Scientific Prospects for Neutron Scattering with Present and Future Sources

An ESF Exploratory Workshop in collaboration with the European Neutron Scattering Association (ENSA)

held, with additional support from EC/TMR and ILL, in Autrans, France, 11 - 13 January 1996

Contents

Executive Summary

This Workshop was undertaken by the European Science Foundation, under the umbrella of its *Framework Studies into Large Research Facilities in Europe*, in collaboration with the European Neutron Scattering Association. It was organised locally by the Institut Laue Langevin, and additional support from the European Community (Training and Mobility of Researchers) and the ILL. The Workshop brought together about 80 scientists in the village of Autrans (near Grenoble, France) in January 1996 to consider, in ten working groups, the future of neutron scattering in Europe. The Workshop concluded with the reports of the 10 individual Group Leaders and a Panel Discussion.

The main elements of this report are an introduction which summarizes the outcome of the working groups and of the workshop panel, an assessment of the results by the ESF Standing Committee for the Physical and Engineering Sciences (PESC), the reports of the ten working groups, and a summary of a survey undertaken by ENSA.

The base line questions put to the Workshop participants were as follows:

(a) What is the 10-year forward look for neutron scattering, with particular attention to the impact of the new techniques such as the new 3rd generation synchrotron sources?
(b) Forward look beyond 2005, with particular emphasis on new frontiers?

The conclusions of the Workshop are as follows:

1. The use of neutrons continues to evolve, both in traditional and in new fields. Given the enormous impact of new materials in technology, no end to this process can be foreseen. The demand for neutrons continues, and we do not see this changing in the next 15 years. The demand for more sophisticated use of neutrons, e.g. polarisation analysis, continues to grow, so that aggressive programmes of instrumentation development are vital to the field.

2. Non-neutron tools for matter investigation, such as synchrotron radiation, cannot substitute the future use of neutron beams.

3. The diversification of neutrons into an increasing number of scientific areas continues. Examples are earth sciences, the pharmaceutical sciences, biology and engineering.

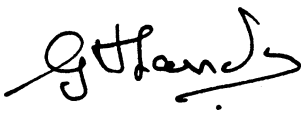
4. The direct impact of neutrons on "wealth creation" is increasing and will continue to do so. Examples of industrial relevance are in the fields of multilayers, polymers, materials science, and engineering.

5. Unless appropriate action is taken, sources of neutrons, and hence the supply, are

likely to *decrease* in the next ten years. Given the existing and future expected demand in Europe this makes it imperative that:

(a) full use be made by European users from the basic and applied sciences, of the present network of medium-flux national sources and the highest-flux sources, i.e. ILL and ISIS, and

(b) a mechanism be initiated by the ESF to co-ordinate the design and funding requests that will allow a truly advanced European Source to be operational within 15 years.



Gerard H. Lander
Workshop Chairman

Hubert Curien
Panel Chairman

ESF Assessment
'Impact and prospects of neutron methods and neutron sources on European science and research'

The European Science Foundation, with the endorsement and engagement of its Standing Committees and Associated Committees, is actively pursuing its function as the multi-disciplinary clearing-house in Europe for large research facilities and large networking enterprises, providing information and advice from the European view point to the decision-making bodies at the European or national scene.

Under its *Framework Studies into Large Research Facilities*, the Foundation initiated and supported *the ESF Neutron Source Studies ('ENS Studies/Task A')* in order to investigate the impact and prospects of neutron methods and neutron sources for European science and research, including applied research. (Task (B) under the ENS Studies is devoted to developing and assessing the scientific case of the initiative for a pulsed highest-flux European spallation neutron source *('ESS project')).*
The central event under Task (A) of the ENS Studies of the Foundation was the Exploratory Workshop in Autrans, France, in January 1996, the Report of which is hereby assessed.

The Report contains the results of the 10 Working Groups which covered the whole gamut of science from particle physics to biology, with industrially important topics especially in engineering and chemistry. The Conference Chairman, Dr G. Lander of the EC Karlsruhe Establishment, and the Chairman of the Panel Discussion, Professor H. Curien, former Minister for Science in the French Government and past President of ESF, summarise the major points of consensus which emerged from the Working Groups and from the Workshop as a whole.

