructure and mechanical properties for high strength steel—the role of neutron diffraction strain scanning*- Mater. Sci. Eng. A 427 (2006) 16–26
- [6] JR Santisteban, A Steuwer, L Edwards, PJ Withers, ME Fitzpatrick- *Mapping of unstressed lattice parameters using pulsed neutron transmission diffraction*- J. Appl. Cryst. 35 (2002) 497-504
- [7] MT Hutchings, PJ Withers, TM Holden, T Lorentzen- *Introduction to the characterization of Residual Stress by Neutron Diffraction*- CRC Press (2005)

The Use of Neutron for the Study of Composite Materials used for Engines

G. Garcés

Fuel-efficient propulsion systems require a decrease in the vehicle's weight and an increase in engine operating temperatures. Therefore, there is a great effort to explore new materials and new manufacturing processes in order to replace traditional systems. **The combination of a ceramic phase within a metallic/ceramic material offers engineers the potential to save weight with sufficient high-temperature strength and creep resistance.** Composites consist of at least two chemically and physically distinct phases, suitably distributed to provide properties not obtainable with either of the individual phases. The reinforcement morphology can be selected depending on the application requirements and they can be commonly grouped together into: Continuous fiber reinforced, short fiber or whisker reinforced, particle reinforced, and laminated or layered composites.

Different examples of new composites used in prototype engine fabrication are the combination of random distribution of short fibers in aluminum or magnesium matrix for diesel



engines (**Fig. 1a**). Such composites with a relatively low volume fraction (<20% vol.) fabricated by casting techniques have coarse grain size. Due to large penetration depth of neutron and large gauge volume, they allow lattice strain measurements in the bulk composite with a good grain statistic.

Another example is the use of ceramic fibers within a titanium alloy. This composite offers engineers the potential to save weight (around 75 %) in highly loaded rotating structures, enabling integrally bladed ring structures (blings) to be considered as an alternative to traditional bladed discs. In this applications, the fiber can be as deep as 10 mm from the surface, and in such cases only neutron diffraction has sufficient penetration to measure their stress.

In the last decades, neutrons have provided key information in metal/ceramic matrix composite measurements of the residual/internal stresses within composites. These residual stresses are developed during their processing and can be generated by elastic mismatch stresses, thermal misfits, plastic misfit,... For example, in the case of metal matrix composites, their constituents, metallic alloy and ceramic reinforcement, have normally a strong differences between their thermal expansion coefficients, which induces a compressive stress state in the ceramic reinforcement and a tensile stress state in the metal matrix.

The presence of residual stresses must be taken into account when considering the mechanical properties of almost any system that is mechanically nonhomogeneous. For the majority of composites, the addition of a second phase include many of performance-limiting characteristics due to the generation of internal stresses that restrict the resistance to thermal cycling, ductility, etc. If the behavior of a composite can be optimized for a particular application, it is therefore important to be able to monitor the levels of internal stress and thus learn how to tailor them to improve it. This might occur by changing the morphology, diameter

or aspect ratio of the reinforcing phase, by modification of the matrix by alloy or heat treatment or by modification of the matrix/reinforcement interphase in order to enhance the efficiency of the reinforcement to strengthen the matrix or to shield the matrix crack.

On the other hand, not only neutron diffraction is used to measure residual stresses but also it is a very flexible technique to carry out experiments during in-situ conditions: tensile/compressive tests, in-situ thermal cycling, in-situ fatigue test.... This kind of experiment gives valuable information about the internal damage that can be suffered by composites during their service. For example, **Fig. 2** shows the experimental set-up for in-situ mechanical test in SALS beamline(Grenoble, France)[1].

The main problem during in-situ experiments using neutron is the large acquisition time needed to obtain reliable diffraction peaks. During this measurement time, the microstructure and the stress state inside the composite can evolve. This fact has limited in-situ experiments mainly to room or cryogenic temperature. ESS will radically shorten the time to acquire the diffraction spectra and it can expand in-situ experiments to high-temperature. This is an important task, because as composite materials find more widespread applications, greater emphasis will be placed on their in service performance. Neutron diffraction in the new ESS can provide information both about the stress distribution during in-service loading, fatigue, thermal fatigue, creep, and so on, and postmortem after-service loading.

Another emergent use of neutron for composite characterization is the neutron tomography. **Because of the non-destructive, deep penetration of neutrons, they are particularly well suited for imaging embedded features inaccessible by any other signals.** Combined with the inherent ability of time-of-flight methods, it is possible to discriminate between different structural components, including magnetic phases. Neutron tomography enables engineers



to relate defects to strength of materials, leading to new design criteria for composite components. For example, **Fig. 3** shows the solder distribution in the joint section between the nozzle (C/SiC composite) and the metal component using thermal neutrons[2]. It is possible to evaluate the presence of pore which can limit the mechanical strength of structural components.

The evaluation of internal damage in composites is an important parameter to estimate their life in service. Tomography can visualize and estimate reinforcement fragmentation or void formation during in-situ experiments or during their life in service. For this purpose, Synchrotron X-ray tomography is widely used due to their short time of measurement. However, since the deep penetration of neutron, it would be possible to explore higher gauge volume which is ideal for real structural component in-service conditions. The new source in the ESS will enable large field (200x200 mm) submillimetre resolution images.

ESS will add a new dimension to real scale tomography and radiography which can be combined with synchrotron tomography on the understanding of fracture of composite structures. However, it is also important to reduce the acquisition time needed to generate a real 3-D image. In other words, because it relies on taking 100 s of radiographs to get a 3-D image, tomographs taking 100 s of radiographs to get a 3-D image, tomographs can take a long time to acquire. ESS will also shorten the time to acquire tomographic images in order to give valuable information for engineers in the development of new composites for structural application in engines.

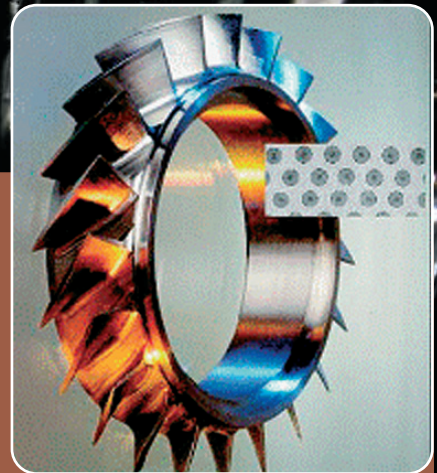
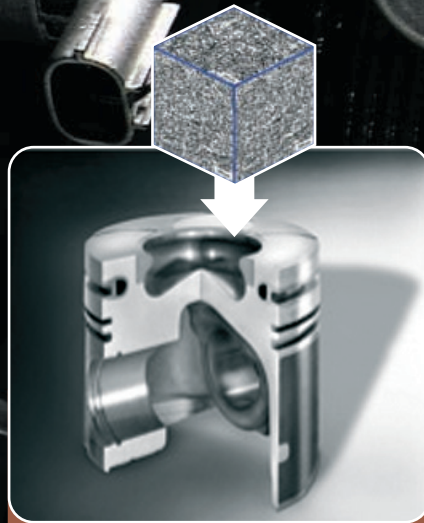


Fig. 1

a) Short-fiber aluminium matrix composite used in diesel engines. The composite is integrated in the aluminium block where high temperature is reached in order to inhibit creep.

b) Bladed ring prototypes of SiC fiber/Ti alloy for highly loaded rotating structure.

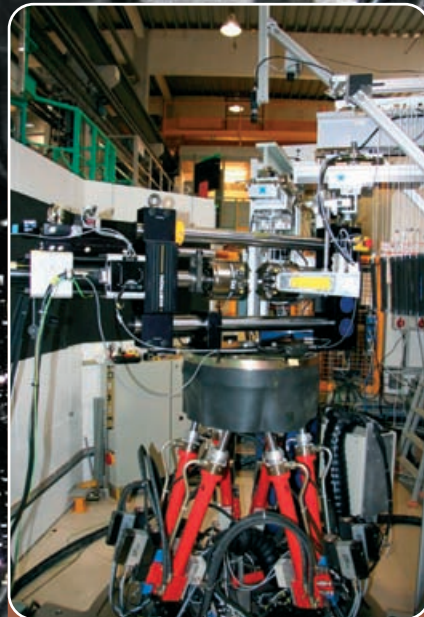


Fig. 2. Experimental set-up for in-situ mechanical test in SALSA beamline, Grenoble.

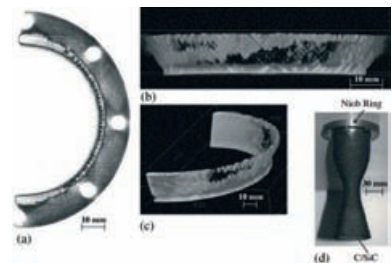


Fig. 3. Connection between the C/SiC nozzle and a metal ring. Neutron tomography reveals that the solder is pore-free.



FURTHER READING

[1] Pirling T, Bruno G, Withers PJ. Mater sci eng A 2006;437:139.
 [2] J.R. Kornmeier, M. Hofmann and S.Schidt, Materials Characterization 58 (2007) 922-927

Environment

6



6.1

Neutron Scattering and in Situ Catalyst Studies

T. Ramirez-Cuesta

6.2

Novel Materials for Magnetic Refrigeration: the Role of Neutron Techniques

E. Palacios

6.3

Neutron's Contribution to more Safe Radiactive Waste Management

M. M. Castellote Armero



Neutron Scattering and in Situ Catalyst Studies

T. Ramirez-Cuesta

Catalysis is the key to both life and lifestyle. There are fundamental catalytic processes related to fuels and energy, emissions, polymers and plastics, life, health and food.

The chemical industry is a major component in the world economy; a single European company like BASF has a yearly turnover of over 4 billion euro. In the US the chemical industry uses catalyst technology to produce over 1 trillion US\$ of revenue. Catalysis is a fundamental issue in chemistry with a wide range of problems and applications. Catalysis is particularly at the heart of the petrochemical industry. Catalysis is therefore critical to the largest industries in the world.

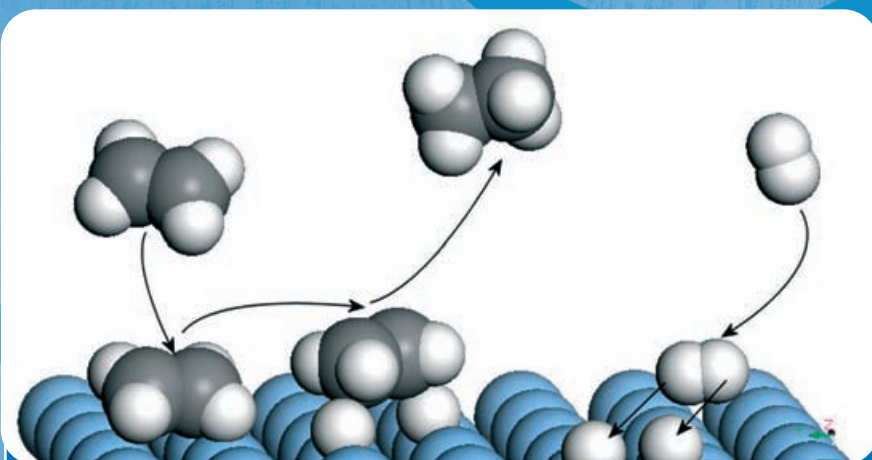
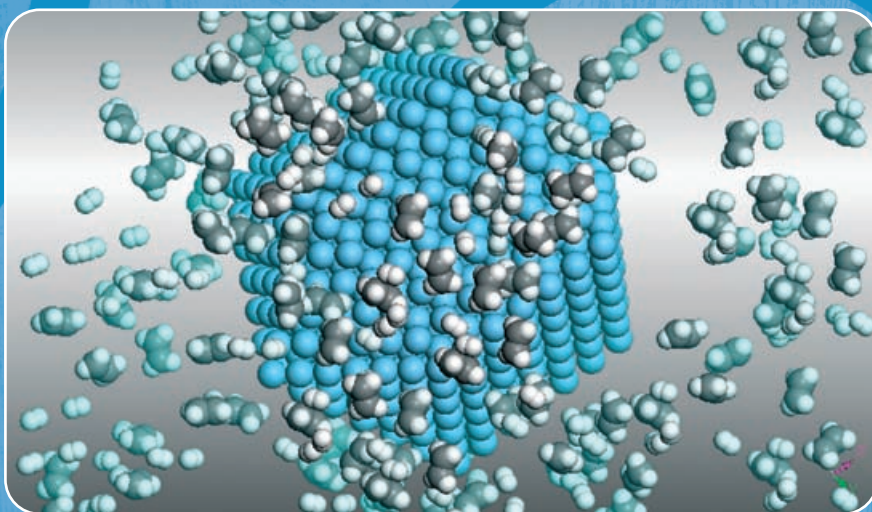


Fig. 1. Sketch of a catalyzed hydrogenation reaction. Top, a nanoparticle is surrounded by the reactants. Bottom, on the surface of the catalyst, the hydrogen molecule splits and hydrogen atoms are now ready to react, a molecule from the gas phase adsorbs and then reacts, after the reaction it goes back into the gas phase.

What is catalysis?

Let us ask: what is catalysis? A definition of catalysis is usually: it is the process in which the rate of a chemical reaction is increased or decreased by the presence of a chemical substance that is called the catalyst. Often the catalyst is not consumed itself.

In most cases what the catalyst does is to lower the energy barrier between two states, one can think that the initial state (the initial chemical compounds) is a village on one side of a mountain range, the final state (the desired chemical products of the reaction) are on the other side, communications between these two places is not easy; it is necessary to climb the mountain to get to the other side (activation barrier). When a catalyst is present it provides a road that goes around the mountain and allows communication between those two places at a lower cost (reduced activation barrier). The road, once built, is not consumed by the transport of products on it. This is a very trivial picture but illustrates the concept. There are a lot of chemical reactions that will not happen unless a catalyst is used. When the catalyst is in a different phase or state than the reactants it is called heterogeneous catalysis (usually solids that improve/control reactions that involve liquids and gases). Catalysis is doing clever chemistry, sometimes making reaction faster, others making the product but stopping undesirable by-products.

Some examples: Clean energy, the hydrogen economy, green chemistry

Hydrogen is an energy carrier, it has to be produced from other sources, but when burned it is a clean source of energy. Hydrogen storage is one of the most active areas of research; so far we still do not have a material that will allow us to implement hydrogen as an efficient fuel for automotive transportation for example. What we need is to catalyse some reactions in such a way that we can operate at a reasonable set of parameters (pressure and temperature) to put and extract the hydrogen from such material. Catalysed reactions are fundamental parts of the workings of fuel cells that together with hydrogen can create a pollution free transport system. Catalysts are used to treat the exhaust gases of cars and buses in order to remove pollutants. In environmental chemistry catalysts are necessary to remove contaminants, to degrade water pollutants and to save energy¹.

Why “in situ” studies of catalysts?

With “in situ” studies, scientists mean studying the materials and processes as close as possible to the real operation conditions. Catalysts and catalytic processes have been used for a long time in industry; however, in most cases we lack the understanding of the nature of the operation of the catalyst. We do not always know why and how they work. In the last decades a great deal of effort has been devoted to study these processes using “surface science”, this approach consists on using models of the real catalyst in order to isolate the contributions and details of the reactions involved. However these models are of limited applicability, they usually require the use of extremely clean conditions, gas pressures of 10^{-13} atmospheres, that is 0.0000000000001 of an atmosphere of pressure (almost perfect vacuum) and special metal surfaces and crystals.

In industry these reactions occur at pressures near and above atmospheric pressure and the materials are usually slurries, with the catalyst immersed into this mixture. The gap between real conditions and the “clean experiments” is called the “material and pressure gap” and it is a very active area of research. A recent editorial of a Journal of the Royal Society of Chemistry in the United Kingdom, stated: “*The resulting profound understanding of surfaces and surface processes does not, however, automatically translate into an equally good understanding of heterogeneous catalysis as one might perhaps expect. Progress in that field has been limited mainly by two big obstacles known as the pressure and material gap in heterogeneous catalysis*”².

Why use neutrons?

As we have seen, one of the main problems in understanding catalysis is the lack of good experiments that can be performed under realistic conditions. Some people study these systems using optical techniques and X rays but because they rely on light as a probe for measurement, they usually require transparent samples or windows in their experimental cells. Some materials are just not transparent, so the use of optical techniques may not be applied.

On the other hand, because of the nature of neutron interaction with matter, neutrons can see where atoms are (diffraction) and what atoms do (spectroscopy). Neutrons also interact with different elements in a different way than other techniques, like optical spectroscopies and X-rays. Neutrons are penetrating; they penetrate deeply into typical samples of the order of millimetres and can go through containment vessels, generally aluminium or steel, so neutrons are usually good at looking at bulk properties of materials. **Neutrons have already been used to study a fundamental problem in catalysis, the poisoning of catalysts.** Although the catalysts are not consumed during catalysis, they often pick up impurities from the reactions and stop working, the identification of the impurities and reactions that poison the catalysts are very important to optimise the processes involved.

Several techniques can be applied to study catalysts using neutrons:

Inelastic neutron scattering (INS) spectra can be readily and rigorously modelled, the measured intensities can be related straightforwardly to the motions of the atoms in the material, and subtraction of backgrounds is also straightforward. INS is sensitive to the motions of hydrogen atoms; optical techniques are usually more sensitive to the motions of heavier atoms, the cross section of hydrogen is more than 10 times larger than any other element so it is a lot more visible. Since hydrogenation/dehydrogenation reactions are some of the most industrially relevant catalytic reactions, INS is in a unique position to study these problems. Technically INS is not subject to selection rules unlike infrared and Raman spectroscopy³.

Small angle neutron scattering is a technique that is used to study disordered materials, making it ideal to study systems like catalysts, exploiting the sensitivity of neutrons to hydrogen it can be used to determine structural information of reactants on surfaces and "in situ" reactions⁴.

Quasielastic neutron scattering can be used to study the translational/rotational motion of molecules in materials such as zeolites, clays, nanostructured porous materials and nanotubes. **Diffusion of hydrogen in hydrogen storage materials can also be studied; neutrons are usually the only technique that is able to look at these properties.**

Neutron tomography consists of taking images of macroscopic objects using neutrons in the same way that we use X-rays to study bones. Because the neutrons penetrate matter so efficiently, we can study a fuel cell during operation by analysing the transmitted spectra, we can quantify the hydrogen contents in different parts of the device.

Neutrons are a very powerful tool in the study of materials; they particularly excel in measuring hydrogen containing materials, a new generation source of neutrons in Europe is a scientific priority. Catalysis is not something that we are very familiar with, but a fundamental part of our daily life; for example, every time we load fuel in our cars, use plastics, consume pharmaceuticals, we use the product of catalysis.

Neutrons are a very powerful and necessary tool in the understanding of catalysts.

The ESS will be a unique opportunity to design and build new and exciting instruments, for example it could have a machine that will be a simultaneous INS spectrometer and Small angle neutron scattering diffractometer, that will allow study of in situ catalyst and reactions structurally and dynamically on one go. **New quasioleptic spectrometers will allow us to understand the mobility of species during reaction.**

The ESS will be the place to study Catalysis; it will have a suite of instruments that will permit these studies to be taken into a new dimension. Some of the studies in catalysis cannot be studied efficiently because the intensity of the current sources is not enough to detect the fine details of the products and reactants. ESS will provide a blank canvas where the best instruments can be designed from the beginning to investigate one of the most important and highest economic impact areas of knowledge.

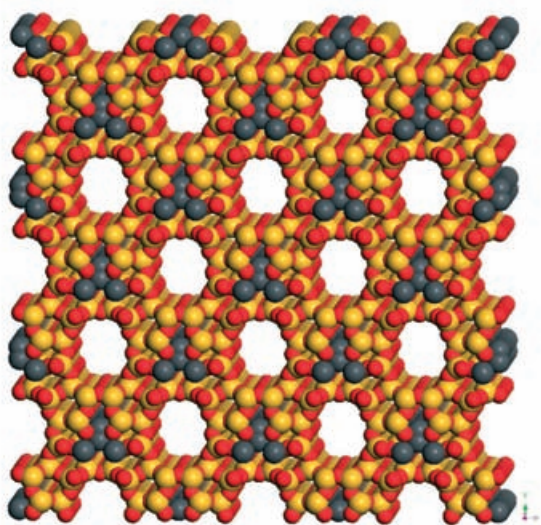


Fig. 2. Zeolites are porous materials that are used in a variety of catalytic reactions, especially hydrogenation. Neutrons are used to study these functional materials.



FURTHER READING

1. Marteel, A. E.; Davies, J. A.; Olson, W. W.; Abraham, M. A., Green chemistry and engineering: Drivers, metrics, and reduction to practice. *Annual Review of Environment and Resources* 2003, 28, 401-428.
2. Imbihl, R.; Behm, R. J.; Schlögl, R., Bridging the pressure and material gap in heterogeneous catalysis. *Physical Chemistry Chemical Physics* 2007, 9 (27), 3459-3459.
3. Mitchell, P. C. H.; Parker, S. F.; Ramirez-Cuesta, A.; Tomkinson, J., *Vibrational Spectroscopy with Neutrons, with applications in Chemistry, Biology, Materials Science and Catalysis*. World Scientific: London, 2005; Vol. 3, p 642.
4. Albers, P. W.; Parker, S. F., Inelastic Incoherent Neutron Scattering in Catalysis Research. In *Advances in Catalysis*, Vol 51, 2007; Vol. 51, pp 99-132.

Novel Materials for Magnetic Refrigeration: the Role of Neutron Techniques

E. Palacios

The standard refrigeration procedure is based on the compression-expansion of a fluid, usually a gas which transforms into liquid when compressed. In this way the fluid expels heat when compressed in thermal contact with the atmosphere and then is put in contact with the device we'd like to cool down or keep at low temperature. For this purpose the traditional substances are CFC's, identified as very dangerous for the ozone layer in the atmosphere. Moreover, the conventional refrigeration methods reach only about 20% of the theoretical limit (Carnot efficiency), at best.

An alternative procedure is the magnetic refrigeration. The atoms or ions of few elements (by instance Fe, Mn, rare earths) in the periodic table have "magnetic moment", that is, they behave as small magnets at atomic scale. Due to the thermal motion, the magnetic moments are randomly oriented in the space ("paramagnetic state"), but when an external magnetic field is applied the moments align with it. The magnetic field can be produced by an electrical current flowing through a coil or by a macroscopic magnet. This process expels heat to the environment, or increases the temperature of the material when thermally isolated. The effect is called "magnetocaloric effect". Conversely, when the field is removed ("demagnetization") the material absorbs heat from the environment or cools if isolated. The process can be done cyclically, as sketched in the **Fig. 1**. Grey thermometers symbolise the temperature of a magnetic material and a system we want to cool. Near room temperature, the demagnetization of a ferromagnetic

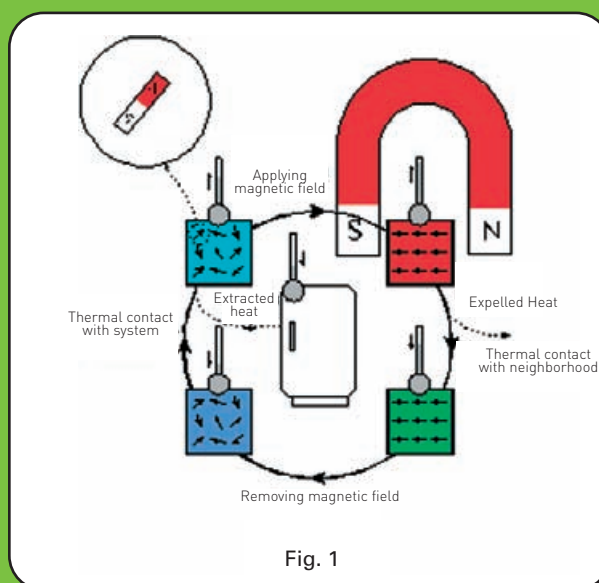


Fig. 1

material is an efficient process for refrigeration. In a ferromagnetic material the magnetic moments align spontaneously, without any external field below some temperature, T_c , called "Curie temperature". Below T_c the material behaves as a magnet. Above T_c the material is paramagnetic, that is moments are randomly oriented. The magnetocaloric effect becomes strong for temperatures slightly above T_c , since a low field is enough to overcome the thermal motion and produces the alignment of the moments, which in any case align spontaneously at T_c . The best ferromagnetic material for refrigeration is gadolinium, with $T_c=20^\circ\text{C}$, and a magnetic

moment three times that of iron. Nevertheless gadolinium is a rare and expensive material.

The magnetic refrigeration became a real alternative to the traditional procedures since the discovery in 1997 by V. Pecharsky and K.A. Gschneidner Jr. of the so-called “giant magnetocaloric effect”, GMCE. To explain with simple words this effect, let us imagine liquid water to be paramagnetic and ice to be ferromagnetic. Let us suppose we have a glass of water at 20°C and we insert it in a magnetic field. As water transforms spontaneously into ice at 0°C, when water is few degrees above, a relatively low field would align the magnetic moments and convert it in ice, in a few seconds. In addition the heat of alignment of the magnetic moments (what would give about 100 J per gram of water) this process would expel 330 joules per gram of water, a total of about four times the “magnetic” heat. Water would heat up to 130 °C, and would transform in ice, hard as a rock! Let us assume now that we leave the glass of ice to cool again down to 20°C, we put it in thermal contact with an object, and then we remove the field. The equilibrium state of water is liquid, but for that it would need to absorb again 430 J to convert ice in water, similarly to what happens when we put ice in a glass of drink. Only one gram of this “magnetic ice” could refrigerate five grams of ordinary drink down to 0°C.

Unfortunately water is not magnetic, but something similar does happen with the GMCE materials, with the only difference that paramagnetic and ferromagnetic states are both solid. Paramagnetic (water-like) and ferromagnetic (ice-like) states have different crystal structures and the transformation between them absorbs heat when passing from the ferromagnetic to the paramagnetic. Therefore the magnetocaloric effect is enhanced giving rise to GMCE. For instance, the first GMCE discovered material, $Gd_5Si_2Ge_2$, has twice the intensity of magnetocaloric effect than

pure gadolinium, although the content of Gd atoms is nearly one half, being Si and Ge non-magnetic. Moreover the proportion of Si to Ge can be varied *ad libitum* which allows tuning the transition temperature according to the desired application. Even in the case that GMCE materials could be poisonous, they do not evaporate and, similarly for batteries, do not contaminate when properly managed. **Moreover, the efficiency of prototypes already tested reach a 60% of the maximum Carnot efficiency, which implies an energy consumption about one third of that conventional refrigerator.** That is, assuming a Carnot efficiency of unity (it depends on the temperature of the cold device, but usually is more than unity) with a conventional refrigerator, to extract one joule of heat from a cold device, it is necessary to expend about five joules of electric energy. With a magnetic refrigerator, only two joules suffice for the same purpose.

Since 2005 a conference about magnetic refrigeration is held every two years, supported by the International Institute of Refrigeration, Paris (France). Since 1997 many other GMCE compounds have been discovered, as $MnAs_{1-x}Sb_x$, $MnFeP_{1-x}As_x$, Ni_2MnGa , $LaFe_{17}Si_2$, $RhFe$, Mn_3GaC , etc. There are instances in which the heat is absorbed or expelled by the effect of structural change alone, without any magnetic contribution, and being the ferromagnetic phase stable at the higher temperature, whereas the lower temperature is antiferromagnetic. The antiferromagnetic array of moments is somewhat similar to ferromagnetic, as the moments are aligned parallel, but in the nearest neighbours have opposite sense. The application of an external field forces the transition from the antiferromagnetic to the ferromagnetic phase and absorbs heat in the same way that the transformation of ice in water. However no heat is absorbed or expelled by the magnetic moments themselves because they are aligned in both ferro and antiferromagnetic states. As a

consequence the magnetocaloric effect is inverse: the sample absorbs heat when is put in a magnetic field and expels it when brought out from the field. In most of cases the chemical composition can be varied around the nominal value and small amounts of substitutes can replace the nominal elements, in order to improve the magnetocaloric effect and to tune the transition temperature to the work conditions.

And, what is the role of the neutrons in this field? The present research in refrigeration materials is mainly empirical. When a compound is reported to show the GMCE, many variants are prepared and studied to search the best composition and substituting the atoms for other chemically similar, many times without a real understanding of the microscopic mechanism driving the magneto-structural transition. **Neutron scattering gives information in several ways about the atomic structure of matter and the best searching criteria.**

Firstly, neutron diffraction allows determining the type of crystal lattice and the position of the atoms in it. This structural properties, at atomic scale, can be in principle studied also by X-ray diffraction but when dealing with magnetocaloric alloys the macroscopic properties depend subtly on the atomic arrangement and very often the problem is to determine the precise position of atoms of very similar atomic number, like Mn, Fe, Ni, Co, etc., which cannot be distinguished by X-rays. Thermal neutron diffraction allows to distinguish near elements and even different isotopes of the same element. By instance in Ni_2MnGa (where properties depend very strongly on small differences around the nominal composition) the structure of austenite, martensite and another irreversible martensite phases could be determined by neutron diffraction. As a second example, in $\text{MnFeP}_{1-x}\text{As}_x$ neutron diffraction showed that dramatic change in the Fe-Fe distance occurs, between -70°C and 30°C , depending on composition, with negligible changes in

other inter-atomic distances. This change produces the transformation from ferromagnetic to paramagnetic and strong changes in the unit cell, responsible of the GMCE in this material.

Secondly, macroscopic measurements of magnetization and susceptibility allow inferring whether a sample is ferromagnetic, paramagnetic or antiferromagnetic, but only neutron diffraction allows determining the value and direction of the magnetic moment of every atom in the solid. Sometimes the type of magnetic order, or its absence, depends critically on a single atom-atom interaction among many. As another example, neutron diffraction has shown that the antiferromagnetic low temperature structure (**Fig. 2**) of Mn_3GaC is formed by layers of moments on Mn atoms antiferromagnetically coupled in the low temperature state. An external field produces the transition to ferromagnetic state and one of the most intense and inverse GMCE.

Very recently (2009), neutron diffraction on magnetic field allowed to determine the magnetic structure and the phase change from paramagnetic to ferromagnetic of $\text{Mn}_{1.7}\text{Fe}_{0.8}\text{P}_{0.8}\text{Ge}_{0.2}$, one of the most efficient GMCE compounds.

Another very useful technique is the neutron inelastic scattering. In a solid, the electric field ("crystal field") due to other atoms determine the magnetic moment of a given atom. Inelastic neutron scattering gives the energy levels and allows predicting the magnetic and magnetocaloric properties.

Today the most intense neutron source in Europe is that of Institut Laue Langevin where about 50% of proposals of interesting experiments are not accepted due to lack of beam time. Therefore alternative sources are necessary. In this context, the project of European Spallation Source would come not merely to fill the already existing gap, but would bring XXI century technology, and enhance the present capabilities.

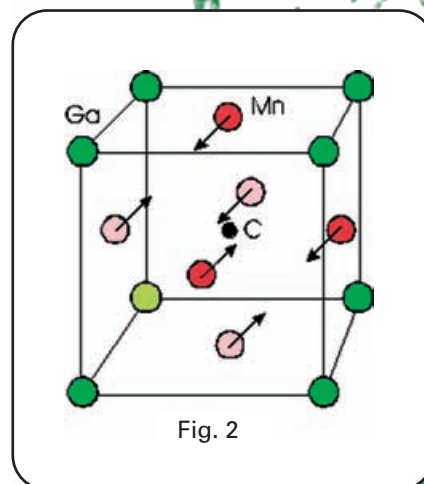


Fig. 2

Neutron's Contribution to more Safe Radioactive Waste Management

M. M. Castellote Armero

Research is one of the key elements in the generation of the know-how and technologies required to guarantee the safety and feasibility of the different stages of radioactive waste management. In order to undertake this research, **neutrons are foreseen as a powerful tool** provided they can give information on **structure** (neutron diffraction), **organisation** of particles in dispersed systems (small-angle scattering), on **binding energies and dynamics** of the systems (inelastic neutron scattering), and in **nuclear fundamental** studies (gamma spectroscopy).

Radioactive waste can be defined as any waste material or product for which no further use is foreseen and that contains or is contaminated by radionuclides in concentrations or levels of activity higher than those established by the regulations currently in force. These wastes have to be managed in the way that they are controlled from its origin to their definite disposal until the radioactive activity decreases to admissible levels, guaranteeing the protection of people and environment. In Spain, this is the mission of ENRESA, which is a public company created by the Spanish Parliament in 1984.

Although there are many types of radioactive waste, from a management point of view, radioactive waste may be classified in two major groups:

1) The so-called **Low and Intermediate Level Wastes (LILW)**, produced both in the generation of electricity by nuclear means and in very diverse non energy-related applications of radioactive materials (as medical applications). In the management of these wastes, the solutions considered in different countries are diverse. Among the countries that have implemented definitive solutions, practically all have adopted what is known internationally as **"near surface disposal"**, which may range from simple "trenches" to overall installations for the management with **engineered barriers**. In Spain they are definitively disposed of at the El Cabril facility (Córdoba), these including the sub-group of Very Low Level Wastes (VLLW) where the disposal facility is a multi barrier system where **concrete is the basic material of the isolation barriers**.

2) The **High Level Wastes (HLW)**, consists of, mainly, spent nuclear fuel and other specifically high level wastes. For their management, apart from **separation and transmutation** to reprocess fuel, mainly two different options are under consideration: On the one hand, the definitive solution of **deep geological disposal**, mainly on **granitic and clay** formations, and **temporary storage** on the basis of a dry storage system guaranteeing the safety and protection of people and environment over the time periods required for their definitive management, based also in **engineered barriers**.

In this context, most countries having radioactive wastes, develop continuous research programs, to increase knowledge and to implement new skills acquired in the management of radioactive wastes.



Aerial view of the El Cabril facility
(from www.enresa.es)

Among other themes, a big deal of research has been focused on:

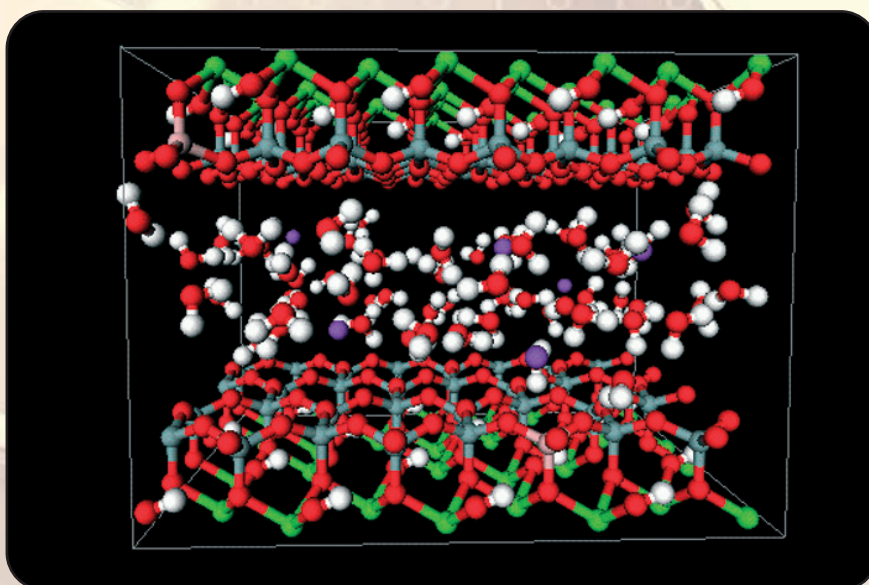
- Improving **knowledge on durability of engineering and geological barriers**, mainly for:
 - **Cementitious matrices, especially concrete.**
 - **Different geological materials, specially several types of clays**
- Feasibility and development of **separation and transmutation technologies**.

Neutron's applications

Concerning the study of **engineering and geological barriers**, it is clear that safe storage of nuclear waste on a long time scale requires **chemical stability** of the host matrix and understanding the **behavior** of the materials. All that can be monitored using different neutron techniques.

In the case of geological barriers, different materials have been studied using neutron techniques: zeolites, granite, etc. But mostly layered silicates, specifically smectite clays and mica, that function as getters for the radionuclides to retard their migration.

Smectite clay minerals consist of negatively charged crystalline aluminosilicate layers. The layers are held together face-to-face by means of several different cations that balance the excess of negative charge resulting in regular stacks of layers with crystallite size of the order of microns. The small size of the crystallites and the relatively poor degree of preferential orientation achievable in aggregates renders the application of conventional crystallographic methods to the study of this kind of interlayer structure very difficult.

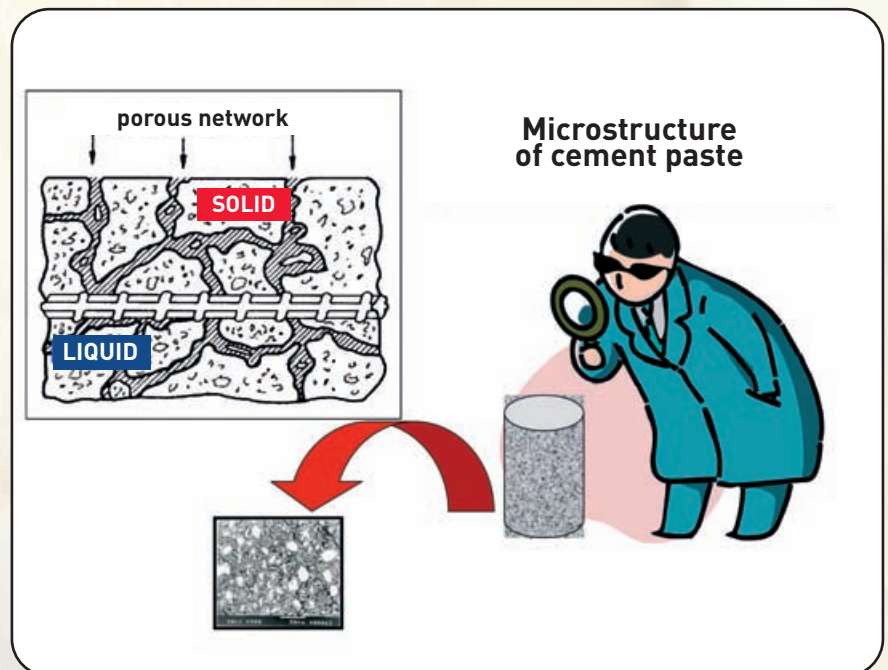


Diagrammatic representation of an Smectite clay (from <http://www.soils.wisc.edu>)

In this context, the use of neutron techniques, especially diffraction, has allowed the study of many of the important properties of clays and other geological materials, regarding radioactive waste management, for example:

- Characterisation of the **water structure** and **coordination** in the **interlayer region**.
- Study of the **swelling properties**, having observed reorientation of clay layers when reaching an specific relative humidity.
- **Isotopic substitution** experiments, that allows the study of the migration of radionuclides in clay containment barriers and in the environment.
- Effect of **radioactive decay** and the associated **radiation** and **thermal effects** in geological materials concerning transport properties, as sorption and cation exchange in different materials.
- **Fluid interactions under pressures and temperatures** relevant to hydrostatic geological conditions and with chemistries relevant to the application as barrier materials.

Concerning **cementitious materials**, as said, **concrete** is a fundamental element regarding the artificial barriers. In addition to the strong **physical barrier** that it constitutes, when the cement is hydrated, a porous network through the material is produced. This network is filled by an **alkaline solution**, in equilibrium with the different **solid hydrated phases**, that favours the immobilisation of wastes that, as a general rule, present a very low solubility at high pH. Additionally, this **microporous system** presents a high specific surface that also favours the adsorption of radionuclides. On the other hand, this



can be a **pathway to several agents to enter into concrete** being able to produce the deterioration of the concrete itself and corrosion of the rebars.

Thus, in order to **assure more durability of concrete**, it is necessary to deepen the study of the **matrices' transport properties**, the **physico-chemical interactions** of different **trapped radionuclides** as well as of **potential**

aggressive agents with the solid and liquid phases of the cement paste, and the **corrosion of the rebars**. In order to undertake these problems, neutron techniques have been used recently as a tool, contributing to understand the fundamentals of the mechanisms regulating the processes. Among many, the following examples can be pointed out:

- Characterisation of the behaviour of **concrete in contact with water** by in situ monitoring **accelerated leaching tests** by application of electrical fields.
- **Electrokinetic phenomena** in concrete: characterisation of the surface charge of the electrical double layer in the porous network.
- Study of the **kinetics of neutralisation** of concrete with reaction with the atmospheric CO₂ (carbonation).
- Behaviour of cementitious matrices under **high temperatures**, of great interest concerning **fire** and **thermal effects of radiation**.
- **Hydrogen embrittlement** of High Strength Steel
- **Hydration and curing studies** under different environments.
- **Microstructure and porosity characterisation**.

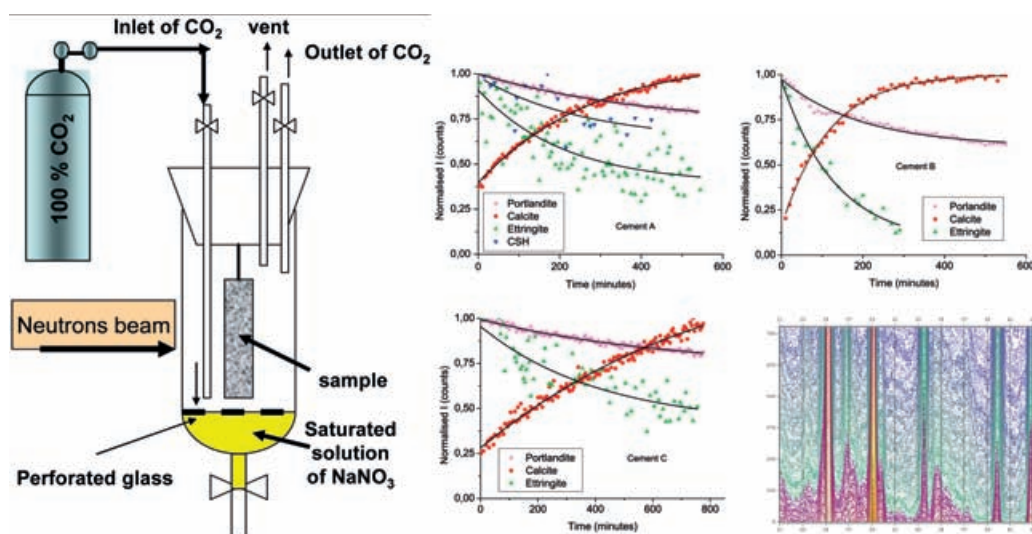


Diagram of the set-up and results of an in-situ neutron diffraction experiment of carbonation of concrete. (From the paper DOI : 10.1016/j.cemconres.2008.07.002)

Concerning **technologies of separation and transmutation**, energy generation from subcritical assemblies boosted by a ESS (neutron spallation source) might be also be considered in waste management as potential means for **the elimination of long-lived radionuclides** by transmutation, providing important reduction of radiotoxicity as well as significant diminution of the required time frames. Additionally, after the fuel is processed, the remaining material is often stored in glass form. Here again, neutrons can play an important role in characterising the encapsulated material and understanding the binding of the actinides into the glass, which is critical for the long-term storage of the radioactive waste. At this respect, neutron diffraction studies have been carried out in order to understand **alkali borosilicate glasses** and **aluminosilicate glasses** structural characteristics and correlate it with

thermal and glass stability in function of the type and amount of specific elements that are introduced in the network, as uranium, modifying and/or stabilizing the structure.