Within ESF the Report has been assessed by the 'ENS Panel'[1] drawn from the ESF Standing Committee for physical and engineering sciences (PESC), in liaison with the Standing Committee for life and environmental sciences (LESC). This Assessment was approved by the Board of the European Science Foundation on 12 July 1996.
ESF-PESC came to the following *observations and assessment:*

The structural investigation of in-animate or animate matter in many R&TD fields of the natural or technical sciences has benefited greatly from the complementary use and exploitation of neutron beams and of synchrotron X-rays, made available at both national and multinational facilities. European R&D has reached a lead position in international competition. With regard to recent developments and constraints it appeared timely for ESF to convene a meeting of scientists working in fields where neutron scattering or competing diagnostic techniques have been (or could be) important in order to assess the impact of neutron techniques, and the future need for neutron sources, for European science and research, both in the relatively short term (10 years) and the distant future. Important in such a discussion is the impact, on the

[1] **Members of the 'Subgroup on Neutron Facilities':** P. Day (Rapporteur, The Royal Institution, London), G. Ertl (Fritz-Haber Institute, Berlin), N. Kroo (Rapporteur, Hungarian Academy of Sciences, Budapest), F.W. Sluijter (Eindhoven University of Technology), D.A.M. Weis (Université Libre de Bruxelles), H.U. Karow (Secretary, European Science Foundation)

science carried out with neutrons of the new horizons opened up by the new generation of synchrotron X-ray sources and, in the longer term, by the emergence of new fields to which neutron scattering could make a decisive contribution.

The assessment points of ESF-PESC is as follows:

1. The contents of the Report on the Autrans Workshop amply demonstrate and document the vitality of science and research carried out with neutrons in Europe at the present time. In particular, neutron scattering techniques remain a vital resource for the structural investigation of condensed matter, including the solution of structural problems in the technical sciences or industrial developments. It should be especially borne in mind that, in the application of neutron scattering to the physical and biological sciences, Europe has established a clear world lead over the USA and Japan.

2. Synchrotron radiation techniques and radiation sources cannot abrogate neutron techniques and neutron sources (which would have been an appealing hope at financially constrained times with regard to the much lower specific costs of soft-X photon beams as compared to neutron beams). The specialists at the Workshop clearly concluded that even in the long term, both techniques and advanced radiation sources including instrumentation of both categories are indispensable to Europe's lead in science, research and technical applications, as the two techniques cannot replace each other (nor be replaced by third methods), but complement and extend each other's range and opportunities.

3. The ideas and proposals for new work presented at the ESF Workshop in Autrans further demonstrate a continued need for high quality neutron sources and their corresponding instrumentation in the foreseeable future. Neutron scattering techniques will make a special impact on newly emerging interdisciplinary fields as they did for example, in the elucidation and understanding of the previously unforeseen field of high Tc superconductors. Examples include reproducing extreme conditions of materials important in the earth sciences, the behaviour of polymer mixtures in flowing reactors in the chemical industry, rationalising the procedures for making zeolite catalysts, understanding the performance of engineering components under operating conditions, and many more. The need to carry out experiments at central facilities will, in itself, encourage the interdisciplinary contacts essential to make progress in such fields.

4. The Workshop also came to the conclusion that further progress in science and research will rely on the availability of two types of neutron beam sources in relation to their time-characteristics: neutron sources generating (quasi) steady-state beams (in specially optimised nuclear research reactors or in accelerator driven spallation sources, generating continuous or long-pulse neutron beams), and neutron sources generating short(est)-pulse neutron beams (i.e., sharply-pulsed neutron spallation sources).

5. Following from the above points, one may state that the R&TD community of neutron users in Europe is large, distinguished, vibrantly active and representative of almost every discipline in the physical sciences, as well as molecular biology and engineering. Finding the optimum means to address the continuing needs of this wide and strategically important R&D community group in both the medium and long term within the scientific-technical-strategic and economic opportunities in Europe should be a matter of the highest priority, ensuring the health of many fields of European R&TD and the European lead achieved in the past.