Other important materials concerning immobilization fo high level radioactive wastes are the **perovskite-type structures**, that can be considered as analogues to the mineral phase which is dominant in the lower mantle. The crystal structures, phase transitions and solid solubilities with other oxides, including the ability of incorporation and trapping of different radioactive elements in the generated sites have been also undertaken using neutron diffraction.

Concerning **irradiated material**, many different tools, but not yet neutrons, are used in the characterisation of nuclear wastes. The main reason neutrons are not used being the **difficulty in examining sizeable samples** of such irradiated materials at user facilities.

However, the **brilliance of the ESS** will allow powder diffraction experiments to be performed on samples as small as a few mg, thus allowing a new tool to be brought to bear on this important problem. The time-of-flight method has a distinct advantage as neutron induced fission can be separated from the diffraction pattern.

Examples of questions that need to be addressed are the **phases present as a function of distance from the barrier** (either the cladding in the case of direct burial, or the container in case of reprocessed fuel), and, in particular, the **metal to oxygen ratio** that is a key parameter on both corrosion and reactivity potentials. Following this ratio as a function of distance from the cladding or barrier, will characterise the waste in a way unavailable today, and might well become a crucial aspect of quality control and monitoring of actinide waste.

Energy

7



7.1 **Application of Neutron
Scattering to the Development
of better Organic Solar Cells**

A. Urbina

7.2 **Hydrogen Storage Materials
and Neutron Scattering
Experiments**

J. Hernández Velasco



Application of Neutron Scattering to the Development of better Organic Solar Cells

A. Urbina



This short chapter will enhance the importance of Neutron Scattering techniques in order to increase our understanding of the structure and dynamics of materials used in a new generation of photovoltaic devices. This is an application that will deliver almost immediate results that link nanoscale phenomena being explored by means of neutron scattering experiments to performance improvement of macroscopic devices designed to transform solar light into electrical power at lower cost than traditional inorganic solar cells. First, an introduction to organic photovoltaic cells' structure will be presented; then the advantage of using neutron scattering as a complementary technique to other spectroscopies such as X-ray, Raman or Infrared will be briefly emphasized before focusing on the particular materials and systems where it could be applied in order to study different parts of the organic photovoltaic devices. Finally, some ideas regarding future experiments that combine light excitation and neutron scattering will be proposed.

The dominant research in the field of organic photovoltaics has been directed towards the dye-sensitized solar cell (DSSC), which could supply solar electricity on a large scale. Those are hybrid devices consisting in nanostructured metal oxide films formed by an assembly of nanoparticles sintered over a conducting substrate which provides a large internal area that can have different functions, specially when combined with organic hole-conductors that fill the voids in the nanostructure. The achievement of efficiencies higher than 11% is already impressive, but one of the main drawbacks of this technology is the use of liquid electrolytes. It has been provisionally addressed with sophisticated encapsulation procedures that limit possible future applications, and it remains a challenge how to provide efficient solid hole-transporting materials in these devices. Several groups have also developed “full-organic” photovoltaic devices (“plastic solar cells”). In 1995 it was observed that the mixture of two polymers formed a bulk distributed heterojunction and led to efficient charge generation within the whole film. Since then, solar cells based on blends of methanofullerenes with derivatives of conjugated polymers have been under investigation. Nowadays, several groups report routinely the fabrication of devices with efficiencies higher than 4%, and tandem devices with polymer/fullerene derivative blends have reached efficiencies above 6%. With this trend in the power conversion efficiencies, a breakthrough in the learning curve of the technology could be achieved if the durability of the devices is guaranteed for more than five years. Very recently some cost analysis and forecasts for this technology have been presented. The use of solid materials, that can be flexible and processed in solid state during the fabrication of the “plastic solar modules”, open a huge range of application that spans from easy architecture integration to portable devices, from flexible coatings to very low cost and low maintenance solar home systems for rural electrification.

As it's been explained in more detail in previous chapters, neutrons are a valuable tool for investigating condensed matter. The de-Broglie wavelength of thermal neutrons is of the order of the interatomic distances in solids and liquids, thus interference effects occur which yield information of the nanoscale structure of the scattering system. Furthermore, since neutrons are uncharged particles there is no Coulomb barrier to be overcome and they are scattered by nuclear forces penetrating deeply into the target. Additionally, the energy of thermal neutrons is of the same order as that of many excitations in condensed matter (a few meV) and therefore the measurement of the energy and momentum of the scattered neutrons provides accurate information of the

structure, dynamics and interactions of the materials at the atomic scale. Finally, if the neutron's magnetic momentum is taken into account and the measurements are performed with polarization analysis, which strongly enhances the sensitivity of the experiment, the elastic scattering gives information on the arrangement of electron spins and density distribution of unpaired electrons and inelastic magnetic scattering gives the energies of magnetic excitations.

All of these advantages of neutron scattering find a nice application in the study of different critical parts of the devices under consideration. In **Fig. 1** we present a draft of a typical organic solar cell, where the different techniques can be applied:

1) Quasielastic neutron scattering to study transitions (melting and/or glass transitions), dynamics of the macromolecule such as backbone and side-chain movements, diffusion, reptation and other order-disorder processes that could lead to controlled self-organization of the materials at the nanoscale. Solutions or bulk samples of conjugated polymers have been studied, also in separate experiments. Nanoparticles' behaviour that will form the “bulk heterojunction” when mixed with the polymers have been studied in solution. It remains a task to study binary or ternary blends of these materials. If good labelling techniques such as selective deuteration could be developed, the study of this mixtures would open a huge field of study by quasielastic neutron scattering.

2) Small angle neutron scattering is used to investigate the formation of large scale structures (aggregates, micelles, rod-like structures, etc.), especially when the nanoparticle component of the blend is dissolved in order to prepare the mixtures prior to deposition on the substrates. The length scales of these structures (of the order of a few nanometers) should be matched to the free path of the excitons created by light absorption. A fine tuning of these parameters is needed in order to improve the quantum efficiency of the photovoltaic devices.

3) Neutron reflectometry is a useful technique to analyse surface and interface properties at the nanoscale. In the organic solar cells, the study of organic/organic as well as organic/inorganic interfaces can only be accomplished by neutron reflectometry techniques and it should benefit from clever proposals in order to enhance the contrast between the materials. Using embedded magnetic layers or selective deuteration will allow us to study the profile of interfaces, diffusion of materials into each other and improvement in the control of the electrode contacts. All of these parameters are important in order to obtain a more efficient recollection of the photogenerated charge carriers in the solar cells.

4) Finally, two other techniques that could contribute to this field should be mentioned. On the one hand, **inelastic neutron scattering** will be useful to explore the phonon density of states and its influence in electron-lattice coupling for charge transfer and transport. Only recently has this interaction started to be taken into account and their full understanding will require input both from experiments and theoretical models. On the other hand, **neutron diffraction** will confirm the calculated lattice parameters of the crystalline structure of the polymers and the relative amount of ordered and amorphous phases that coexist in the devices. This is, again, important for a better understanding of the charge transport phenomena.

In the near future, new experiments should be designed with special focus on the characterization of the conjugated polymers that are the core of the organic solar cells. Two ideas for future development that need to be explored take into account the combination of excitation of the materials with an intense light beam while simultaneously measuring neutron scattering with very high resolution in the energy range of a few meV: 1) to study the collective structural deformation that propagates with the photogenerated excitons, also called solitons or polarons; and 2) to measure the selective population of singlet and triplet states and the exchange energy in the different conjugated polymers using polarized neutrons and if necessary, spin-echo techniques.

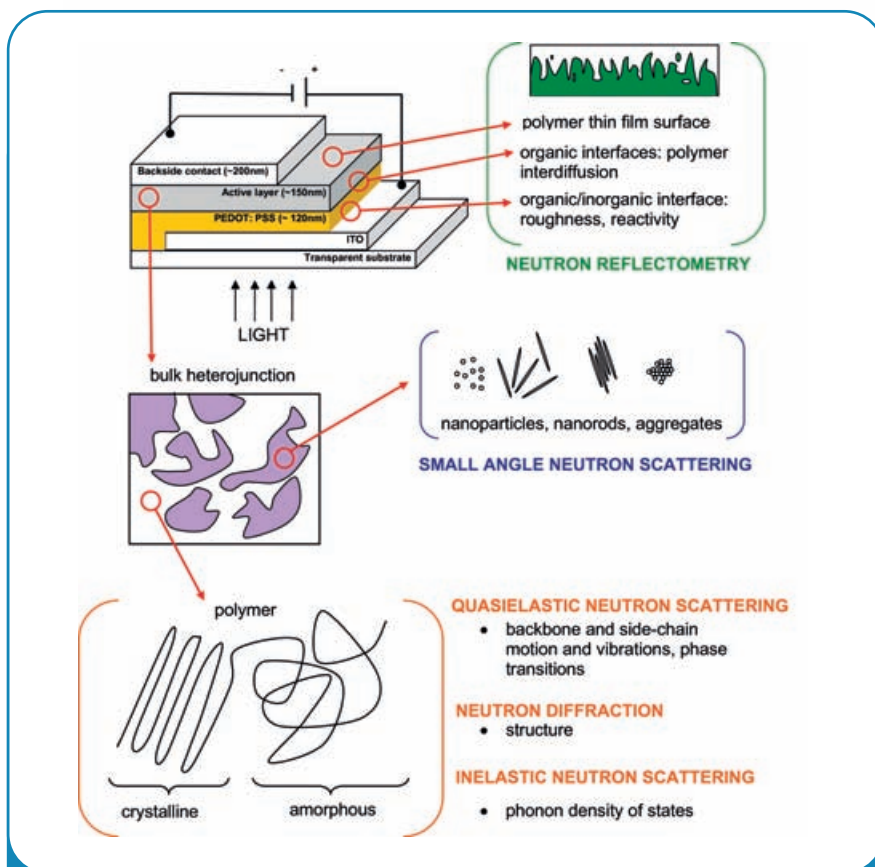


Fig. 1. Draft of an organic solar cell showing the different parts of the device where neutron scattering experiments can be useful in order to increase the knowledge of the structure and dynamics of the materials at the nanoscale.

FURTHER READING

Bai Y. et. al 2008. High-performance dye-sensitized solar cells based on solvent-free electrolytes produced from eutectic melts. *Nature materials*, 7: 626-630.

Brabec C. J., Sariciftci N. S., Hummelen and J. H. 2001. Plastic Solar Cells. *Advanced Functional Materials*, 11:15 – 26.

Brabec C. J., Dyakonov V., and Scherf V., 2008. Socio economic impacts of Low Cost PV Technologies, pages 531-567, chapter 20 in *Organic Photovoltaics: Materials, Device Physics and Manufacturing Technologies*, Wiley-VCH, Germany, ISBN: 978-3527316755.

Grätzel M, 2001, Photoelectrochemical cells. *Nature*, 414:338 – 344.

Halls J. J. M., Walsh C. A., Greenham N. C., Marsaglia E. A., Friend R. H., Moratti S. C., and Holmes A. B. 1995. Efficient photodiodes from interpenetrating polymer networks. *Nature*, 376:498 - 500.

Kim J. Y., Lee K., Coates N. E., Moses D. , Nguyen T.O., Dante M., Heeger A. J., 2007. Efficient Tandem Polymer Solar Cells Fabricated by All-Solution Processing, *Science*, 317, 222 – 225.

Urbina A., Miguel C., Delgado J.L., Langa F., Díaz-Paniagua C., and Batallán F., 2008. Isolated rigid rod behavior of functionalized single-wall carbon nanotubes in solution determined via small-angle neutron scattering, *Physical Review B*, 78:045420(5).

Yu G., Gao J., Hummelen J.C., Wudl F., and Heeger A. J., 1995. Polymer Photovoltaic Cells: Enhanced Efficiencies via a Network of Internal Donor–Acceptor Heterojunctions. *Science*, 270:1789–1792.

Hydrogen Storage Materials and Neutron Scattering Experiments

J. Hernández Velasco

Why hydrogen?

Currently there is a great interest in the investigation of hydrogen gas (H_2 molecules) interaction with different materials. The reason is that hydrogen is regarded as a promising alternative to fossil fuels which will, inevitably, become a scarce and unsustainable energy source, also because of environmental issues.

Nowadays, the combustion of carbon and oil based fuels is the most important cause of carbon dioxide (CO_2) emissions into the atmosphere, besides other pollutants. This “greenhouse effect gas” contributes to the global warming.

On the contrary, hydrogen has many advantages as an energy carrier. It is highly abundant, light in weight and, when it is burned in combination with oxygen or used in fuel cells, it generates no emissions other than non polluting water vapour. **Fig. 1.**

Thus, it is not surprising that hydrogen technology attracts such an enormous attention because it is key to solve both energy supply and environmental problems simultaneously.

Hydrogen is an energy carrier that can be generated from various primary energy resources (hydrocarbons, coal, biomass, waste fuels, from water using electrolysis or photochemical water splitting, etc.) Then, hydrogen is a fuel that can be converted from/to electricity.

In this sense, hydrogen fuel cells are emerging as a major alternative energy supply for transportation among other

applications. So vehicle manufacturers are investing huge funds in research and development of fuel cell based cars (Toyota, Honda, GM, etc.) or hydrogen combustion (BMW, Ford, etc.) to allow a transition away from the use of diminishing petroleum resources and towards a dramatic reduction of CO_2 emissions. Hybrid cars, zero pollution prototypes and hydrogen urban buses have already come out.

However, advances in the production and storage of hydrogen are required to achieve the so called “hydrogen economy”. One of the critical challenges of the ongoing intensive effort towards the acceptance and generalised use of hydrogen as an energy carrier concerns its efficient storage with respect to a large number of operating requirements including appropriate temperature, fast release, high storage capacity, etc. Current technologies, using tanks in which H_2 is stored as compressed gas (under high pressure about 350-700 atmospheres) or in liquid state (cooled at low temperatures around $-253^\circ C$), fall far of the mobile targets due to the required tank volume, safety reasons (hydrogen is highly flammable) or energy balance.

Alternatively, hydrogen might be stored in a solid material. These materials could absorb hydrogen more densely packed than in pressurized gas or liquid hydrogen under moderate pressure and temperature. The research to produce new materials for the safe, efficient, and compact storage and retrieval of hydrogen is fundamental to the recognition of hydrogen as a commercially competitive energy carrier.

Which materials?

Hydrogen contains more energy on a weight basis than any other substance but, as the lightest chemical element, it also has a very low energy density. For transportation use, a suitable material for on-board storage should be able to store a high weight-percent and high volume density of hydrogen while rapidly discharge/charge this amount of hydrogen at acceptable temperatures (around 50 to 120°C) and not very high pressure. Low cost, low toxicity and low reactivity with moisture or air are desirable.

Although some chemical compounds meet some of these targets, fully satisfactory materials have not been identified yet. In this sense, public funds from governments have been provided to research projects devoted to such investigation within the European Union and other countries *e.g.* USA, Japan, Canada, Australia, etc.

For a high storage capacity the US Department of Energy has set the objective and timelines of minimum 6 weight % abundance of hydrogen in the storage system by year 2010 and 9% over the next decade. So, optimal materials should be light-weight then, including chemical elements of low atomic number. Heavy elements would enter the composition of materials in a rather low quantity to improve the storage properties.

The absorption and release of hydrogen in a reversible way and the range of temperature and pressure for the process will depend on how strongly the hydrogen is bonded to the material. It can store the H₂ molecule "as it is" by weak links (so called physisorption) or either transform into another chemical compound with bonding to H atoms (chemisorption).

In the former group, diverse nanoporous solids are explored as storage materials including: zeolites, Metal Organic Frameworks (MOFs), and several carbon structures such as fullerenes, nanotubes, nanofibers and activated carbons. "Nano-" prefix deals with the small dimensions of the atomic arrangement in the scale of 10⁻⁹ meters.

In the latter type of materials, intermetallic alloys, light elements hydrides, complex hydrides and some organic compounds are investigated. Multi-component systems or composite materials are examined as well, showing potential enhanced capacity. As an example, carbonaceous materials doped with small quantities of metals improve the hydrogen absorption of both separated substances.

Fig. 2.

Why neutrons?

The knowledge about the structure (position and order of atoms) and dynamical behaviour of hydrogen storage materials is a crucial step towards designing and producing more efficient systems. In this sense, neutron beams could be used successfully to study the physics and chemistry of hydrogen in these materials. When an incident beam of neutrons hits a sample, some are "scattered", the changes of direction and speed of neutrons can be measured and provide information about the structure and motion of atoms inside the material.

In comparison with X-rays produced in laboratory sources or synchrotron radiation facilities, neutrons are small subatomic particles without electric charge that interact with the atomic nucleus revealing its position. By contrast, X-rays are scattered by the electron clouds surrounding the nucleus. Heavy atoms have larger number of electrons and do scatter X-rays more effectively than light atoms.

Neutron scattering techniques are unrivalled to locate the position of light atoms like hydrogen, that become almost invisible for X-rays. Furthermore, neutrons can distinguish contiguous elements much better than X-rays and are unique to recognize different isotopes of the same element, like common hydrogen and deuterium, **Fig. 3.**

Moreover, because neutrons are scattered from collisions with nuclei, they penetrate deeper into the materials than X-rays do. This makes possible the study of samples inside large equipments like engines or complex environments to apply extreme pressures and temperatures, in such cases only neutrons can easily cross along the shielding that surrounds the material.

Within the highlights of neutron research in hydrogen storage materials we could mention the arrangement determination of H₂ molecules absorbed in MOFs, the range of bonding sites and strengths are keys to hydrogen storage capacity and release in these materials. Also, it has been possible to study and differentiate ordered and disordered (amorphous) alloys and metals with distinct hydrogen contents.

On the hydrogenation process, atomic order tends to be changed and these structural changes can be followed *in situ* during uptake and desorption of H₂. Neutron scattering techniques are the most suitable tools to reveal the hydrogen storage mechanisms at the atomic scale. In this sense the construction of the European Spallation Source (ESS) with high neutron flux and high resolution instrument devices could lead such experiments to an unsurpassed level by the existing facilities.

Fig. 1. Hydrogen Life Cycle

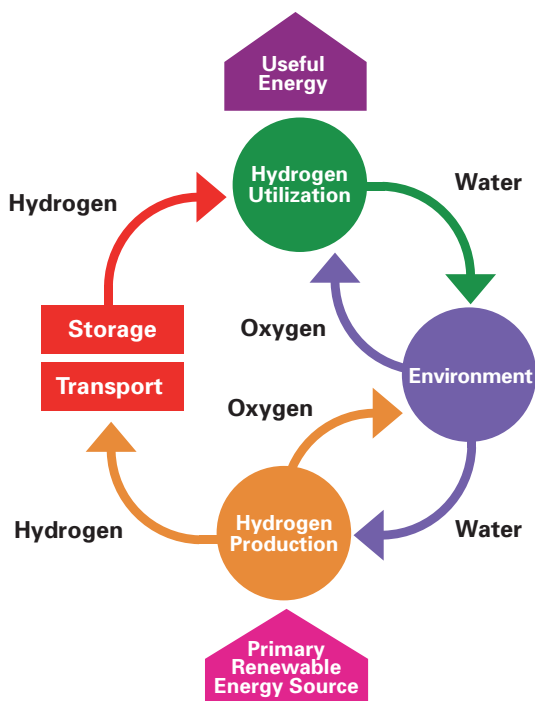


Fig. 2. Scheme of tentative hydrogen storage mechanism in carbon-metal composite. H₂ molecules attach to metal surface and after breaking H-H bond, H atoms diffuse to the carbon support.

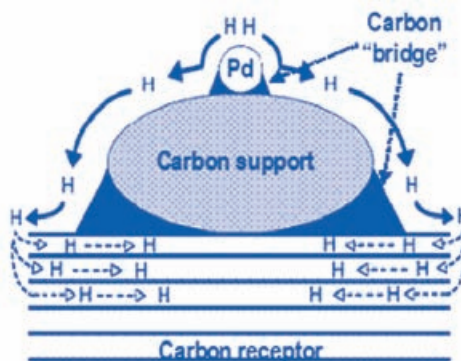
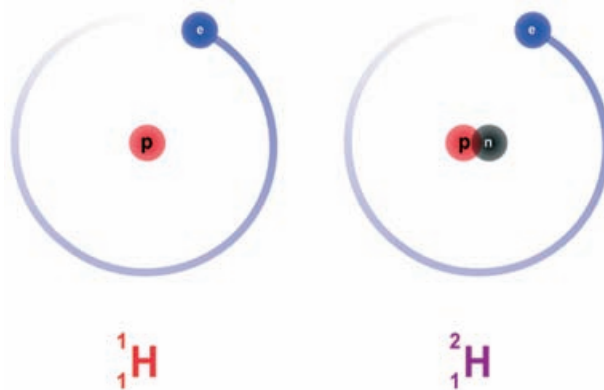


Fig. 3. Scheme of ¹H common hydrogen and ²H deuterium isotope. e=electron, n=neutron, p=proton. Different nuclei interaction with neutron beams allow to discriminate isotopes. Structures can be determined by contrast variation.



New basic science

8



8.1

Quantum Phenomenology

R. Ballou

8.2

**Spin Dynamics of Heavy
Fermions/Valence Fluctuation
Systems at Thermal and
Epithermal Neutron Energies**

A. P. Murani

8.3

**Cold Neutrons, Gravitation, and
Forces in the Universe**

H. Abele

8.4

**Neutron Science and the
Hydrogen Bond in Water**

L. R. Falvello

8.5

**Magnetism without Static
Magnetic Moments: Quantum
Spins and Low Dimensionality**

J. E. Lorenzo, L.P. Reganult

8.6

**Synergy between Neutron
Scattering and Complementary
Experimental Techniques**

J. A. Blanco



Quantum Phenomenology

R. Ballou

The technological capabilities achieved nowadays in the material synthesis open more and more the Pandora box of novel phenomena accessible to experimental investigations. Quite illustrative in that respect was the progress made in the field of molecular magnetism: it was in a compound prepared by the methods of molecular chemistry that for the first time the predicted odd - even half integer quantum spin parity effect in spin chains could be confirmed. Another phenomenon that attracted considerable attention and could be approached in great details was quantum tunneling, in assisting or decohering environments, of nanometer-sized molecule moments through anisotropy energy barriers. A number of other discoveries in this field could be brought to light, not to mention many of its other facets, for instance those dealing with molecular electronics and molecular spintronics, photo-magnetism and more generally multifunctionality, biocompatibility, ... but this would bring us too far in the descriptions. A profusion of phenomena are materialized in other classes of materials as well, oxides, metals, for instance the different avatars of superconductivity, the quantum phase transitions, the fermi-liquid behaviors and its breakdowns, ... to name a few among a sizeable list, the investigations of which by neutron scattering is often decisive to get deep insights into the mechanisms, but it also will not be doable to even take a quick look at them. Occasionally, there might be concepts at a first sight trivial but which unexpectedly reveal themselves a source of a wealth of novel behaviors when brought to fruition in actual materials. An example of this is geometrical frustration that emerged as a domain of intense experimental and theoretical investigations and that allowed finding out the spin liquid and spin ice phases, more precisely those of classical nature featured by specific spin-spin correlations, the quantum analogs being still actively searched. Another fishpond

of novel phenomena are certainly the artificial structures prepared by the methods of nanotechnology.

Neutron scattering was crucial in evidencing the spin parity effect in spin chains for directly probing by inelastic scattering the spin gap in the energy spectrum inherent to the quantum disorder phase associated solely with integer spins. Of course, boosted by the discovery, a number of neutron investigations were performed, inelastic or quasi-elastic, using polarized incoming neutrons and analyzing the outgoing neutron polarizations or by neutron spin echo methods, on a wide variety of new materials, oxides as well as molecular. This provided further experimental characterizations of the quantum disorder phase: the value of the spin gap with respect to the spin amplitude and exchange interactions, the exponential decay with the distance of the spin-spin correlations and the associated correlation length with respect to the spin amplitude could be measured with accuracy and confronted to numerical and theoretical works. The critical phase associated with half odd integer spins was examined by neutron means in great details as well. The soliton excitation (spinon) continuum in the energy spectra was probed. The dyon effect, which allows evidencing through transitions between spinon modes that the spinon carries a spin $1/2$, was observed under transverse magnetic field in anisotropy gaped energy spectra. The algebraic decay with the distance of the spin-spin correlations was proven. Although quite fertile these results were far to close up the topic: many other novel states and excitations could be found out according to the spin parity, the dimensionality of the spins and the exchange interactions between them, these eventually extended to next neighbors or alternated in amplitude and defining the so-called spin Peierls model or else combining bilinear and biquadratic contributions. As examples we might call to mind the free fermion phase, the

spontaneously dimerized phase or more generally polymerized phase, the spin-Peierls phase, the valence bond states, to name a few. **Neutron scattering is an invaluable tool to identify and characterize these phases, by allowing probing the excitation spectrum and measuring the spin-spin correlations.**

Another extension of this physics is concerned with coupled chains forming spin ladders or spin tubes. Attention was paid to finite-length spin chains as well, either open or closed, but essentially on the theoretical side and not that systematically. A new odd-even parity effect then comes out, now associated with the number of spins. In the case of the quantum disorder for instance two effective spins $1/2$ emerge at the ends of an open chain, which interact ferromagnetically to stabilize a triplet state if the number of spins is odd and antiferromagnetically to stabilize a singlet state otherwise, namely if the number of spins is even. This strongly supported the idea that the quantum disorder in chains of integer spins with isotropic first neighbor exchange interactions should be a valence bond states phase where this number parity effect appears natural. A few magnetostatic and resonance measurements were in fact performed on finite-length spin chains, for instance in a closed chain with an odd number of spins, which was interpreted as a magnetic Moëbius strip, but neutron scattering experiments being the way accessing the spin-spin correlation are usually lacking and awaited to get deeper insights.

Quantum tunneling of giant spins through anisotropy energy barriers, in arrays of magnetically isolated nanometer-sized molecules belongs to that class of phenomena which cause a stir when discovered and generate an entire new field of research. A unique opportunity there was open to study an essentially quantum dynamical phenomenon under the influence of decohering environments and therefore to improve our understanding of the crossover from quantum to classical. A macroscopic expression of the quantum escape of the molecule spins out of their anisotropy barrier is experimentally found in the stair-

case hysteresis cycle of the macroscopic magnetization of the whole array under magnetic field parallel to the magnetization axis, which, quite interestingly, is observed because of a broadening of the resonances due the dipolar interactions between the spins of the molecules. A fast quantum relaxation is measured at the tunneling resonances the in-depth investigations of which could be performed at different temperatures and on different time ranges, showing a variety of behaviors and suggesting strong relevance of the environments, in particular nuclear spin and dipolar interactions. A basic parameter inferred from magnetization measurements under sweeping magnetic field parallel to the magnetization axis and controlled by magnetic fields transverse to the magnetization axis is the tunnel splitting. Its investigations allowed finding out the predicted odd – even half integer spin parity effect associated with topological interferences, namely, on increasing from zero the transverse magnetic field, the quantum tunneling for odd half integer collective spin is at first absent then oscillate a few times between zero and a maximum before monotonously increasing whereas for even half integer collective spin it is at first maximum, then oscillate before monotonously increasing as well. It appears that so far the tunnel splitting were not directly probed by neutron scattering most probably either because in zero transverse magnetic field the energy transfer is too weak to be discerned or because not enough large single crystal could be investigated under transverse magnetic field. A few polarized neutron diffraction experiments on single crystals were performed to probe the spin polarization distribution within the molecules in attempts to visualize the spin-spin exchange paths and the formation of the collective spin from its ionic components. Neutron investigations proved advantageous in allowing the accurate determination of intra-molecular and inter-molecular exchange interactions and anisotropy parameters from excitation spectra measured by inelastic scattering. This gave deeper insights about the formation of the collective spins and of the energy barriers from

ionic contributions, which are of great help to design the chemical strategy for the synthesis of new materials with improved single molecule magnet properties.

An environment by essence is decohering, although in certain circumstances it might be assisting to a quantum escape out of an energy barrier by providing the necessary energy coincidence according to its own dynamics as for instance with the dipolar interactions with the other molecules moments themselves subject to tunneling. Of importance is to identify it, to understand its distinctive features, and to examine the possibilities to remove or at least to attenuate it. An environment that can be avoided by merely lowering the temperature is the phonon bath, which couples to the collective spin through magneto-elastic interactions. The mutual influences of the dynamics of the collective spins can be made weaker as well by chemically canceling the eventual intermolecular exchange interactions and increasing the distances between the molecules to decrease the dipolar interactions. The spin bath associated with the hyperfine interactions with the nuclear spins appears the more difficult to escape and, involving subtle decohering mechanisms, the most effective in destroying quantum coherence. The anticipated coherent manipulation of nanometer-sized molecule moments, more precisely preparation and processing of entangled states relevant to quantum computers, is thus found extremely delicate to materialize. A lot of efforts are targeted towards achieving this goal but is so far still in its start. In most instances the experimental works focuses at the single quantum bit processes, by eliminating as much as possible the interactions between them, and extremely few is understood about the coherent manipulation of a collection of spins in decohering environments as it should be the case in an actual quantum computer. Investigations of quantum phase transitions can be insightful in this regard and neutron scattering of prime relevance as a spatially resolved probe of dynamics.

A quantum phase transition, unlike the ordinary transitions which are driven by thermal fluctuations, occur within a ground state and is driven by quantum fluctuations controlled by an intensive parameter other than the temperature, such as a pressure or a magnetic field. It essentially was scrutinized in heavy fermion compounds and high temperature superconductors with the hope that it could help in the understanding of the unconventional behaviors of these complex systems. Its exploration in a single crystal of giant spins blocked in rotation by an anisotropy energy and fluctuating by tunneling through the barrier under finite transverse magnetic field offers the great advantage in principle of being more tractable theoretically. The neutron investigations so far performed are extremely scarce, but already demonstrated a strong influence of the spin baths on the length scale over which the excitations could be entangled. A main difficulty in carrying more systematic neutron experiments is clearly the need of large single crystals for the measurements

No doubt that with a neutron source as ESS, with two orders magnitude in flux higher than those presently available in the other neutron centers all over the world, this extremely fascinating domain of investigations will be called to a strong expansion.

Any set of spins with mutual interactions, which competes in such a way that no spin configuration can minimize all of the interactions simultaneously, is, by definition, frustrated. Identified at first as a basic ingredient of spin-glass behaviors of amorphous materials with a random-looking mixture of positive and negative exchange interactions, this phenomenon of frustration can occur in crystalline materials. It is distinguished as geometric when it is inherent to the geometry of the network of spins. It then may give rise to macroscopic degeneracy of the ground state with classical spins, which results in an extensive entropy at zero temperature. Accordingly, magnetic orderings are inhibited except if secondary interactions are relevant, in which case the stabilized orders are complex, non collinear and/or multi-propagating. A subtle mechanism of order

by disorder can be at work, but is not fully effective in all the instances and can be thwarted by degeneracy allowed local deformations of the spin configurations or by the quantum tunneling between degenerate spin configurations separated by an energy barrier. When the different degeneracy breaking effects are absent or not efficient enough novel magnetic phases are foreseen: spin liquids, valence crystals, multi-spin orders associated with the breaking of only space isotropy (nematic liquid) or only time reversal and parity invariance (chiral liquid), topological glasses. It will be not possible to go into the details of the huge amount of experiments performed on geometrically frustrated magnets, except emphasizing that the neutron scattering experiments proved invaluable in discovering spin liquids and spin ices through measurements of the spin-spin correlations. Other anticipated or unexpected phases are presently actively being searched.

A final point that merely could be signaled is the neutron investigation of the magnetism of nano-objects, which potentially could strongly benefit from the ESS. Generally nano-objects are too small to be investigated by most of the neutron scattering methods, safe in ensembles. New spectrometers are however foreseen for small angle neutron scattering and grazing incidence small angle neutron scattering using polarized neutrons, which, it is expected, would allow probing the magnetic density distributions in systems with a size in the 2nm to 1000nm range with the presently available neutron flux. A visualization of the different modes of the magnetization reversal in a magnetic nanowire, buckling, curling, coherent rotation, would then become possible. Quantum motions of domain walls out of pinning centers could be opened to observations as well. With a flux higher by two orders of magnitude higher precision measurements could be achieved. It is not unlikely that inelastic scattering then could be made feasible as well. This would open the possibility to probe for instance such phenomena as the finite length cut off of the long wavelength spin wave propagation in a magnetic nanowire.

In short neutron scattering provides the most complete information we could expect in a spin system by giving access to the generalized dynamical susceptibility. An extremely wide range of spatial correlations and time window can be covered from hot to ultra-cold incident neutrons and magnetic information can be experimentally extracted from other signals through the appropriate polarization analysis. Neutron proved an invaluable tool in more than an instance to directly measure the relevant effect of a given phenomenon, such as spin gaps, spin baths thwarting of excitation softening, spin fluidity, to name a few of quantum nature. An only limitation appears to be the necessity to use a quite large amount of samples, in particular large single crystal to get significant signals.

The ESS with its flux would open the possibility to investigate a number of quantum phenomena momentarily out of reach.



FURTHER READING

- J.P. Renard, M. Verdaguer, L.P. Regnault, W.A.C. Erkelens, J. Rossat-Mignod, W.G. Stirling, *Europhys. Lett.* 3 (1987) 945
- L. Thomas, F. Lioni, R. Ballou, D. Gatteschi, R. Sessoli, B. Barbara, *Nature* 383 (1996) 145 – J.R. Friedman, M. Sarachik, J. Tejada, R. Ziolo, *Phys. Rev. Lett.* 76 (1996) 3830
- W. Werndorfer, R. Sessoli, *Science* 284 (1999) 133
- H.M. Ronnow, R. Parthasarathy, J. Jensen, G. Aeppli, T. F. Rosenbaum, D.F. McMorrow, *Science* 308 (2005) 389
- R. Ballou, E. Lelièvre-Berna, B. Fak, *Phys. Rev. Lett.* 76 (1996) 2125 – I. Mirebeau, I. Goncharenko, I.N. Cadavez-Perez, P. Bramwell, S.T. Gingras, *Nature* 420 (2002) 54
- S. T. Bramwell and M. J. P. Gingras, *Science* 294 (2001) 1495 – T. Fennel, S.T. Bramwell, D.F. McMorrow, P. Manuel, A.R. Wildes, *Nature Physics* 3 (2007) 566

Spin Dynamics of Heavy Fermions/Valence Fluctuation Systems at Thermal and Epithermal Neutron Energies

A. P. Murani

Heavy *Fermions*, the highly correlated electron systems generally involving the rare earths Ce, Yb or the actinide U as one of the constituents, exhibit some very interesting physical properties, amongst which their most distinguishing Fermi-liquid characteristics are: i) enhanced, constant magnetic susceptibility $\chi(0)$ at low temperatures, $T \rightarrow 0$ K, ii) large linearly temperature dependent low temperature specific heat, $C = \gamma T$, and iii) low temperature electrical resistance varying as the square of the temperature, $R = AT^2$, with the coefficient A roughly proportional to γ^2 .

The heavy-Fermion character derives from the mixing, i.e. hybridization, of the electrons forming the magnetic shell on a given lattice site with the conduction electrons or other outer electrons of the neighboring sites. This interaction is responsible for the heavy mass 'quasi-particles' at the Fermi surface and the apparent 'transformation' of the system into the low temperature non-magnetic state. At first sight it may appear paradoxical that as the strength of the interaction between the local-moment and conduction electrons (i.e. hybridization) *increases* the 'effective' mass of the quasi-particles, deduced from the linear specific heat coefficient γ , *decreases*. Increasing hybridization or 'mixing' with conduction electrons induces faster temporal fluctuations of the f-shell occupancy as well as increased deviations from integral valence. Systems with low to moderate values of $\chi(0)$ and γ in which hybridization is very pronounced are usually referred to as *valence fluctuation systems*.

Some Yb-based systems, for example YbAl₂ which has a practically temperature independent magnetic susceptibility below room temperature, were initially considered as divalent with a full 4f shell, hence non-magnetic. In the case of Ce

metal, the early theories of the transition from the γ to the α phase proposed that the single 4f electron of trivalent γ -Ce is promoted, or pushed out, to the s, p, d conduction band leaving behind a tetra-valent Ce⁴⁺ state in the α -phase with zero 4f occupancy. The latter interpretation was, however, shown to be inconsistent with subsequent experimental findings from positron annihilation experiments that detected little change in the number of s, p, d conduction electrons at the transition to the α -phase. An alternative theory then postulated a transformation of the localized 4f state in γ -Ce into a narrow 4f band in α -Ce. While this is, apparently, still a widely held view it is in contradiction with the results of high-energy neutron studies, presented below, that show an energy-broadened 4f state in α -Ce which is, nevertheless, substantially localized.

A number of investigations of spin dynamics of heavy Fermions/valence fluctuation systems reviewed below have required the use of epithermal neutrons. In general, the paramagnetic response from these systems is broad and Lorentzian in spectral form whose maximum represents the characteristic energy T_K . Since neutrons of incident energies of $\sim 3T_K$ to $\sim 10T_K$ are necessary to study such a response adequately, we have performed measurements using incident neutron energies as high as ~ 2000 meV on systems with characteristic energies T_K reaching ≥ 500 meV. **It is useful to recall that magnetic inelastic neutron scattering studies on reactor sources have generally been limited to the energy region below ~ 200 meV. The advent of the spallation neutron source has permitted the energy range to be extended by more than an order of magnitude opening up possibilities of research into domains, such as this, that were inaccessible previously.**

The $\gamma \rightarrow \alpha$ phase transition in Ce:

The $\gamma \rightarrow \alpha$ phase transition in Ce has remained enigmatic ever since its discovery in 1927 by Bridgman. A detailed pressure experiment performed many years later shows clearly that an abrupt, ~ 6 fold, drop in the susceptibility of Ce occurs above ~ 9 kbar as the metal transforms from the γ to the α -phase. This is accompanied by a 14 % volume reduction but there is no change in the crystalline structure that is fcc in both phases. A similar drop in magnetic susceptibility of Ce (alloyed with a small concentration of Sc or Th to prevent β -phase formation) also occurs as a function of temperature around ~ 120 K, below which the susceptibility is practically temperature independent.

Indeed, hybridization between the local moments and the outer electrons occurs, although moderately, in the γ -phase of Ce also. In fact, the strength of the hybridization and hence its effect on the physical properties vary from moderately weak, as in γ -Ce, to being extremely strong as in α -Ce and α -Ce-like systems, particularly CeFe_2 and CeRu_2 . The relatively weak hybridization in γ -Ce-like systems, particularly CeAl_3 , CeCu_2Si_2 and many others which exhibit a very large specific heat coefficient γ (or C/T) at low temperatures, and to which the classification heavy Fermions was originally applied, manifests as

broadened crystal field states. Thus, in γ -Ce the neutron inelastic scattering data down to 120 K, show a quasi-elastic distribution of moderate width associated with the crystal field ground state and an inelastic peak of similar width corresponding to the excitation from the ground state to the higher-lying cubic crystal field state. In the α -phase, however, the magnetic response consists of a very broad Lorentzian spectrum centered on the characteristic energy of ~ 170 meV. This is very similar to the single-ion spectral form calculated by Kuramoto and Müller-Hartmann for the Anderson model, **Fig. 1**. The characteristic temperature is given as $T_K \sim D \exp(-\pi|\epsilon_f|/N\Delta)$ where D is the conduction electron bandwidth, ϵ_f the position of the 4f state relative to the Fermi level E_F , N the degeneracy of the 4f state and $\Delta = \pi V^2 \rho(E_F)$, where V is the strength of the interaction and $\rho(E_F)$, the density of conduction electron states at E_F .

We have determined the magnetic form-factor $F^2(Q)$ by integrating the spectral intensity within ± 30 meV around $T_K \sim 170$ meV as shown in **Fig. 2** where the continuous curve represents the Ce^{3+} form factor and the dotted curve is the form factor for the itinerant 4f band calculated by Hjelm et al. It is evident the latter curve deviates significantly from the measured data which, however, closely follow the single-ion Ce^{3+} form factor.

The ' $\gamma \rightarrow \alpha$ -like' phase transition in YbInCu_4 :

A very similar phenomenon to the $\gamma \rightarrow \alpha$ transition in Ce is observed for the compound YbInCu_4 . On cooling, the magnetic susceptibility of the compound drops abruptly below ~ 40 K, in a manner quite similar to that at the $\gamma \rightarrow \alpha$ transition in Ce at ~ 120 K, becoming practically temperature independent at lower temperatures. Neutron data at low energies show that in the high temperature phase, $T > 40$ K, well-defined crystal field excitations are observed, **Fig. 3**, which disappear abruptly below 40 K from the energy window of the data, having transformed to a broad Lorentzian spectral distribution observed in neutron energy loss spectroscopy with a high incident energy of ~ 150 meV, **Fig. 4**. The Q -dependence of the integrated intensity around the maximum ($T_K \sim 32$ meV), shown in the inset to **Fig. 4**, follows closely the Yb^{3+} magnetic form-factor. This is similar to the Ce^{3+} single-ion form-factor exhibited by the Q -dependence of the integrated intensity within a small energy range around the characteristic energy T_K of ~ 170 meV of α -Ce, **Fig. 2**. Hence, these results clearly indicate that the energy-broadened 4f states remain localized across the transition from the γ to the α -phase in both Ce metal and YbInCu_4 .