6. The foregoing conclusions lead to several proposals for action by national agencies, the EU, and the Foundation itself.

(i) In the medium term, means should be found to ensure the most effective exploitation of the existing portfolio of neutron sources in Europe, both of the national medium flux type and those centres of excellence such as ILL and ISIS having the highest fluxes available in the world in their respective categories.

Medium flux sources remain important as regional training grounds for young researchers, for developing novel instrumentation and conducting preliminary or speculative experiments before they are transferred to the high flux sources where beam-time is in greater demand. In this regard, access for scientists from other European countries should be supported by the EU.

The small number of highest flux sources provide benchmarks for the science conducted with neutrons at the world level. Arrangements must be made by the ESF sponsoring agencies to ensure that the fullest possible use is made of such sources, by optimising the number of instrument days available to users and ensuring that as many beamlines as possible are furnished with state of the art instruments. Neutrons are scarce and should not be wasted!

(ii) In the longer term it is appropriate to actively continue to define the technical specification and design parameters of an advanced 'European Neutron Source' which would become operational when the existing high flux sources reach the end of their lifetimes, say in 15 years.

(iii) The ESF-PESC Inter-Committee Working Group on Large Research Facilities is dealing with the issues arising at the European level in the provision of facilities shared by large communities of researchers. ESF-PESC together with its Member Organisations (which represent the major research councils and funding agencies in Europe) is pursuing its function as multi-disciplinary scientific-strategic 'clearing house' in assessing the needs of European R&D communities with regard to large facilities. A particular issue is the provision of qualified access of non-national users to such facilities.

In the light of this ESF is prepared to provide advice or to take action in the co-ordination of access to regional medium-scale neutron sources operated in various European countries. An important issue should be to promote networking between the regional sources, instrumentation centres, and user communities, through the development of helpful and acceptable networking concepts for the participating communities, institutions, and funding organisations.

The ESF should provide the continuing focus for the scientific-strategic case of a future European Neutron Source.

7. The Autrans Workshop demonstrated the pervasiveness and vitality of both basic and applied science conducted with neutrons and Europe's leading position in this field. It is for the ESF Member Organisations and the European Union to devise mechanisms whereby this lead can be maintained. The European Science Foundation and its Standing Committees are prepared to collaborate on this issue.

Introduction

Background

Neutrons beams have now been in use for about 50 years. The first experiments in condensed matter research were performed in the late 1940s, and the two pioneers in neutron scattering, Bertrand Brockhouse of Canada and Clifford Shull of the USA received the 1994 Nobel Prize in Physics. During those 50 years the intensity of thermal neutron sources has increased by about a factor of 100. This is small when compared with many other techniques, e.g. NMR capabilities or the rapid rise in laser (or X-ray synchrotron) intensities after the first inventions. What has increased enormously in the field of neutron scattering is what may be loosely called the "utilisation factor" of neutrons. This includes (a) source tailoring such as cold sources to give neutrons of long wavelength that were not even considered in the early days of neutron scattering, (b) optical elements such as monochromator, mirrors, neutron guide, and analyser and (c) improvements in detector technology and design. In such a utilisation factor the advances have been considerable and certainly account for another factor of 100, (much more for cold or hot neutrons) so that, together with the increases in flux, the experiments performed today bear little resemblance to those performed in the 1940s. Neutron experiments are, however, still always intensity limited.

What has not changed in 50 years of neutron scattering is the uniqueness of the scattering cross section (see next section). It is these unique features of the cross section that has allowed neutron scattering to prosper. But what will be the position 10 or 20 years from now?

Europe now has the two best neutron sources in the world, the Institut Laue Langevin in Grenoble, France, a steady-state reactor, and the ISIS spallation source at the Rutherford Laboratory near Oxford in the UK. Many other smaller national sources, primarily reactors, also exist in Europe. Most of these were built in the 1960s. Without major refurbishment, facilities such as these can be expected to last ~35 years. The problem of age, together with the escalating safety requirements, means that many of these are expected to shut down [OECD report by the late T. Riste] in the next 5 to 15 years. What then is the future of neutron scattering?

Consequences of the neutron cross section: basis for optimism about the future

Neutrons are now used across an enormous breadth of science. The principal reason for this is the unique features of the cross section:

(a) that it is a neutral particle and penetrates deep into materials. Neutrons react to all known forces, except the electrostatic force.
(b) that its principal cross section is nuclear in origin. In particular, the cross section for hydrogen is much greater than that for any other element and it is *different* from

that for deuterium.
(c) that it is a heavy particle so that changes in energy may be easily measured by its change in velocity. Thermal neutrons (25 meV) have an energy well matched to that of elementary lattice or magnetic vibrations, whereas at the coldest end of the spectrum (μeV) the technique overlaps with the frequency range covered by NMR techniques.
(d) that it possesses a magnetic moment which interacts with unpaired electrons in solids, allowing the details of microscopic magnetism to be examined. Polarised neutrons can also be exploited in their interaction with both electron and nuclear spins.
(e) that the cross section may be readily calculated in most cases within the first Born approximation, so that eigenvectors as well as eigenvalues may be determined.

As stated above, none of these are new, but they are *unique* - and the way in which they can be exploited continues to evolve. We shall highlight some of the recent advances, as well as those foreseen, in the following summary.

The Workshop

To discuss the future potential of neutron scattering ~80 scientists gathered in the small mountain village of Autrans (near Grenoble, France) on 11-13 January 1996. The ESF Exploratory Workshop was run in collaboration with the European Neutron Scattering Association (ENSA) with additional support from the European Commission (Training and Mobility of Researchers) and the Institute Laue Langevin. The basic tasks of the Workshop were to examine:

(a) the 10-year forward look, with particular attention to the impact of the new techniques such as the new 3rd generation synchrotron sources, and
(b) the forward look beyond 2005, with particular emphasis on new frontiers.

The scientists attending the Workshop were divided into ten groups to cover the various fields of science that use neutron beams. Their summaries are attached and form the main body of this report. A list of the groups is given in Appendix B. This group of scientists contained relatively few (16 in total) affiliated to European neutron facilities, and the groups contained ~30 scientists who did not use neutrons primarily in their research activities. This large number of non-neutron professionals was to ensure that other modern techniques were well represented amongst the participants. The 83 participants came from over 10 countries within Europe, with ~2/3 coming from the three larger countries, France, Germany and the UK. Five came from outside Europe. The emphasis of the Workshop deliberations was completely on science or engineering that can be addressed by neutron techniques; no considerations were given to either detailed instrument design or to comparisons between capabilities at steady-state and spallation sources [*].

[*] The closest reference to the present activity is that of the Shelter Island Workshop in 1984 [Nucl. Inst. & Methods B 12, 525-561 (1985)], although this document contains more details of instrumentation than the present report. Other documents are the Report of the Abingdon Workshop on "Instrumentation and Techniques for the European Spallation Source, June 1992, RAL-92-040 (published by Rutherford-Appleton Laboratory, UK), and "Technology and Science at higher-power Spallation sources" May 1993, published by Argonne National Laboratory, Illinois, USA, 1994.

At the conclusion of the working sessions the Group Leaders gave presentations to all those attending. The conclusions of all the groups were extremely positive with respect to both the short- and long-term future of neutrons.

Workshop Panel

The Workshop ended with a Panel discussion, chaired by H. Curien, former French Minister for Research and a past ESF President, with the following as members of the Panel: G. Aeppli (A T & T Bell Labs, USA), P. Day (ESF-PESC Observer, The Royal Institution, London), G. H. Lander (Workshop Chairman, European Commission, Karlsruhe, and Chairman of the Workshop), Y. Petroff (ESRF, Grenoble), D. Richter (ENSA Chairman, KfA, Jülich), R. Scherm (ILL, Grenoble). In addition to the above speakers there were many contributions to the discussion from the floor. The overwhelming consensus was that neutrons have a large role to play in future research and technology across an ever widening field of subjects. The diversity was a recurring theme of the discussion. However, this diversity, while one of the main strengths of neutron research, made it difficult to propose "one" crucial experiment that could be sold to the scientific community. Neutron scattering in most cases, research on fundamental physics often being an exception, is characterised by *small* science at a *large* facility. In a presentation at the beginning of the Panel discussion, D. Richter, representing ENSA, gave the results of a recent survey of the neutron community in Europe.[#] Two crucial points from this survey are:

(1) The European community consists of ~3500 users of neutrons, but at least half of them class themselves as "casual" users, i.e. they use neutrons for less than 25% of their research or development work.
(2) The majority of the neutron users are <u>not</u> physicists, but a combination of chemists and materials scientists.