Fig. 1 The magnetic spectral response from α -Ce plotted as $\chi''(\omega)/\omega$ fitted to the Lorentzian (LOR) and the Kuramoto and Müller-Hartmann (K-MH) spectral forms.

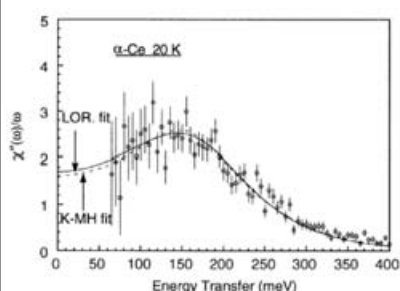


Fig. 2 Integrated intensity within ± 30 meV around $T_K \sim 170$ meV plotted as function of Q . The continuous curve shows the Ce^{3+} form factor and the dotted curve is the form factor for the itinerant 4f band.

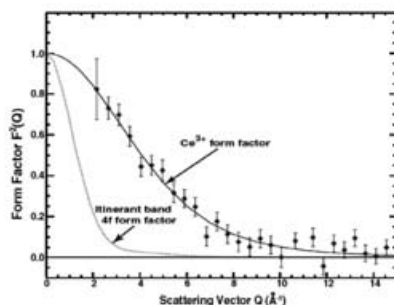


Fig. 3 Crystal field excitations observed for $T > 40$ K in YbInCu_4 using the time-of-flight neutron energy-gain spectroscopy.

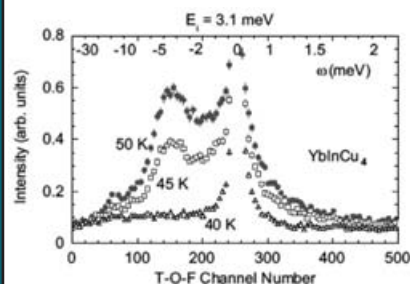
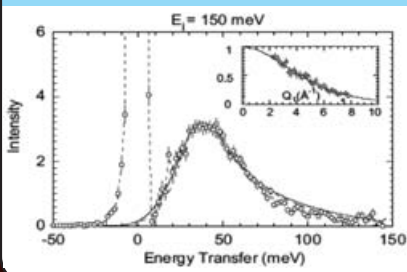


Fig. 4 Magnetic scattering at $T = 35$ K in YbInCu_4 . The inset shows the Q -dependence of the intensity at the maximum fitted to the Yb^{3+} form factor.



Spin-Orbit excitations in heavy Fermion systems:

One of the most fascinating observations for both the Ce and the Yb-based heavy Fermion systems, still awaiting a detailed theoretical interpretation, is that of spin-orbit excitations that occur at significantly higher energies compared with the free-ion values. Measurements of the difference spectrum between the γ and the α phases of Ce at the same temperature of 125 K, making use of the hysteresis in the transition, were performed using neutrons of incident energy 2000 meV at ISIS. The residue of the data relative to the fit clearly shows the spin-orbit excitation in γ -Ce at ~ 260 meV as well as a hump in the negative part (i.e. the α -Ce part) of the difference spectrum representing the spin-orbit excitation in α -Ce. In order to ascertain this remarkable finding we have also performed measurements using the beryllium filter spectrometer on the hot source at ILL which has a very high luminosity for neutrons of energies up to ~ 700 meV, and possibly beyond. The data reproduced in **Fig. 7** clearly indicate a well-defined excitation at ~ 260 meV in the γ -phase which disappears in the α -phase having been transformed into a broad hump at around ~ 500 meV, representing the spin-orbit excitation in

the α -phase. A similar observation for the spin-orbit excitation energy has been made for the compound YbInCu_4 across the ' $\gamma \rightarrow \alpha$ -like' transition in this compound, **Fig. 6**. Although the observed excitations are broad and resolution limited, due to the use of high-energy neutrons, a shift of $\sim 50 \pm 30$ meV is clearly seen in the spin-orbit excitation energy in the ' α -like' low temperature phase.

Fig. 5 Scattering intensity as a function of energy transfer in the γ and α -phases of Ce. The well-defined spin-orbit excitation at ~ 260 meV in γ -Ce transforms into a broad excitation around ~ 500 meV in α -Ce.

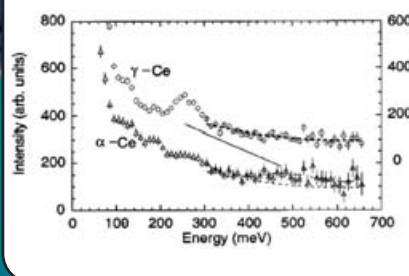
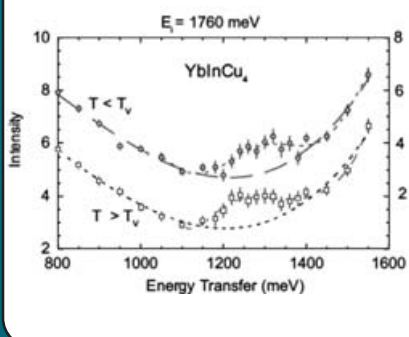


Fig. 6 Observed high-energy excitations across the ' $\gamma \rightarrow \alpha$ -like' phase transition in YbInCu_4 showing an energy shift of $\sim 50 \pm 30$ meV in the α -phase ($T < T_v \sim 40$ K).



Well-defined spin-orbit excitations at enhanced energies have been observed in systems with characteristic energies T_K in the region of several tens of meV. **Fig. 7** shows data on CePd_3 ($T_K \sim 55$ meV) taken with neutrons of incident energy 900 meV. The data are fitted to a Lorentzian spectral function and the inset shows the residue with respect to the fitted curve. It represents the spin-orbit excitation at ~ 370 meV which corresponds to an enhancement of ~ 100 meV ($\sim 2T_K$) over the free-ion value. Also, in the series of compounds $\text{CeIn}_{3-x}\text{Sn}_x$ ($0 < x < 3$) the energies of the spin-orbit excitations as well as their widths, **Fig. 8**, are found to increase progressively with x such that the enhancement in energy above the free-ion spin-orbit value and the width Γ are both roughly twice the magnitude of the characteristic energy T_K of the ground state.

The observed enhancement of the spin-orbit energy by about 1.5 to 2 times the ground state T_K can be understood qualitatively in terms of the higher characteristic energy T_K of the upper spin-orbit level due to its closer proximity to the Fermi level, hence stronger hybridization with the conduction electrons. As a result, the upper spin-orbit state should also transform into a broad hump centered on $\Delta_0 + T_K$, where Δ_0 is the free-ion spin-orbit energy. Thus, the enhancement of the spin-orbit excitation energy provides a measure of the characteristic energy of the upper spin-orbit state of the ion.

Fig. 7 The observed magnetic spectral response from CePd_3 fitted to a Lorentzian spectral function. Inset shows the residue representing the spin-orbit excitation at ~ 370 meV.

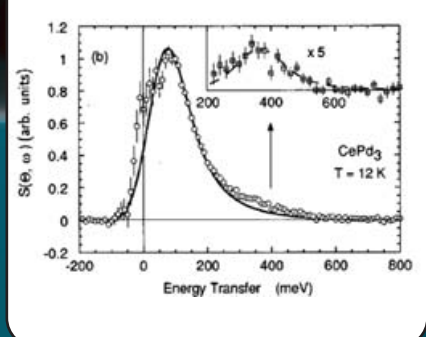
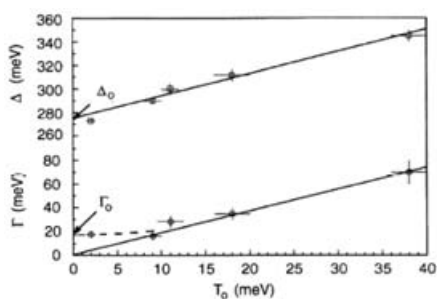


Fig. 8 Spin-orbit energy and the width Γ as a function of the ground state characteristic energy T_0 (i.e. T_K) for the series of compounds $\text{CeIn}_{3-x}\text{Sn}_x$ ($0 < x < 3$).



Conclusions:

We have briefly reviewed above some high-energy neutron experiments on moderately heavy Fermion systems that are often classified as valence fluctuation systems. We find that the magnetic states become progressively broader and their spectral widths correspondingly larger with increasing hybridization. It is very interesting that a substantial single-ion character of the 4f state is preserved not only in α -Ce ($T_K \sim 170$ meV) but also in the very strongly hybridized systems such as CeFe_2 and CeRu_2 ($T_K \sim 500$ meV). Epithermal neutrons have proved essential for the investigation of the broad, high-energy ground states of these materials as well as the spin-orbit excitations that occur at significantly enhanced energies compared to the free-ion values.

One of the investigations reviewed above has helped to establish that the high luminosity of the hot source at ILL can permit measurements to energies reaching ~ 700 meV, or higher, except that the beryllium filter technique used there imposes relatively high Q-values. In general, however, investigation of magnetic systems requires a focus on the low-Q region that can, indeed, be accessed readily using time-of-flight spectrometers. The latter are well developed and represented within the instrument suite at ISIS but are somewhat disadvantaged in the investigations of systems with intrinsically weak signals, for example dilute alloys, due to the limited source flux. **The proposed spallation neutron source ESS together with state-of-the-art, high-energy, time-of-flight spectrometers served by appropriate moderators could provide an order of magnitude increase in flux at high energies and prove extremely valuable for many interesting and challenging scientific problems of the future.**



FURTHER READING

- J.M. Lawrence, P.S. Riseborough and R.D. Parks, Rep. Prog. Phys. 44, 1 (1981)
- D.R. Gustafson, J.D. McNutt and L.O. Roelling, Phys. Rev. 183, 435 (1969).
- B. Johansson, Philos. Mag. 30, 469 (1974).
- P.W. Bridgeman, Proc. Am. Acad. Arts Sci. 62, 207 (1927).
- M.R. MacPherson, G.R. Everett, D. Wohlleben and M.B. Maple, Phys. Rev. Lett. 20, 26 (1971).
- A.P. Murani, Z.A. Bowden, A.D. Taylor, R. Osborn et al. Phys. Rev. B 48, 13981 (1993).
- Y. Kuramoto and E. Müller-Hartmann, J. Magn. Magn. Mater. 52, 122 (1985).
- D.L. Cox, N.E. Bickers and J.W. Wilkins, J. Appl. Phys. 57, 3166 (1985).
- A.P. Murani S.J. Levett and J.W. Taylor, Phys. Rev. Lett. 95, 256403-1 (2005).
- A. Hjelm, J. Trygg, O. Eriksson, B. Johansson and J. Wills, Phys. Rev. 50, 4332 (1994).
- A.P. Murani, D. Richard and R. Bewley, Physica B 312 -313, 346 (2002).
- A.P. Murani, J. Reske, A.S. Ivanov and P. Palleau, Phys. Rev. B 65, 094416 (2002).
- A.P. Murani, R. Raphael, Z.A. Bowden and R.S. Eccleston, Phys. Rev. B 53, 8188 (1996).
- A.P. Murani, A.D. Taylor, R. Osborn and Z.A. Bowden, Phys. Rev. B 48 10606 (1993).

Cold Neutrons, Gravitation and Forces in the Universe

H. Abele

Galileo Galilei would be somewhat surprised. At least, when neutrons become ultra-cold and fall in the gravity field of the earth. Today his famous fall experiment shows quantum aspects of the subtle gravity force in the sense that neutrons do not fall as larger objects do. Neutrons as quantum particles show characteristic departures from classical behavior. We find them only on particular energy levels, when they come close to a reflecting neutron mirror, where only small quantum leaps are allowed. This phenomenon, known as quantum bouncer, is neatly explained by a general rule of quantum mechanics in the sense that bound states must have discrete energy levels. The hydrogen atom, the electromagnetically bound system made out of a proton and an electron, is such an example. The conventional picture is not sufficient to explain the buildup of this atom, and the energy levels are calculated quantum mechanically. A gravitational bound neutron on the mirror corresponds to the electromagnetic bound electron in the hydrogen atom. But with neutrons, the energy levels have values that are smaller by many orders of magnitude compared with an electromagnetically bound electron in a hydrogen atom. From the physicist's point of view, gravity has a special position, because it is much weaker than other fundamental forces of nature. A promoting interest in such low-energy experimentation with neutrons is the unexplained role of gravity in modern theories and the realization that for basic open questions a deeper understanding of gravitation is needed. **Neutrons do now test speculations on large extra dimensions of submilli-meter size of space-time or the origin of the cosmological constant in the universe, where effects are predicted in the interesting range of such experiments and might give a signal in an installation at an ultracold neutron source at ESS.**

Neutron Source

At ESS, neutrons are produced in a spallation source. At production, these neutrons are very hot corresponding to 10^{10} degrees. In a first step, spallation neutrons are slowed down to room temperature by passing through heavy water. Cold neutrons are obtained in a second moderator stage at ~ 25 K. These cold neutrons have a velocity spectrum around 800 m/s. For particle physics, a flux of more than 10^{10} $\text{cm}^{-1}\text{s}^{-1}$ over a cross section of 6 cm x 20 cm is available at existing neutron sources. Some experiments profit from high intense cold neutron beams at ESS, other experiments need even colder neutrons, so called ultra-cold neutrons. The corresponding temperature is a thousandth degree above absolute zero. These neutrons are so cold that they are reflected from surfaces and can be stored in "neutron bottles". On this side of the scale, the gravity experiment uses neutrons having 10^{18} times less energy than spallation neutrons at the beginning of the moderation process.

Sensitivity

Experiments with neutrons have obtained an extreme level of sensitivity and precision. For example ultracold neutrons at a milli-Kelvin temperature make energy changes down to 10^{-23} eV measurable and changes in neutron momentum can be measured to 10^{-11} . This number is remarkable: 10^{-11} corresponds to a sensitivity of the size of about an atom over a distance of 9 m.

Although it is difficult to determine an exact range, basic questions – relating the standard theory of particle physics, the Standard Model, to cosmology and other areas of physics and astronomy – come into reach for low-energy experimentation, were tiny signs from corresponding effects are detectable, but remain so far and in the future mostly unaccessible for high-energy accelerator experiments. **Therefore, due to their extreme precision, low-energy experiments can be sensitive to processes occurring at much higher energies than accessed with today's accelerators.** The experiments provide the zero-energy values of the Standard Model, improve its internal consistency, and define the point of departure for new physics beyond the Standard Model. This field of research with neutrons is related to highest energies right after the Big Bang, when gravity was as strong as other forces like the electroweak or the strong force of the Standard Model of particle physics. The Standard Model of particle physics is usually studied by highest beam energies in accelerator experiments. **Neutron physicists however use "low energy" or cold and ultra-cold neutrons, neutrons that are much colder than the molecules around us.**

Forces in the Universe and Cosmology¹

The combination of quantum mechanics and gravitation by studying quantum states in the gravitational field of the earth is just one example for new techniques for measurements of fundamental properties. Neutrons react to all known forces and are a powerful tool for addressing questions from the domains of particle physics, nuclear physics and astronomy. A nice example is cosmology. We think that all started dense and hot with the so called "big bang". Since then, the universe has been expanding and has been cooling to the situation we find today. We believe that the universe followed a number of different phase transitions into states of

successively lower symmetry in a sequence as follows: Planck scale, Grand Unified Theory (GUT) transitions, Inflation, electroweak transition, baryogenesis, nucleosynthesis, atomic freeze-out, galactic freeze-out. Hence, our understanding of the development of the universe is based on the knowledge about phase transitions, a subject that has been studied in all their varieties with neutron experiments vigorously over the past 30 years. On all states, neutrons test these very early stages of the universe with a variety of observables, see **Table 1**. Some observables require neutron physics, for other questions the neutron provides one of several ingredients.

¹This section updates "Neutrons and the origin of the universe", H. Abele, W. Fischer, H. Rauch, in: New Science and technology for the 21st Century. ESS Council, 2002.

a Planck Scale, the Very Early Stage

We discuss different stages of our universe and start at the Planck scale of 10^{19} GeV or 10^{-35} m, the length scale of quantum fluctuation of space time geometry. Here, right at the beginning, theorists try to formulate a unified theory of gravity together with the other basic forces, still one of the great and unsolved challenges in modern physics. Such a theory can be formulated consistently in space with six or seven extra dimensions. How can it be tested? If our universe has really six additional dimensions, we should observe new phenomena related to the existence of these dimensions. **If large extra dimensions existed, we would find deviations from Neutron's gravity law in the $1 \mu\text{m}$ to $100 \mu\text{m}$ range with suited experiments.** Deviations from Newton's law are also expected from so called axion couplings. Axions are hot topic dark matter candidates and best limits on axions are derived from experiments with neutrons. In any case, as we have no means to reach the Planck scale of 10^{19} GeV or 10^{-35} m, this symmetry must be inferred from low energy measurements, be this at 1000 GeV in present day's "high energy" experiments, be this at 10^{-23} eV in present days "low energy" experiments".

b Grand Unified Theories

The basic idea of Grand Unified Theories is that the three forces – the strong, the weak and the electromagnetic force – are actually components of one single unified force. An underlying symmetry relates one component to the others so that all is described by a single force law. The same symmetry implicates that particles like electrons, quarks and neutrinos are basically the same. On the other hand we know that these particles nowadays behave very differently. Thus, the theory is constructed such that the symmetry is spontaneously broken in the present universe. The detailed mechanism of symmetry breaking is related to the analogous mechanism in condensed matter phase transitions, a complicated interplay between large numbers of electrons and atomic nuclei and has been revealed with neutrons. Thus, particle physicists profit from models developed in condensed matter physics.

Grand Unified Theories also bring new features to neutron physics which have drastic new implications. To give an example, **many Grand Unified Theories foresee a conversion of a free neutron into its antiparticle, an antineutron. But we have no indication for neutron-antineutron-oscillation from experiments so far.** The present experimental limit for neutron anti-neutron oscillations is $t > 10^8$ s.

Neutrons are neutral. The experimental limit of less than 10^{-21} electron charges is a clear indication for physics beyond the Standard Model and points directly to Grand Unified Theories. The Standard Model does not have electric charge quantization, so neutron's charge could be anything. The small size of this value may be considered as to speak for Grand Unified Theories, where neutron's charge is equal to zero.

C

Electroweak Transition

Most theories about this early stage of the universe expect a high degree of symmetry, e.g. no difference between left and right or between particles like fermions and bosons. The situation of high symmetry is very different from what we find today, where only left-handed neutrinos or electrons can be found in neutron β -decay due to the weak interaction and differences between particles are obvious. We speak about the observed breaking of symmetries for example of parity P, of time reversal T and of combined charge conjugation and parity CP. We explain this difference between now and before with the assumption that the universe evolved through a number of different phase transitions into states of successively lower symmetry, a scenario, which, if true, would mean that the neutrinos today should carry a small right-handed component. Limits on the right-handed currents have been derived from free neutron and muon decay experiments. We have reached the energy scale of the Standard Model of particles and fields.

Neutron β decay determines Standard Model parameters. The number of independent observables offered by neutron β decay is considerably larger than the small number of parameters describing this decay in the Standard Model. In 2008, the Nobel prize in physics was awarded for achieving CP violation with so called 'quark mixing' in three generations via the CKM matrix. The first element of this matrix is one of the two parameters describing neutron decay within the Standard Model. The other parameters in the prediction for the energy consumption in the sun and the solar neutrino flux, the light elements in the primordial nucleosynthesis (see next section), and neutron star formation. The parameter is also used for the calibration of neutrino detectors. **All these particle cross-sections used in cosmology, astrophysics and particle physics today thus have to be calculated from neutron decay data.**

d

Baryogenesis and Nucleogenesis

About a second after the weak interaction drops out of equilibrium, we can follow what a gas of interacting baryons (protons and neutrons) does when the universe expands and cools. About one hundred seconds later, nuclei can survive and neutrons and protons are converted into deuteron, triton and Helium. Big Bang nucleosynthesis made helium with traces of deuterium and Lithium. The protons left over remain as hydrogen. The primordial mass fraction of He is $\sim 0.25\%$ and agrees well with the observed helium abundance in our universe. The theory of primordial Big Bang nucleosynthesis is considered to be very powerful since all inputs entering the calculations are known from laboratory experiments. In the past 15 years, finer details of the results have been taken into consideration. For example,

the more types of relativistic particles exist, the greater is the energy density and as a consequence, the faster is the cosmological expansion rate, yielding a higher neutron to proton ratio. A higher neutron to proton rate ends up in more helium. On the other hand, a short neutron lifetime lowers the neutron to proton ratio thus yielding less helium. **As a consequence, neutron lifetime measurements together with the observed helium abundance have made a definite prediction about the number of particle families.** The formal statistical result provided a reasonable fit to three particle families but making a fourth neutrino family exceedingly unlikely. Later on, particle accelerators were beginning to probe to the cosmological level of sensitivity. At C.E.R.N., the existence of three particle families has been brilliantly verified with a measurement of the decay width of the Z-boson.