With the presentation of Y. Petroff, (Director of the ESRF in Grenoble) the question was brought to the fore of the relationship with the new 3rd-generation synchrotron sources. Certainly the results emerging from these machines are very impressive, inelastic scattering with a few meV resolution, and magnetic scattering from surfaces. The enormous brilliance of these machines may result in a decrease of neutron activity in some areas, but the complementarity of the synchrotron technique was emphasised by many speakers. For many scientific questions the combination of both techniques is more useful than either one of them; some specific examples are given in the report. As has been recognised for a long time, the opening of new subjects by synchrotron radiation is likely to *increase* the need for the information available with neutrons. This question is closely related to that of "increasing complexity" in research and development on materials and life sciences. As the complexity of the materials and technologies increases so we need more microscopic techniques, and both neutrons and X-rays fall naturally into that category.

[#] A complete analysis of this survey is being printed as a separate ESF report, but we present an abbreviated version as Appendix C of this report

Much discussion centred on the inter-relationship between the small and large sources, and the need to preserve this mutually beneficial relationship. Many of the most important developments in neutron scattering techniques have been pioneered at the smaller sources, then exploited at the larger facilities. However, it is inevitable that many of the smaller sources will be shut down, and there are only two new sources (PSI Villigen and Munich University) assured in Europe, although the pulsed source in Austria (AUSTRON) is still seeking realisation.

Many opportunities exist for new and/or improved instrumentation at both steady-state and spallation sources. These were discussed by a number of speakers, and are clearly a high priority for both the scientific output and the need to encourage young people to enter the field. In this respect a number of speakers expressed the view that some changes in the operational procedures of the larger facilities were necessary to accommodate more long-term research. The Collaborating Research Group (CRG) mode at ILL is one example, and, in general, there was agreement that the large facilities must find creative ways to fully exploit their capabilities, and, at the same time, remain at the forefront of both instrumentation as well as research.

In concluding the Panel discussion, the Chairman H. Curien made the point that the neutron community should be aware of the great demands on government funding today, and the difficulty in setting priorities. He cautioned that huge projects, such as the ANS (the large research reactor in the US that was cancelled in 1995 after almost 10 years of planning) did great harm to the public perception of the field. He urged that reasonable (in budgetary terms) solutions be initially sought, and that a major source *must* have the full backing of a wide and diverse European scientific community. The Panel Chairman was optimistic that the case was a good one, but much work remained to be done.

Conclusions of the Workshop

1. The use of neutrons continues to evolve, both in traditional and in new fields. Given the enormous impact of new materials in technology, no end to this process can be foreseen. The demand for neutrons continues, and we do not see this changing in the next 15 years. The demand for more sophisticated use of neutrons, e.g. polarisation analysis, continues to grow, so that aggressive programmes of instrumentation development are vital to the field.

2. Non-neutron tools for matter investigation, such as synchrotron radiation, cannot substitute the future use of neutron beams.

3. The diversification of neutrons into an increasing number of scientific areas continues. Examples are earth sciences, the pharmaceutical sciences, biology, and engineering.

4. The direct impact of neutrons on "wealth creation" is increasing and will continue to do so. Examples of industrial relevance are in the fields of multilayers, polymers, materials science, and engineering.

5. Unless appropriate action is taken, sources of neutrons, and hence the supply, are likely to *decrease* in the next ten years. Given the existing and expected future demand in Europe this makes it imperative that:

(a) full use be made by European users from the basic and applied sciences of the present network of medium-flux national sources and the highest-flux sources, i.e. ILL and ISIS, and

(b) a mechanism be initiated by the ESF to co-ordinate the design and funding requests that will allow a truly advanced European Source to be operational within 15 years.