At this stage of cosmological expansion, a serious problem becomes evident: Where remains the anti-matter? According to the standard big bang theory equal amounts of matter and antimatter were created in the primordial explosion. In the subsequent process of annihilation of matter and antimatter only very few heavy particles ("baryons") and an equal number of antiparticles from this early period could survive. Our mere existence contradicts this expectation; there remained about 10^8 times more baryons in the universe than predicted and almost no antibaryons have survived. So far, the only viable solution of this problem is the violation of charge-parity symmetry (CP) which, on all reasonable expectations, is equivalent to a violation of time reversal symmetry (T) that could have led to a small excess of particles before the annihilation stage. The most direct access to these questions lies in the detailed investigation of neutron decay parameters or in measurements of its electric dipole moment (EDM). The existence of an EDM violates time reversal and also charge parity (CP) symmetry. EDM measurements started in the fifties and increased their sensitivity by one order of magnitude every seven years. **Current theories of the baryon asymmetry of the universe is related to an EDM of about 10^{-28} e cm, a limit that is accessible with one flagship experiment for the ESS. The current upper limit is $3 \cdot 10^{-26}$ e cm.**

Atomic and Galactic Freeze-out

At this stage of cosmic expansion about 300000 years after the big bang, the universe is cold enough for the build-up of atoms through electron recombination driven by the electromagnetic force. **The fine structure constant α defines the strength of this force, and has been determined – astonishingly enough – from neutron experiments. Other experiments are more precise right now, but new neutron measurements are underway.**

Today, our universe populated by billions of galaxies appears to be expanding at an accelerating rate. The rate is governed by a new form of energy: dark energy. The observation of the accelerated expansion was a big surprise a decade ago that has driven the current revolution in cosmology. 70% of the cosmos consists of dark energy and no one is sure what it. There are ideas for what it might be, but they remain vague. One speculation links the magnitude of the dark energy in the universe to the modification of gravity at small distances, again in the range of gravity experiments with neutrons.

e

8.3

Table 1: Left: phase transitions in the early universe; middle: observables in neutron-particle physics; Right: related physical questions. This table is based on [1]

Phase transitions in the early Universe	Observables in neutron particle physics:	Related physical questions
Planck	Spin, mass, gravitational bound quantum states, quantum interference	Dark matter search, search for gravity-like forces expected from large extra-dimensions, equivalence principle
GUT transition	Charge, electric dipole moment, magnetic dipole moment, electric polarizability	Supersymmetry, baryon asymmetry in the universe, charge quantization, GUT's Quark models
Inflation		
Electroweak transition	Angular correlation coefficients in neutron decay, lifetime, Energy spectra: of electrons, protons, of various correlation coefficients, of inner bremsstrahlung Neutron decay into hydrogen, Parity violating effects: Spin rotation in nonmagnetic medium, Neutron polarizing action of nonmagnetic medium, n-p g-asymmetry, n-p circular polarization	Supersymmetry, left/right symmetry, Time reversal symmetry, quark mixing and CKM matrix, scalar and tensor interactions
Baryogenesis	electric dipole moment	baryon asymmetry in the universe
Nucleosynthesis	Angular correlation coefficients, Lifetime	$^3\text{He}/^4\text{He}$ abundance in the universe, neutrino freeze-out
Atomic freeze-out	m_n/n_p , h/m_n	strength α : value of electromagnetic interaction
Galactic freeze-out	gravitational bound quantum states, quantum interference	Dark energy and accelerated expansion of the universe in some models

[1] D. Dubbers, Nuclear Physics A654 297c (1999)

Neutron Science and the Hydrogen Bond in Water

L. R. Falvello

Water is a superb enigma -- a substance whose molecules are composed of just three atoms and which nevertheless is the most plentiful and arguably the most important component of living creatures, the most complicated and least understood of nature's creations. Only two elements, oxygen and hydrogen, contribute their atoms to water, H_2O , and yet the complexities of its properties have still not been completely unrevealed by science. The molecule of water has a simple shape, like the letter "V", but its presence is essential for almost all of the enormously complex processes that take place in living beings. *What is it about water that makes it at once so simple to picture and so difficult to understand?*

Water is everywhere in the world around us, a total of 1360 million cubic kilometers (326 million cubic miles) of it. Only a small amount of it, though, some 3%, is freshwater, directly useful to humans. And of that, only one-third of one percent is on the surface of the earth in liquid form – rivers, lakes, ponds. Two-thirds of freshwater is to be found in glaciers and icecaps, and some 30% of freshwater is in the ground. So like the Ancient Mariner of Coleridge's poem, humanity in its ever-increasing numbers is faced with the problem of "Water, water every where/ Nor any drop to drink." We are correct to wonder what the future of water will be for life on earth. Among the many answers to potential problems – a drier future? – is scientific study. Water, one of the substances most familiar to humans, is still an object of continuous scientific exploration. Much is known about it. Much remains to be discovered. On a large scale, the future management of global water resources depends ever more importantly on advances in our understanding of the properties of water.

On a far smaller scale, the future use

of many of our molecular artefacts, such as the pharmaceuticals that work in the water-rich environment of the human body, also depends on our advancing knowledge of water and its interaction with the other molecules of life.

The study, or at least the contemplation of water is not new, dating back famously at least as far as Aristotle, who described water as one of the four fundamental elements – along with air, earth, and fire. Even before Aristotle, Thales of Miletus had urged the scholarly mind to "Meditate on water!" an injunction to which even modern science willingly conforms.

The imperatives of resource usage and medical applications, if not extant, would not be necessary in order to inspire science to study water. The immediate questions suggested by water and its properties are not less than imposing. How is it that such a simple molecule forms substances with such odd properties? The melting and boiling points of water, to begin with, are out of line. They do not agree with the

predictions derived from the chemical periodic table (using the properties of compounds formed from the congeners of oxygen). How can it be that a molecule with just three atoms is necessary for complex physiological processes? What is it that permits water to dissolve ionic substances, like table salt, as well as certain complex molecular substances, like sugars? The molecular simplicity of water is a stunning counterpoint to its functional complexity, and despite the latter it is colorless, odorless, and tasteless. There is still more – water has one very anomalous characteristic that has been essential to the scheme of things in a world full of life. Its liquid form is more dense than the solid – ice floats on water, and more importantly, lakes and ponds freeze from the top, not from the bottom. If the opposite were true, cold weather would bring lakes frozen solid from bottom to top; nothing would continue to live within them. Our vibrant surface water – and perhaps the entirety of Earth – would be lifeless.

So what is it about water that permits it to be and to do all of this?

The water molecule, as represented in **Fig. 1**, has two strong chemical bonds linking the two hydrogen atoms to the oxygen. These are shown as shaded lines in the drawing; in the actual molecule they consist of two electrons each and serve as the submicroscopic glue that holds each O—H atom pair together. But the water molecule is actually able to do more – it is a "social" molecule that can form attractive relations to its neighbors. These "intermolecular" interactions are directional, which means that they act principally in certain directions, not just anywhere. These attractions are called hydrogen bonds, and they are one of the key features responsible for the remarkable properties of water.

The hydrogen bond is one of those natural phenomena that are so pervasive that the exact moments of their discoveries cannot be pinpointed. Although the term "hydrogen bond," as a more or less formal name for it, did not appear until some time after 1930, its effects had been observed a long time before that and the fact that something special was present in certain systems had been concluded by scientists in the preceding decades. Indeed, a very important class of compounds, known as the gas clathrates, which depend on hydrogen bond formation for their existence, had been observed as early as the first quarter of the 19th Century by Davy and by Faraday.

The hydrogen bond in water is responsible for its anomalously high melting and boiling points. The water molecules attract each other as shown in **Fig. 2**, where the hydrogen bonds, which are not nearly as strong as the covalent O—H bonds, are shown as dashed lines in keeping with a tradition followed by chemists. Because the molecules are attracted to each other, and because the attraction is directional, giving rise to a certain degree of order,

it turns out that separating them, for example by boiling liquid water to transform it to a gas, is harder than it would be if these attractions were not present. The directions of the hydrogen bonds are simple. Hydrogen bonds radiate out from a given molecule in four directions. If we take the direction of the oxygen atom as the center point for our considerations, as in **Fig. 1**, then two of the directions are simply continuations of the directions of the O—H covalent bonds. The two hydrogen atoms can form attractive interactions to as many oxygen atoms of neighboring molecules. The other two directions also form a V-shaped pattern, but they are on the naked side of the oxygen atom, in a plane that is perpendicular to the plane of the H—O—H ensemble. The oxygen atom can attract two hydrogen atoms from molecular neighbors in these directions.

When water freezes, the degree of order suggested by the directionality of the hydrogen bonds, and which is challenged by the continuous motion of molecules in the liquid, becomes a fixed, unvarying structural feature of the solid ice. This has the effect of opening up the overall structure as compared to the liquid form, and this is why ice is lighter than liquid water.

How is it that science has managed to reveal all of this, and how are the properties of water being studied today? Science has applied many techniques, not to mention much thought, to the study of water. And ever more sophisticated techniques – neutron science prominent among them – are being applied today. **The use of neutron science, which we can subdivide into neutron spectroscopy and neutron scattering, can tell us a great deal about both the structure and the dynamics of water in all of its forms.** And that includes much valuable information about the hydrogen bonds that attract neighboring water molecules to each other.



Why neutrons? First of all, what it is – neutron science is one example of the use of radiation to study matter. Scientists use most forms of radiation, such as electromagnetic radiation (including x-rays, visible light, infrared and microwaves), and the particulate radiations such as neutrons, to study the structures, internal motions, and transformations of matter in all its forms. To keep it simple, we can divide radiation experiments into two general types, those in which radiation is absorbed by the specimen and those in which it is deflected (or scattered, as per scientific terminology) by the specimen. If we vary the energy of the radiation that is incident upon the sample, we can see just which energies of radiation are absorbed; this is called spectroscopy. Scattering experiments, in which the amount of radiation deflected in different directions is measured, provide an enormous amount of information about the internal structure of a specimen – that is, how atoms and molecules are arranged within it. In spectroscopy and scattering, neutron radiation has turned out to be very useful, because the same energy ranges can often be used both for structural studies (scattering) and for experiments to determine how molecules vibrate (spectroscopy). This can be contrasted with electromagnetic radiation, for which we need to use x-rays to study structure but infrared radiation to study vibrations. Neutrons bring another useful capacity to bear on structure analyses, because they interact very well with the ubiquitous hydrogen atoms. The x-radiation used for structural studies is not deflected well by hydrogen atoms. And this brings us back to water.

Science has the good fortune to be able to study water in all its forms using neutron beams – as a bulk liquid, as frozen ice, and also within other substances. In liquid water we need to know how individual molecules vibrate and how they tumble over their molecular neighbours. These characteristics are intimately related to the presence of hydrogen bonding. Neutron spectroscopy is ideal for this purpose. And neutron scattering

provides accurate information about how far water molecules are from each other in the liquid – again, a property strongly influenced by hydrogen bonding. In solid water, structure analyses based on neutron scattering give a clear three-dimensional picture of how the atoms of hydrogen and oxygen are arranged on the nanometer and sub-nanometer scale, and how the molecules are related to each other. Hydrogen bonds are thus revealed in intimate detail, and their presence and detailed geometries can be related to the bulk properties of water. Neutron science can be used to study the different forms of ice, and there are many. The studies of all the various forms of water are more than just intellectual exercises, because they also provide information that is needed by those who analyze the data from spacecraft, those interplanetary explorers that have been sent to look, among other things, for signs of life beyond Earth. Here on Earth we can study the structures and properties of the forms of water that might exist under the conditions present, say, below the surface of Mars or on the moons of Jupiter. We can then compare data from our homemade samples to the data received from outer space.

But there is more. Because water is so ubiquitous on our planet, it must be studied in countless natural contexts. Water molecules, for example, are also held by hydrogen bonding to the surfaces of proteins, where the protein molecules both direct hydrogen atoms at the oxygen atoms of water molecules and also have oxygen (and some other) atoms present to "receive" hydrogen from the surrounding water. Neutron diffraction techniques have been and continue to be adapted to study the surface structure of proteins in detail, because neutrons are the probes *par excellence* into the exact locations of the hydrogen atoms in the middle of the hydrogen bonds. **Smaller biological molecules - pharmaceutical agents, toxins, flavourings, indeed anything whose interactions with living beings are to be studied for their mechanisms of action, can fruitfully**

be studied with neutrons, because hydrogen bonding is very likely to be involved in the approach to and anchoring of the smaller molecule (the "substrate") to its molecular host in the biological system.

Water has still more tricks up its sleeve. The gas clathrates mentioned above and known for some two centuries, have remarkable structures and properties. They are solids composed of water, which forms a hydrogen-bonded cage around a "guest" molecule, which is normally a molecule of a compound, such as methane or carbon dioxide, which is usually found as a gas. The possible applications of gas clathrates (which have other names, include clathrate hydrates) are plentiful and potentially important. Can we sequester carbon dioxide, our problematic greenhouse gas, as a clathrate hydrate? Can we mine and use the methane that is trapped on the ocean floor in the form of methane clathrate?

(The quantity of methane, a combustible fuel that we know how to use, thus trapped is estimated to be more than six trillion tons.) There is more, but first it is imperative to understand these remarkable substances. **Neutron spectroscopy and scattering have already been applied, and much has been learned about the structures and properties of the gas clathrates, whose principle structural glue consists of the hydrogen bonds among the water molecules that form cages around the guests.** Much more remains to be discovered, and the potential social and economic benefits are substantial. And as you can probably imagine, it is suspected that clathrates exist in substantial quantities elsewhere in the solar system and beyond.

8.4

NEW BASIC SCIENCE → Neutron Science and The Hydrogen Bond in Water

What has been done so far? Literally hundreds of articles have been published reporting studies in which neutron scattering was applied to an understanding of water in its many contexts. Titles from the 1980's such as "The structure of liquid water by neutron scattering," or "Hydrogen-bond spectroscopy of water by neutron scattering," are among many instances of the application of neutron techniques to structure and dynamics of liquid water and hydrogen bonding. But interest in studying water did not begin then – keeping in mind that the neutron itself was discovered in 1932, we can see the perceived utility of studying water in the fact that publications reporting neutron scattering investigations were reported as early as 1935! **In all, there are now more than 2.500 literature references which either report or interpret neutron experiments involving water in one form or another.** And the value of neutron scattering data is not static; as our ability to understand complex states of matter improves, existing data can be interpreted in terms of more sophisticated theoretical models. At the same time, as neutron sources and instrumentation improve, we can study water in ever more complex systems, and ones that have very important practical applications. The water structure around protein molecules has been the subject of at least 250 published reports. Many score structural studies of clathrate hydrates by neutron diffraction have been reported, beginning more than 30 years ago.

The Role of ESS. ESS will change both the time and space scales on which water in all its forms can be studied. The strong radiation source, the wide spectrum of wavelengths available, and the fact that instrumentation technology has advanced by leaps and bounds, mean not only that existing data can be improved, but also that new types of measurements can be made. We hope that the structure of water, pure or as a solvent in its many and diverse solutions, can be monitored in real time as a sample passes through thermodynamic thresholds such as freezing or melting. We expect that hydrogen bonds will be characterized with even higher resolution, permitting a detailed description of the electron densities around the atoms involved – detailed enough to match the quality of modern theoretical models. **Materials of great potential importance to the future of our global ecosystem, such as the hydrate clathrates, will be studied with much higher resolution and under ambient conditions that better reflect their natural circumstances -- such as the pressures that exist at the ocean floor where huge quantities of methane clathrate are trapped, or at the pressures and temperatures found on the Jovian moons where water may be found.** The water structure around proteins will be the object of far more routine and frequent measurements than is possible today. And there will be more, because as always happens with new research, the results obtained with ESS will suggest further experimentation, whose details are today beyond the prudent limits of imagination.

Closing comment. In bulk water, in plants and animals, in exceedingly important inanimate substances such as the clathrate hydrates, hydrogen bonding among water molecules is a critical determinant of the structures and properties of substances that define our existence and which may be vitally important to our future well-being. Neutron science is a key player in understanding the hydrogen bond in all of these contexts, and it is expected that the modern neutron science centers being constructed and proposed will advance our ability to understand this deceptively simple interaction.



FURTHER READING

The structure of liquid water by neutron scattering. III. Calculations of the partial structure factors, by Ohtomo, Norio; Tokiwano, Kazuo; Arakawa, Kiyoshi, *Bulletin of the Chemical Society of Japan* (1984), 57(2), 329-33.

Hydrogen-bond spectroscopy of water by neutron scattering, by Chen, Sow Hsin; Toukan, Khaled; Loong, Chung Keung; Price, David L.; Teixeira, Jose, *Physical Review Letters* (1984), 53(14), 1360-3.

The scattering of neutrons in water and lead, by Deizenroth-Muisovskii, M.; Kurchatov, I.; Latushev, G.; Muisovskii, L., *Physikalische Zeitschrift der Sowjetunion* (1935), 7, 659-69.

Diffusion of slow neutrons, by Bayley, D. S.; Curtis, B. R.; Gaertner, E. R.; Goudsmit, S., *Physical Review* (1936), 50, 461-6.

Reinterpretation of the liquid water quasi-elastic neutron scattering spectra based on a nondiffusive jump reorientation mechanism, by Laage, Damien, *Journal of Physical Chemistry B* (2008), 113(9), 2684-7.

Small-angle neutron scattering study of crude oil emulsions: structure of the oil-water interfaces, by Alvarez, G.; Jestin, J.; Argillier, J. F.; Langevin, D., *Langmuir*, (2008), ACS ASAP.

Neutron diffraction study of the crystal structure of ethylene oxide deuterohydrate at 80°K, by Hollander, E.; Jeffrey, G. A., *Journal of Chemical Physics* (1977), 66(10), 4699-705.

Fig. 1. One molecule of water, with the chemical bonds shaded. The O---H distance is approximately one-tenth of a nanometer. The dashed lines represent the general directions in which this molecule can form hydrogen bonds.

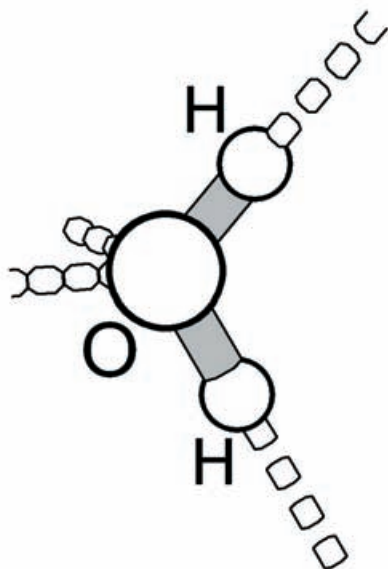
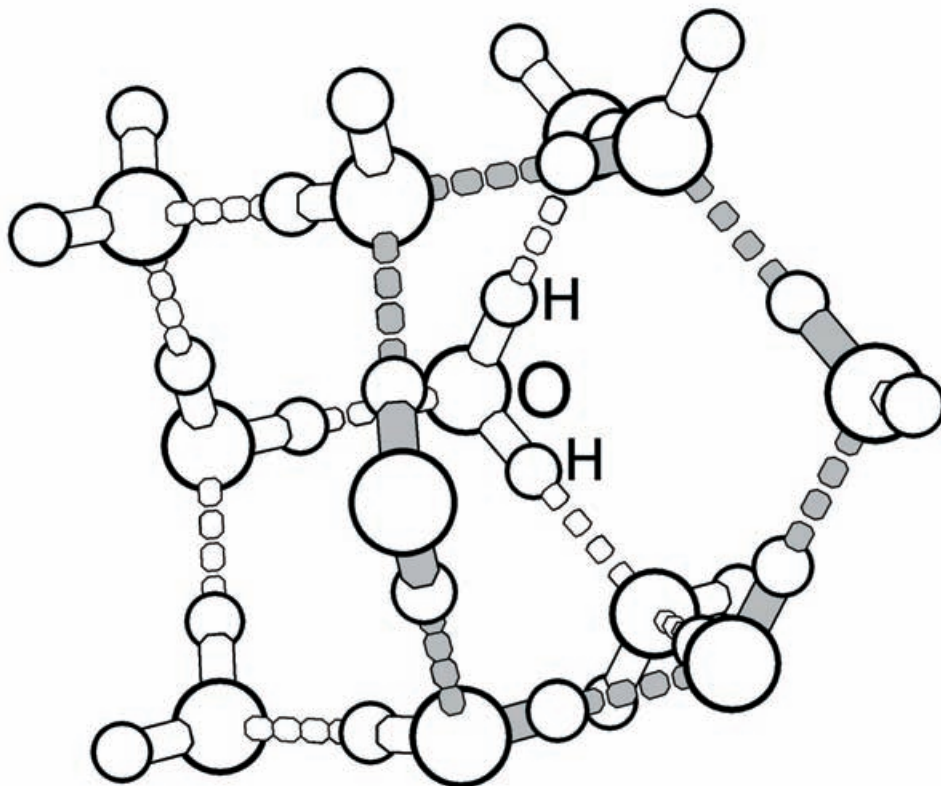


Fig. 2. The extended structure of ice -- in one of its many forms -- showing how hydrogen bonding lends rigidity and openness to the arrangement of water molecules. One of the rigid rings is shaded for emphasis.



Magnetism without Static Magnetic Moments: Quantum Spins and Low Dimensionality

J. E. Lorenzo, L.P. Reganult

The well-known paradigms that explain the physics in higher dimensions (Fermi liquid theory) no longer apply to one dimension (1D). This has motivated theorists to develop new concepts and techniques in order to understand the peculiarities of low dimensional systems. For instance one of the genuine concepts that appear in 1D is the collectivization of excitations. Indeed in 1D an electron or a spin that tries to propagate has to push its neighbors and no individual motion is possible: any individual excitation has to become a collective one. As a result quantum effects get enhanced and the corresponding excitations acquire remarkable quantum features. In parallel experimentalists have succeeded in turning these dreams into reality, producing an impressive and ever increasing array of experimental realizations of quasi-1D systems, from the molecular to the mesoscopic---spin and ladder compounds, organic superconductors, carbon nanotubes, quantum wires, Josephson junction arrays and so on.