Working Group Summaries

The group "***Particles and Nuclei***" covered the fascinating field of physics in which the neutron is used as a particle for investigating some of the fundamental questions of physics. A good example is the search for the electric dipole moment on the neutron, which has gone on for almost 40 years now. However, recent values of the upper limit are close to those predicted by currently popular "grand unified theories", so that there is strong motivation to continue this search. Another example is neutron decay. Since this involves all four particles of the first generation (down quark $\rightarrow$ up quark + electron + antineutrino), many tests of the standard model are possible. An important "flagship" experiment that would require much more flux than presently available is the observation of the free decay of a neutron into hydrogen. This would give a definite answer to why the universe is "left handed". Other fields covered by this group include nuclear physics and neutron optics. Again in these fields there are a number of important experiments testing fundamentals of physics, and it must be remembered that although these fields may seem exotic today, they often drive the instrumentation and methods that can later be exploited in both condensed matter physics as well as industrial applications. Nuclear medicine is an obvious example, as is the development of sources for cold neutrons.

Magnetism and superconductivity is, of course, one of the traditional areas of neutrons in condensed matter and one might, perhaps, expect a slowing of activity. Far from it. The discovery of heavy fermions, of high-T_c superconductors, spin-Peierls transitions, C_{60} and all its derivatives, and the explosive growth in multilayer science, have provided a plethora of new phenomena in the last decade that are perfectly adapted to neutron techniques. At the more exotic end are the studies at very low temperature, now down to 500 pK, on nuclei spin ordering, opening a completely new field of science. The centre of activity has, of course, been in the study of high T_c materials, and, together with heavy fermions, there is a realisation that the breakdown of so-called Fermi scaling, in which the imaginary part of the susceptibility $\chi''(q,\omega) \alpha \omega/q$, and the emergence of behaviour in which $\chi''(q,\omega) \alpha \omega/T$ heralds a profound revolution in the way we think about electron correlations at low temperature. It is quite unclear at this stage where this research will lead, but a central goal is the understanding of the interplay between magnetism and superconductivity. This problem was thought "understood" 20 years ago, now it becomes one of the central problems in condensed matter science.

As with the previous section on neutron physics, activities in solid-state physics frequently drive instrumentation, which is then used in other fields (the spin-echo spectrometer, which extends the resolution down to the meV range, being a good example from the past). The development of techniques to measure high-energy excitations (>100 meV) from single crystals at ISIS, the CRYOPAD 3-dimensional polarisation technique at the ILL, the research on ^{3}He polarisers centred at the ILL,

but involving many atomic physics laboratories, the ultra low-temperature techniques at HMI, and the flux lattice measurements on SANS equipment at Risø and ILL are notable examples, and many more are projected. The development of neutrons as a local probe with resolution 50 x 50 μm^2, time resolved experiments (already started at ISIS), quasielastic SANS to investigate the dynamics of flux lattices are for the future.

Magnetism and superconductivity studies in neutron scattering are driven by new materials and the need for more microscopic information on them, Given progress in general condensed-matter science for the first, and in neutron techniques for the second, the demand for neutron scattering is more than assured for the next 20 years.

For ***amorphous materials and liquids*** the principal scientific question is the description of the complex interactions, both static and dynamic, in the absence of long-range order. Although advantages such as H/D substitution and the kinematics of neutron inelastic scattering are important, the crucial advantage of neutrons is the simplicity of their cross section in the scattering process. This well-understood cross section allows detailed comparison with theory, and it is theory, perhaps more than any other technique, that drives the understanding of these fields. The group emphasises the importance of *accurate* neutron data; a simple example to demonstrate this will suffice. In the description of the atom-atom correlation function, ~80% of the significant part can be obtained from a hard sphere model, so that it is in the remaining 20% that all the details of the many-body interactions are to be found.

The study of aqueous solutions, which are now moving towards biological systems, depends heavily on the isotope substitution method, and the need to subtract data sets that differ by only small amounts underlines the need for better statistics. In these experiments H/D labelling is important, and the use of polarisation analysis would be beneficial provided the present associated loss of intensity (and hence statistical accuracy) could be avoided.