Interestingly quantum antiferromagnetism offers basic prototypes for different phases of strongly interacting quantum systems. In addition to a rich array of classically ordered states, including Néel order and non-collinear states, there are several different types of quantum disordered states: valence bond solids, valence bond liquids, dimer solids, etc. These different quantum states can be accessed by tuning various couplings. One of the most remarked achievements concerns superconductivity. A class of superconductors, including high T_C cuprates, is obtained by doping the Mott insulating states with a valence bond liquid, a quantum antiferromagnetic order. Other approach to

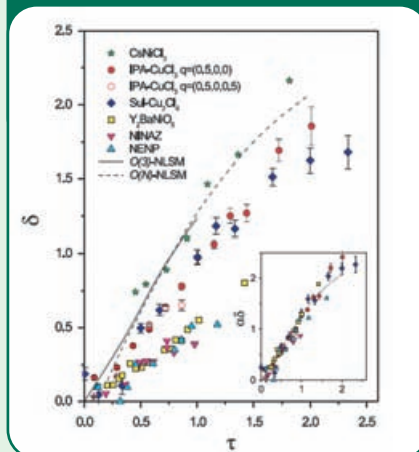
render superconductivity is obtained from a symmetry rotation of the quantum antiferromagnetic state.

Certainly one of the most thoroughly studied low-dimensionality systems is that of the quantum $S=1/2$ and $S=1$ Heisenberg antiferromagnetic chains. In a seminal work dating back to 1983, Haldane predicted that the ground state is a non-magnetic singlet displaying an excitation gap and exponential decay of spin-spin correlation functions when S is integer, while it is gapless with algebraic correlation functions when S is half integer. While the second conjecture was further proven rigorously (Lieb and Matthis theorem), the first one on the occurrence of a gap in the integral-spin Heisenberg chains is still unproven. A lot of progress has been made towards a full description of the so-called "Haldane phase". In particular, Affleck, Kennedy, Lieb and Tasaki (AKLT) provided a microscopic understanding of the nature of this correlated ground state. The AKLT ground state is made up solely of nearest-neighbors singlets (in what we usually call a valence bond solid), and the gap corresponds to the energy needed to break a bond. An interesting property of the $S=1$ quantum spins is that they can be viewed as pairwise entangled spins that make them as prototype systems for quantum information processing. We can conclude this introductory part by stating that **the study of the magnetic excitations in low-dimensionality quantum spins is relevant to a wealth of problems in physics and serve as testing bank for theories in areas such as superconductivity, quantum information, quantum wires, etc.**

The physics of low dimensional gap systems have been the object of countless neutron scattering studies for the last 20 years. The different phase diagrams as a function of pressure, magnetic field, doping, etc. have been traversed along many directions and in many different compounds. Today research studies cover a great deal of compounds and in the following we will illustrate the phenomenal richness of this area by describing three selected examples that may serve to put in perspective the activities that one would like to develop thanks to the foreseen capabilities of the future ESS.

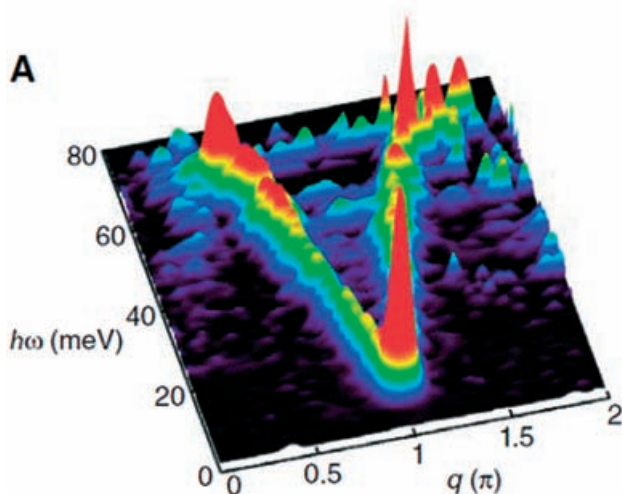
Macroscopic phase coherence in a quantum fluid. Magnetic-neutron-scattering experiments has revealed the development of mesoscopic quantum phase coherence in a one-dimensional spin chain Y_2BaNiO_5 , a quantum spin fluid where no classical, static magnetic order is present. In the cleanest samples, the quantum coherence length is 20 nm, almost an order of magnitude larger than the classical correlation length of 3 nm. Although disordered by the quantum fluctuations the ground state is coherent in the sense of the more complex string correlation function. The narrow peak observed in the dispersion curve of

Fig. 2: Scaling law of the reduced gap as a function of reduced temperature.



excitations in Y_2BaNiO_5 reveals such long correlation length of the triplet excitations mean free path (**Fig. 1**). The peak broadens significantly when the sample is warmed or doped by chemical impurities, indicating that quantum coherence in this system requires low temperatures and perfect crystallinity. The observation of phase coherence in a 1D spin chain is a pure quantum effect whose implications are still under study in the context of other complex coherent states like superconductivity.

Fig. 1: Spin dispersion curve with the intensities. The mesoscopic quantum phase coherence is revealed by the strong peak at the bottom of the dispersion



Another interesting result issued from neutron-scattering experiments is the scaling of the temperature dependence of the gap (D) in the quasi-one-dimensional $S=1/2$ gapped quantum magnets (IPA-CuCl_3 and $\text{Su-Cu}_2\text{Cl}_4$) and in the $S=1$ Haldane spin chain (NENP , NINAZ , Y_2BaNiO_5). It is found that when the $T=0$ energy gap is used as the temperature scale, all experimental and theoretical curves are identical to within system-dependent but temperature-independent scaling factors of the order of unity (**Fig. 2**). This quasi-universality extends over a surprising broad T range, at least up to $T \sim 1.5D$. An identical relationship can be established with the gap energy width. Deviations from unity of these factors reflect the inadequacy of the non-linear sigma model (NLSM) mapping which is rigorously exact only in the limit $S \gg 1$. It should be interesting to test similar D/T scaling laws with compounds that lie in different universality classes.

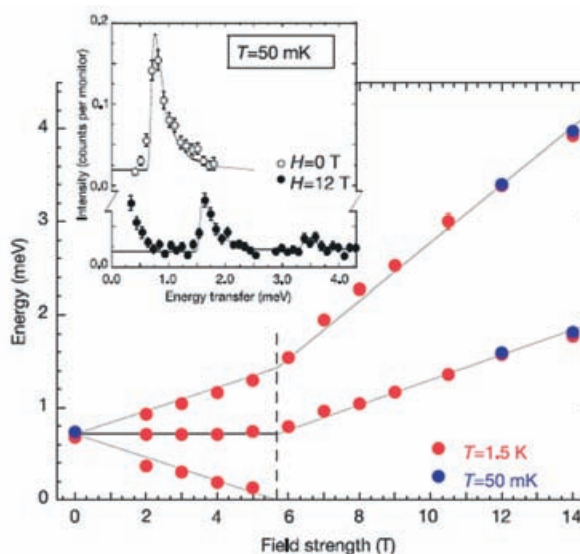
The Bose-Einstein condensate (BEC) is a fascinating state of matter predicted to occur for particles obeying Bose statistics. After the discovery that helium-4 became a new kind of fluid, now known as a superfluid, at temperatures less than 2.17 K (lambda point), it was quickly realized that superfluidity was due to Bose-Einstein condensation of the helium-4 atoms. The first "pure" Bose-Einstein condensate was created by cooling a dilute vapor consisting of approximately two thousand rubidium-87 atoms to below 170 nK. Shortly afterwards a condensate made of sodium-23 containing a hundred times more atoms allowed to obtain several important results such as the observation of quantum mechanical interference between two different condensates. Cornell, Wieman and Ketterle won the 2001 Nobel Prize in Physics for their achievement.

The Bose-Einstein condensation also applies to quasiparticles in solids. A magnon in an antiferromagnet carries a

spin 1 and thus obeys the Bose–Einstein statistics. The density of magnons is controlled by an external magnetic field, which plays the role of the magnon chemical potential. This technique provides access to a wide range of boson densities from the limit of a dilute Bose gas to that of a strongly interacting Bose liquid. A magnetic ordering observed at the point of condensation is the analog of superfluidity. In 1999 Bose condensation of magnons was demonstrated in the antiferromagnet TlCuCl_3 . The condensation was observed at temperatures as large as 14 K. Such a high transition temperature (relative to that of atomic gases) is due to a greater density achievable with magnons and a smaller mass (roughly equal to the mass of an electron). In 2006, condensation of magnons in ferromagnets was even shown at room temperature, where the authors used pumping techniques.

Here we will briefly review the neutron-scattering results on the formation of the BEC in the quantum antiferromagnetic $S=1/2$ dimer compound TlCuCl_3 (Fig. 3). An unusual kind of magnetic order occurs in these materials when the Zeeman energy $g\mu_B H$ (where g is the Landé factor, μ_B is the Bohr magneton, and H is the magnetic field) overcomes the spin gap between the $S=0$ singlet ground state and the $S=1$ excited triplet states (S denotes the quantum number for the total spin). Below a critical field, H_{c1} , the ground state is a quantum-disordered paramagnet formed by the singlet sea (triplon vacuum) and can be approximated by the direct product of singlet states on each dimer with $S^z=0$. Once the spin gap is closed at H_{c1} , a Bose condensate is formed. Because the bottom of the triplon band is located at a non-zero wave-vector k_0 , the wave-function of the condensate varies in space as $\exp(ik_0 \cdot r)$. In this phase the state of an individual dimer at position r is well approximated by a coherent superposition of the singlet and the $S^z=+1$ triplet, where the amplitudes of the superposition depend on the magnetic field H .

Fig. 3: Dependence on the external magnetic field H of the magnetic excitation energy measured in TlCuCl_3 . Data are shown for fixed $T=1.5$ K (red symbols) and $T=50$ mK (blue symbols). Data are extracted from least squares fits to the neutron scattering spectra (inset), curves reflect a Zeeman model. The quantum critical field $H=H_{c1}$ is denoted by the dashed boundary.



The BEC quantum phase transition has been observed in a growing number of dimer-based magnetic insulators, such as ACuCl_3 ($A = \text{Ti, K, NH}_4$), $\text{BaCuSi}_2\text{O}_6$, $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{D}_2\text{O}$, $\text{Cs}_3\text{Cr}_2\text{Br}_9$, $(\text{CH}_3)_2\text{CHNH}_3\text{CuCl}_3$ and $(\text{C}_4\text{H}_{12}\text{N}_2)\text{Cu}_2\text{Cl}_6$, that represent good realizations of 1D, 2D and 3D dimer compounds. Advances in growth techniques may enable us in the future to study in detail the effects of disorder on bosons. Here Bose glasses, which can be made by adding bond disorder or site dilution, are of current interest, as is the influence of defects on the quantum critical states. Other directions include thermodynamics of strongly interacting bosons and quantum coherence at the mesoscopic scale.

Spin-Peierls transition: Quantum uniform Heisenberg spin chains are unstable against fluctuations that drive them to an ordered Néel state by means of transverse couplings. This is the fate of many of the $S=1/2$ chain compounds, usually at temperatures given by the relationship $T_N \sim \tilde{O}J_{\parallel}J_{\perp}$ (or $T_N \sim J_{\perp}$), with J_{\parallel} and J_{\perp} are the spin exchange coupling along the chains and perpendicular to the chains, respectively. However another less common mechanism to lower the magnetic energy is to open a gap between a non-magnetic ground state and the first magnetic excited states. This is done with the help of a structural phase transition that breaks the chain uniform spin-exchange coupling and promotes the formation of spin-dimers. This is the spin-Peierls phase transition, in analogy to the Peierls transition in quasi-1D conductors. The magnetic excitations that were massless and fractional at high temperatures ($S=1/2$ spinons) become massive (because of the opening of a gap) and bosonic ($S=1$ dimers) below the spin-Peierls phase transition. This state was first observed in an organic compound, $\text{TTFCuS}_4\text{C}_4(\text{CF}_3)_4$, and it was thoroughly studied in the mid-nineties thanks to the discovery of the first inorganic compound displaying such fascinating properties: CuGeO_3 . This transition has been the object of countless studies with neutrons and here we are going to mention the study of the excitations.

Fig. 4: Magnetic excitation spectrum in CuGeO_3 , showing the singlet to triplet gap at 2meV and the double gap structure above 4 meV.

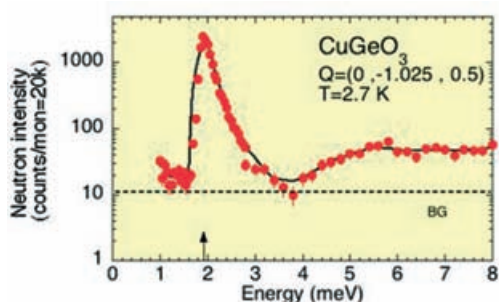


Fig. 5: Splitting under an applied magnetic field of the first excited state in CuGeO_3

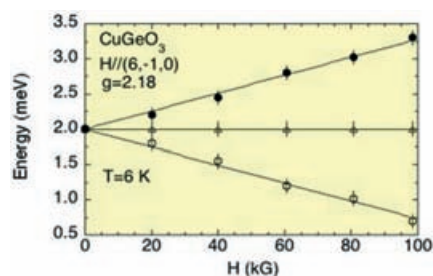
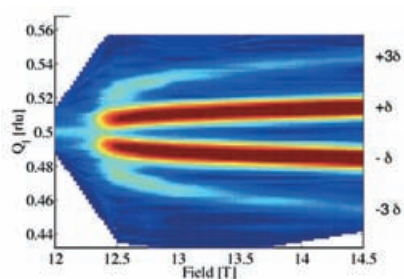


Fig. 6: Soliton lattice above H_c in CuGeO_3 . The new ground state is characterized by the appearance of incommensurate structural and magnetic peaks.



Inelastic-neutron-scattering experiments have revealed the presence of a triplet of excitations at $D \approx 2.0$ meV, that under a magnetic field decomposes into their intrinsic components (Fig. 4 and 5). The critical field required to suppress the gap is of the order of 12.5 T. Below this field the lattice dimerization is progressively destroyed and a solitonic phase appears, as it is shown in Fig. 6. Neutron-scattering experiments have revealed that in addition to the singlet to triplet gap, there is a continuum of magnetic excitations that extends up to 33 meV and that is separated from the spinon branch by second gap in energy of value D . Finally the transition bosonic-fermionic excitations occurring at the spin-Peierls phase transition has been studied with polarized neutrons but definitely more work needs to be done to fully understand the features of this transition.

Benefits of the future ESS. This field of research would benefit of a forthcoming neutron spallation source in different ways. **First the small beams (high brilliance) that one may envisage at this source will allow working with smaller samples and enable the use of extreme condition environments.** Indeed it is important to understand how pressure and magnetic field affects the aforementioned properties and explore the phase diagram of these compounds. A second important feature that is important in these compounds is to have a quick picture of the excitations in order determine whether or not it is worth pursuing more sophisticated studies in a given compound. This can be achieved by making use of detector arrays that cover a good portion of the space around the sample.



FURTHER READING

M. Hase et al., Observation of the spin-Peierls transition in linear Cu^{2+} (spin 1/2) chains in an inorganic compound CuGeO_3 , Phys. Rev. Lett. 70, 3651 (1993).

M. Ain et al., Double gap and solitonic excitations in the spin-Peierls chain CuGeO_3 , Phys. Rev. Lett. 78, 1560 (1997).

H. M. Rønnow et al., Neutron scattering study of the field-induced soliton lattice in CuGeO_3 , Phys. Rev. Lett. 84, 4469 (2000).

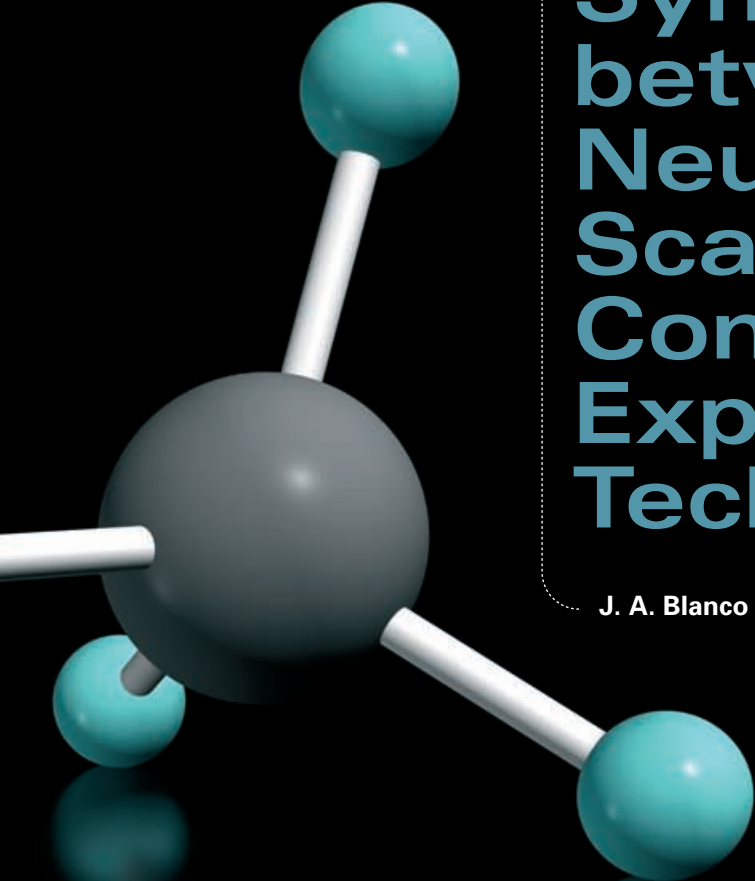
Guangyong Xu, et al., Mesoscopic Phase Coherence in a quantum spin fluid, Science 317, 1049 (2007).

A. Zheludev, et al. Extended Universal Finite-T Renormalization of Excitations in a Class of One-Dimensional Quantum Magnets, Phys. Rev. Lett. 100, 157204 (2008).

http://en.wikipedia.org/wiki/Bose-Einstein_condensate

C. Ruegg, et al., Bose-Einstein condensation of triplet states in the magnetic insulator TlCuCl_3 , Nature 423, 62-65 (2003).

T. Giamarchi, et al., Bose-Einstein condensation in magnetic insulators, Nature Physics 4, 198-204 (2008).

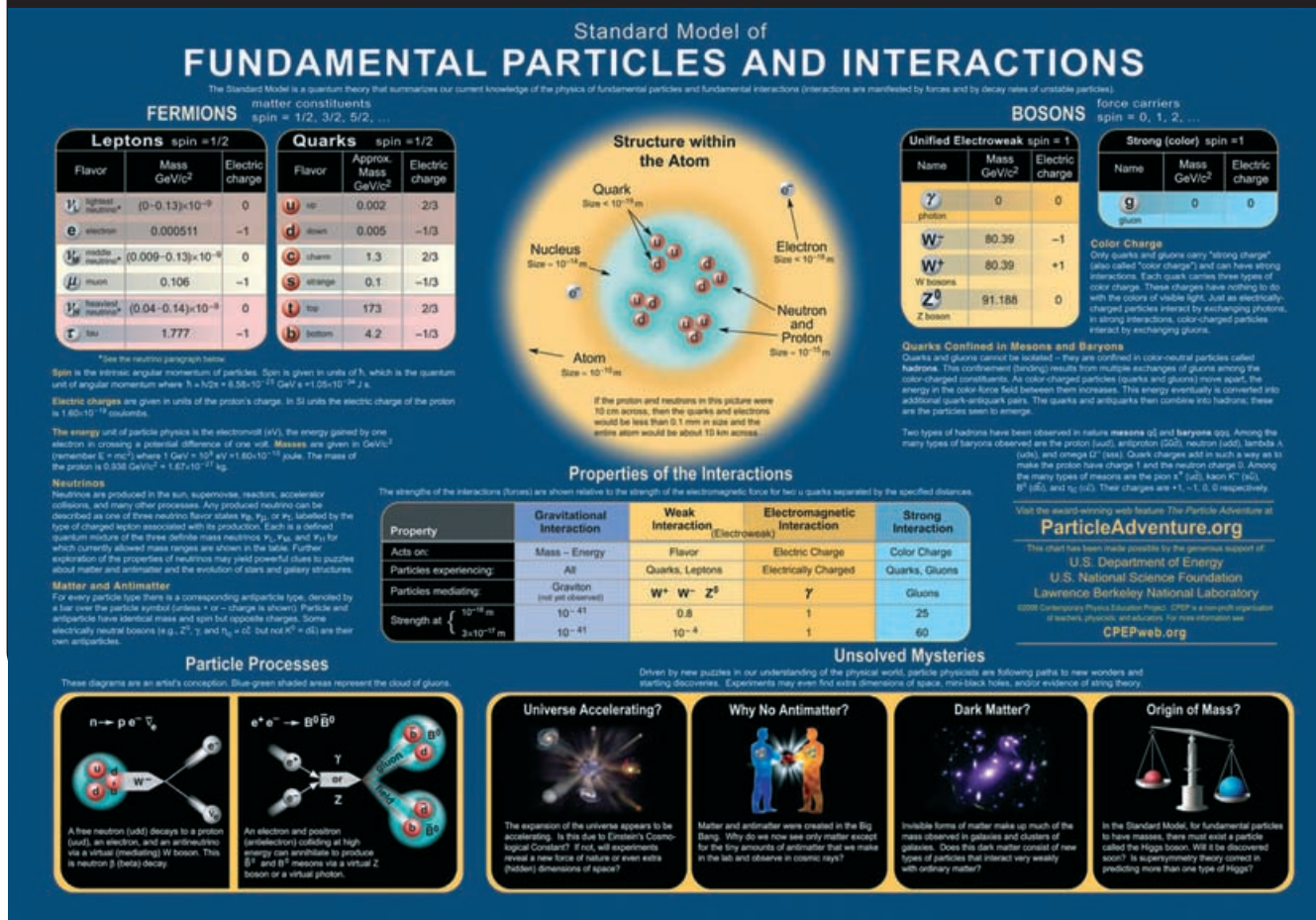


Synergy between Neutron Scattering and Complementary Experimental Techniques

J. A. Blanco

The physical world that we know consists on a great number of systems formed by many particles in interaction. In the outline of the **Fig. 1** we show the particles or elementary constituents of matter that can be found in the 5 % of our Universe, while the 75% is dark energy and the rest 20% is dark matter. This picture summarizes the knowledge of the fundamental particles and their interactions. It is the result of the investigation and discoveries that the humanity has performed during the last centuries, through projects and efforts, being done either individually or collectively, whose consequences have been primordial for the development, prosperity and well-being of our civilization.

Fig. 1. Schematic view of the standard model of fundamental particles and the properties of the interactions.
Source: http://www.particleadventure.org/frameless/chart_frame.html.



In particular, the understanding of the laws and the rules that govern the interactions among these elementary constituents are essential to be able to know where the atoms are and what they are doing, when a beam of photons, neutrons, electrons or muons impact on the matter or materials under study. Moreover, neutrons that do not possess electric charge, act like probes that can penetrate more easily inside the materials, without causing any damage. On the other hand, when one seeks to study and to see the behaviour of glasses, plastics, metals, proteins, amino acids or magnetic materials, the scientists and engineers can obtain by using neutrons a direct vision of the internal structure of the matter. Between the most specific

issues where the use of the neutron techniques has a remarkable advantage with regard to other techniques, we could mention: to be sensitive to the "magnets" or internal magnetic moments that exist inside certain materials; to be able to "see" all the nucleus of any atom, so much if they are weighed as light nucleus; to be able to distinguish regions in organic and inorganic structures in those that an isotopic substitution has been made; to sound regions in the materials that can possess thicknesses bigger than centimetres; and, lastly, an important aspect to consider is that **the interpretation of the results with techniques based on neutron beams is simple in comparison with the one obtained starting from other probes.**

Due to all these mentioned features, the neutron techniques will always be an indispensable tool for the study of the structure and the dynamics of the materials that cannot be replaced with other techniques. However, the results of the studies using neutrons acquire a considerable value, as much when they are combined with the results obtained by means of other experimental techniques to extract complementary information, as when experimental data found by other methods are compared with those obtained by means of the use of neutrons. It is important; nevertheless, to have in mind that there is not a unique experimental technique that can provide all the information that is necessary to completely understand the whole set of

8.6

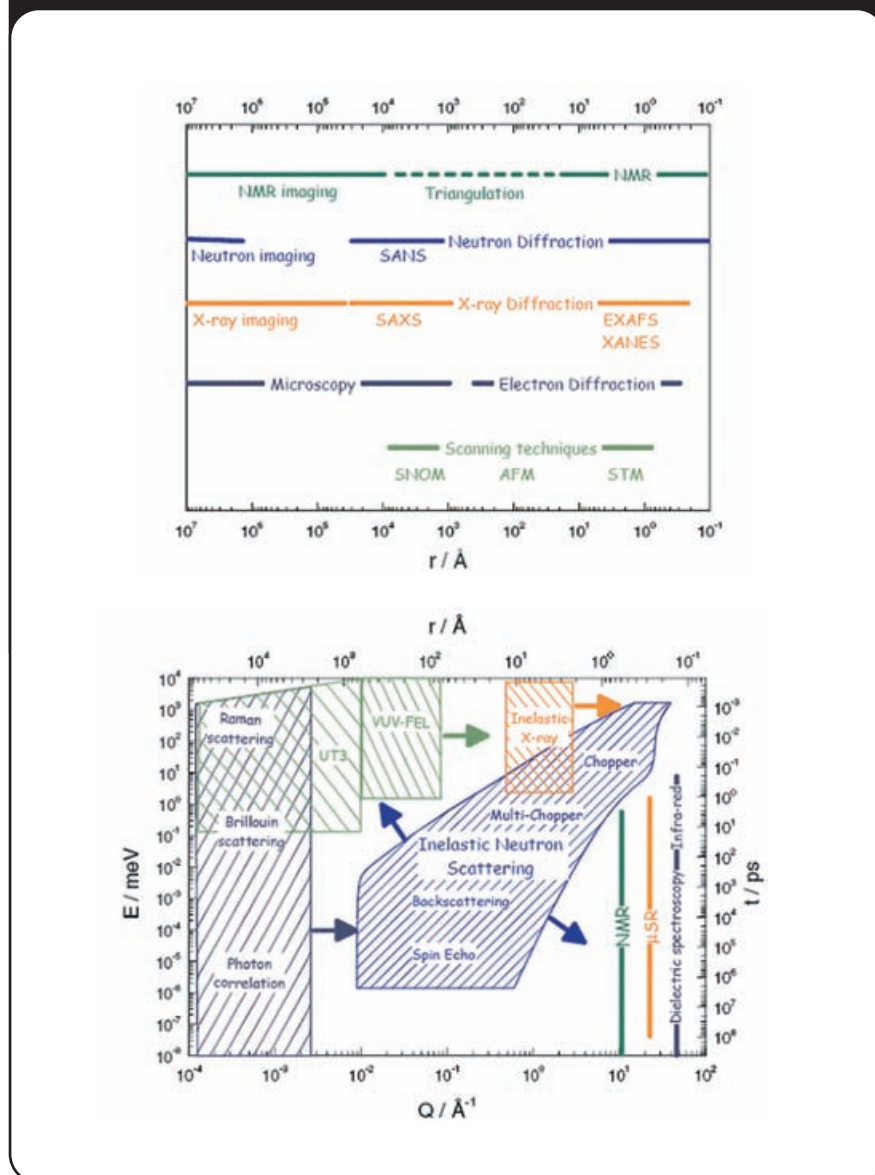
physical-chemical properties of a particular material. Hence, the use of diverse experimental techniques, based on different physical processes, will provide enough information to explain its behaviour under different ambient conditions (temperature, pressure, magnetic or electric field), which is indispensable if the enhancement of the material functionality is pursued. Also, **because the systems in study are more and more complex, it is of crucial importance to investigate the same systems by means of diverse and complementary experimental techniques.** There are, obviously, a great number of techniques that could be presented, and, in consequence, an enormous number of combinations, so it is not possible being exhaustive. Hence, we will focus on a reduced and representative number of techniques, such as: Synchrotron radiation, Magnetic Nuclear Resonance, Laser of free electrons and the muon-spectroscopy that possess clear complementarities with the techniques of neutrons beams, and whose effects of synergy are clear, because the combined effects of all the techniques are much better to the sum of the individual effects.

Synchrotron radiation is, without a doubt, the next and complementary technique to the neutron beams, when using photons as investigation probe. The crystallography of x-rays is the most powerful technique and broadly used in the determination of crystalline structures of all type of substances or materials. In particular, this technique is, *par excellence*, the more employed in the determination of protein structures, nucleic acids (DNA/RNA) and its complexes, whenever they can crystallize with appropriate sizes of good quality. However, the atoms of hydrogen that constitute of the order of 50% of the biological material cannot be located by means of x-rays. Moreover, neutron diffraction allows finding (with a space resolution of 2 Å) the positions of these atoms of hydrogen/deuterium. Likewise, an experiment of x-ray absorption allows obtaining so much information of both the electronic structure and the local

order (XANES / EXAFS, to see **Fig. 2**). On the other hand, starting from the interaction of photons with matter, firstly we can also obtain information about magnetic structures of the materials, ending up being able to separate the contributions to the magnetic moment coming from the orbital and spin angular momentum. Furthermore, the resonant X-ray diffraction, i.e., when the energy of the photons that impact on the matter, in the diffraction experiment, is close to the difference of energies between the internal atomic levels of certain chemical

species, it allows discriminating between the different magnetic contributions coming to the distinct magnetic ions. A fundamental advantage of the resonant X-ray Bragg diffraction is the possibility to determine the arrangement of both magnetic moments as well as electric moments of order higher than the dipole moment (quadrupoles, octupoles, hexadecapoles, triakontadipole, hexacontatetrapole...) in a direct way, while by means of neutron beams we can only have indications of the existence of these arrangements in an indirect way.

Fig. 2. Upper part: Spatial range of the neutron diffraction and other complementary experimental techniques. Lower part: ranges of the inelastic neutron scattering and other experimental techniques for dynamical studies.



Nuclear magnetic resonance (NMR) and neutron scattering have the possibility in common to be able to observe the structure as well as the dynamics of materials, although in many cases the spatial and time scales are different (**Fig. 2**). The atomic selectivity can be different, but both techniques are favourable to study light atoms, particularly hydrogen. However, the information obtained from NMR does not allow showing the spatial and time correlations that can be extracted from the dynamic structure factor with the use of neutrons. Also, the experiments of NMR can present serious limitations in certain cases, and they require a special care and experience in the setting up of the experiments, and, mainly, in the interpretation of the results. On the other hand, the techniques of NMR are over most the method for the determination of structures in solution, and in particular when in biology the proteins are difficult to crystallize, although it is restricted to relatively small (< 30-40 kDa) structures. The average structural parameters derived from NMR are much less necessary than those obtained by means of neutron diffraction. However, NMR provides direct information on hydrogen positions, and it can be used to study the interaction of proteins and the dynamics of enzymatic reactions. **The spectroscopy based on NMR is able to access to scales of time that are totally complementary to the neutron scattering (Fig. 2)**, and the combination of both can provide a more complete description of macromolecular dynamics. Furthermore, the $\text{H}_2\text{O}/\text{D}_2\text{O}$ contrast variation with neutrons of low resolution can be used to locate lipids, detergents and other disordered groups in glasses that cannot be found by means of the X-ray analysis.

The X-ray free electron lasers (XFEL) will generate beams of extremely intense X-rays that will be able to be used in fields of solid state, soft matter and life sciences. The scientific case of this type of Large Facility is broadly justified, as the ESS project, due to its unique peculiarities of brightness, spatial coherence and time structure of X-ray beams that will suppose a gain of several orders of magnitude with regard to the

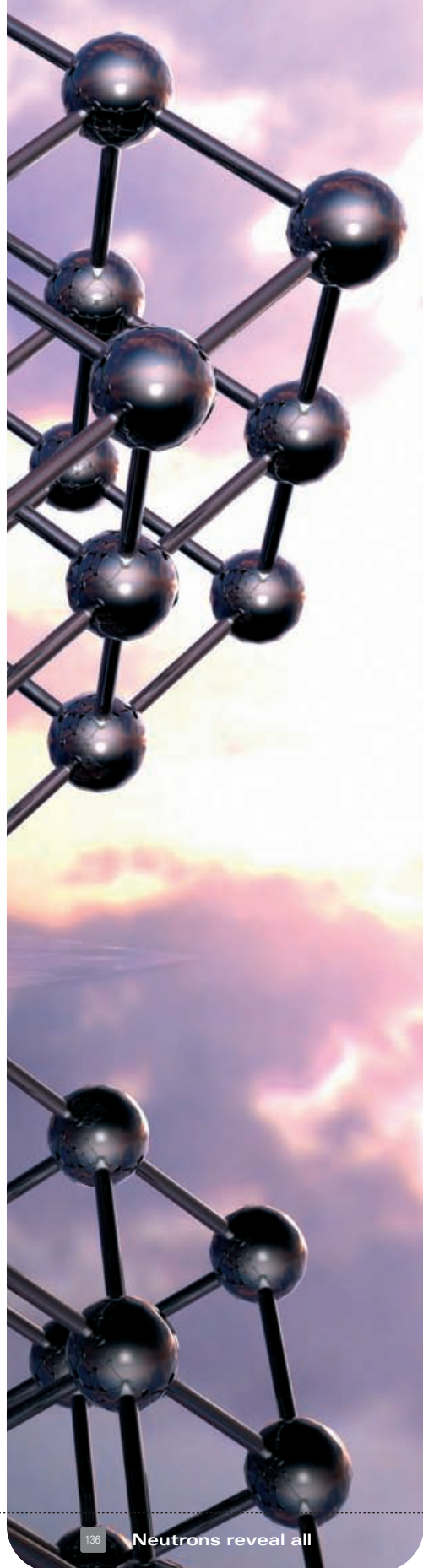
storage rings based on synchrotron radiation sources. With the XFEL source it will be possible, for the first time, to directly study new states of the matter in scales of time and atomic length, i.e., with space and temporary resolutions, of 0.1 nanometers and 1 femtosecond, respectively. In this way, one will be able to follow the temporary evolution of structures of the solid state and chemical reactions in those mentioned spatial-time scales; to solve bio-molecular structures without necessity of being crystallized; to explore the non-linear properties of the matter in the range of X-rays; and the dynamics of fluctuations in those previously mentioned time and spatial scales.

Large Facilities like ESS and XFEL, far from being in competition and excluding themselves, can provide information from opposed points of view on the same scientific problem.

In particular, an area of apparent competition could be in the region of high energy and high transferred moment (**Fig. 2**). Historically, this area of study has been reserved to the inelastic neutron scattering, but the development of three-axes X-ray spectrometers to carry out inelastic scattering will allow to access to a wide region of overlapping between both techniques. In specific cases, such as for example in the determination of phonon dispersion relations at high energy, the neutrons will be always the dominant technique, due to their low speed. However, in comparative measurements in liquids and gas, the different chemical specificity of the two techniques mainly makes both of them highly necessary and complementary for elementary and simple systems.

Another probe that is complementary to the use of neutron beams is the resonance, the relaxation, and the rotation of muon spin (mSR). The rotation describes the phase-out of the spin of the muons under the local magnetic fields inside the sample, in the presence of a traverse field to the direction of the spin of the muon. The relaxation defines how the spin of the muons loses its polarization with the time under the internal magnetic fields, either without





applied magnetic field or with a low field parallel to the direction of the spin of the muon. While the resonance is observed in presence of a radiofrequency magnetic field. As well as the neutrons, the muons can only be produced in large facilities, such as the European Spallation Source (ESS). The great advantage that presents the muon technique is that it is a highly sensitive probe to the distribution and the dynamics of extremely small magnetic fields that usually exist in the interstitial places of a crystalline lattice. In contrast, the NMR provides information of the internal magnetic fields on the regular positions of the crystalline sites.

The mSR technique is not in itself a technique for the structural resolution, but it is complementary with the neutrons in the determination of magnetic structures, mainly, in cases where the resolution using powder diffraction leads to ambiguities.

The ability of muons to be able to measure very small internal fields has allowed detecting the existence of magnetic moments of very-low magnitude, $0.01 m_B$, and even smaller. The identification of processes where this type of magnetic arrangements can exist, as it is the case of high-temperature superconductor oxides, heavy fermions or molecular magnets, is in the limit of sensibility of neutrons. Such studies will even become more important when the ESS increase the limits of sensibility, thus providing the possibility for searching, through new mechanisms, where to locate magnetic moments and the appearance of magnetic order. Nevertheless, the neutron beams are the most adequate technique for the study of magnetic spin fluctuations, giving information of the spatial-time correlations. Nowadays, the similar complementarities between mSR and the neutrons are being exploited in studies about the dynamics of nanoparticles and the magnetic storage. The possibility to use radiofrequency will allow to reorient the spins of the muons inside the sample (in a similar way to the NMR spin echo), and it will complement the technique developed during the last decade, the 3D-spherical neutron polarimetry that is, without a doubt, the most advanced available method for the determination of magnetic structures.

Other techniques as the electronic microscopy and the atomic force microscopy, both sensitive to the electronic density, can benefit with the extension of new focalization techniques for the small angle neutron scattering that allow having access to smaller angles. In particular, these two microscopy techniques offer difficulty in the characterization of solutions, where the role of the neutrons can be decisive. Another research field where the appearance in scene of ESS can be very decisive it is in the computational techniques, in particular by means of simulations based on the Monte Carlo method and the molecular dynamics.

In summary, the challenge that the very numerous European community in Materials Science has in these first years of the XXI century, is the possibility to build an spallation source, just as it is the ESS project, whose return, synergy with other experimental techniques and potential applications in different scientific and technological issues would bring advance, prosperity and well-being for our society of the XXI century.

In consequence, **the success of the ESS project will allow Europe to be again the leader for the worldwide activity in neutron techniques, like it was during the last quarter of the last XX century.**

This leadership, at the present time, is centred in the American (SNS) and the Japanese (J-Parc) spallation sources. Hence, if the new European Science&Technology Materials community does not want to miss the train of modernity and competitiveness for this century, it needs infrastructures and appropriate support that will assure its ability to attack the challenges and coming objectives in Materials Science.



FURTHER READING

Particle Physics, B. Martin, and C. P Shaw, 3rd Edition, Manchester Physics Series, 2008

New Science and Technology for the 21st Century, The ESS Project, Volume II, Ed. D. Richter, 2002.

List of Authors and Affiliation

J. Campo

ESS-Bilbao & Materials Science Institute of Aragón

E. López Cabarcos and J. Rubio Retama

Department of Pharmaceutical Physical-Chemistry, Faculty of Pharmacy, University Complutense of Madrid. Spain

F. Palacio

Instituto de Ciencia de Materiales de Aragón. CSIC - University of Zaragoza. Spain

G. González-Doncel

Dept. Physical Metallurgy, CENIM, C.S.I.C., Madrid. Spain

V. Lauter

Spallation Neutron Source at Oak Ridge National Laboratory. USA

S. Magazù

Department of Physics, University of Messina, Messina. Italy

A. De Francesco

CNR-INFM, CRS-SOFT c/o OGG Grenoble. France

L. Fernández Barquín

Depto. CITIMAC, Universidad de Cantabria, Santander. Spain

G. Chaboussant

Laboratoire Léon Brillouin (CNRS-CEA) CEA Saclay, Gif sur Yvette. France

A. Millan

Instituto de Ciencia de Materiales de Aragón. CSIC-Universidad de Zaragoza. Spain.

F. Boué

Laboratory Léon Brillouin, CNRS-CEA Saclay, Gif-sur-Yvette Cedex. France

F. Luis Vitalla

Instituto de Ciencia de Materiales de Aragón, CSIC-University of Zaragoza, Spain.

G. Artioli

Dipartimento di Geoscienze, Università di Padova. Italy

C. Mondelli

CNR-INFM SOFT, Institut Laue Langevin, Grenoble Cedex 9, France

R. Rinaldi

Dipartimento di Scienze della Terra, Università di Perugia. Italy.

J. Ruiz Hervías

Universidad Politecnica de Madrid. Departamento de Ciencia de Materiales ETSI Caminos. Spain

M. Ceretti

Sciences Chimiques de Rennes, CNRS Université Rennes 1 Campus de Beaulieu. Rennes cedex, France

G. Bruno

Corning SAS, CETC, Avon. France

G. Garcés

Department of Physical Metallurgy. CENIM-CSIC, Madrid. Spain.

T. Ramirez-Cuesta

ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire. United Kingdom

E. Palacios

Instituto de Ciencia de Materiales de Aragón. CSIC. University of Zaragoza. Facultad de Ciencias. Spain

M. M. Castellote Armero

Institute of Construction Science "Eduardo Torroja" IETcc-CSIC. Spain

A. Urbina

Departamento de Electrónica, Universidad Politécnica de Cartagena. Spain

J. Hernández Velasco

Instituto de Ciencia de Materiales de Madrid, CSIC. Spain

R. Ballou

Institut Néel, C.N.R.S. & U.J.F. Grenoble, France

A. P. Murani

Institut Max von Laue - Paul Langevin, France

H. Abele

Atominstytut der Österreichischen Universitäten, Wien. Austria

L. R. Falvello

University of Zaragoza - C.S.I.C., Department of Inorganic Chemistry and I.C.M.A. Spain

J.E. Lorenzo

Institut Neel, CNRS, Grenoble. France

L. P. Reganult

CEA-Grenoble, DRFMC-SPSMS-MDN, Grenoble. France

J. A. Blanco

University of Oviedo, Spain



ESS Bilbao Head Office

Gran Vía, 35 - 2nd floor
48009 Bilbao - SPAIN

Phone: +34 94 607 66 20
Fax: +34 94 607 66 21

ESS Bilbao R&D Centre

Bizkaia Technology Park
Laida Bidea, Building 201-Gate 4
48170 Zamudio - SPAIN

Phone: +34 94 607 68 52
Fax: +34 94 607 66 21

essbilbao@essbilbao.com
www.essbilbao.com



ESS
bilbao