Amorphous materials are widespread in industry; some important materials are fibre optics, amorphous semiconductors, liquid crystal displays, and magnetic devices for magneto-optical recording. Although the research performed on these is basically long-term and thus underpins industrial use, with higher intensity the direct involvement of neutrons, for example by using reflectivity in monitoring the growth of films or powder diffraction associated with new batteries, can be seen in the production process.

The Group sees a continuing need for development and research on instrumentation. On polarisation analysis, on the application of spin echo to SANS, on neutron Brillouin scattering, and on more intense reflectometers using polarised beams.

Polymer and soft matter is one of the major growth areas of neutron scattering; moreover much of the research in this area has direct industrial implications. The two

crucial points for the application of neutrons in this area are the ability for H/D labelling, and the fact that the slow time scales of molecular motions are within the range of observation of slow neutron techniques, especially of the spin-echo method.

Neutrons have already played a major role in understanding aspects of polymer conformation and rheology. SANS remains the pre-eminent technique for establishing the conformation of polymers. Recently, the neutron spin-echo method has been able to demonstrate some important aspects of the validity of the widely accepted reptation model, thus adding appreciably to our knowledge of the topological constraints present in polymer entanglement. Of importance for industrial processes is understanding the deformation and relaxation of polymer melts, and their response to shear and strains. The latter are always present in the production of polymers, and yet the effects on the properties of polymers are poorly understood. Neutrons shed unique light on this problem, again as a result of the capability of H/D labelling.

Another large class of materials are surfactants and self-assembling systems. Again, these are widely used in industry, for example in both the oil and detergent industry. X-rays are often very useful, but, again, the ability of the H/D substitution gives neutrons the key role. A technique that has become of major importance is that of reflectivity. At the moment the majority of experiments look at the specular reflectivity, which gives the profile of the scattering density along the surface normal into the material. With greater flux it is possible to examine the off-specular reflectivity, which gives information on the ordering *within* one layer of the material, i.e. perpendicular to the surface normal.

Experiments are now being performed on polymer/protein interfaces, and clearly there is much room in the future for these kind of studies. Higher fluxes are mandatory for many of the applications envisaged, as is the development of polarisation techniques for separation of the coherent and incoherent scattering, and development of an order-of-magnitude improvement in the Q_{min} that can presently accessed by in small-angle scattering experiments.

Biological studies with neutrons rely extensively on the H/D contrast. Many experiments with small-angle scattering, low-resolution crystallography, quasielastic scattering, and reflectometry (principally on membranes) are providing invaluable information on both structure and function in a large variety of biological systems. It must be remembered that diversity is a key point in biology, differences between systems are as intriguing as similarities. In the domain of molecular structure the use of X-rays remains supreme, and neutrons have no way of competing. However, paradoxically perhaps, the success of synchrotrons is posing more questions for the use of neutrons. Knowing the structure of a protein is vital, but this often requires not only knowing the positions of the "heavy" atoms, C, N, and O, but also the location of the key H atoms, particularly in the active site of an enzyme or in the surrounding

water molecules. Neutrons, with their ability to "see" hydrogen, both in a static and dynamic sense, are ideally suited to answering these questions, so that synchrotrons, far from putting neutrons out of business, will actually generate more business for them. Business, moreover, that lies at the heart of biological function, whether it be the hydrogen network that holds a substrate in the correct conformation for cleavage, or the motions of the protein molecule that, through conformational flexibility, allows access of a ligand to its binding site.

Neutrons, either by SANS or low-resolution crystallography, can tell where these water molecules are located and start (by quasielastic scattering experiments and associated computer simulation) to answer the question of how the movements are related to function. Thus inelastic scattering is a unique tool for probing the internal dynamics of biological macromolecules.

Studies in biology are extremely time consuming and intensity limited. Even the fastest technique, SANS, usually requires many different levels of contrast variation and the most relevant results are those at the smallest concentration. A more concrete example is the hope to obtain data on the same crystal by X-ray and neutron techniques. To perform this we are down by at least a factor of 500! Some of this may be made up by more efficient neutron detectors (e.g. wider angular coverage in Laue diffraction) but clearly stronger sources would have an immediate impact in biology. A similar advantage would accrue to studies with reflectometers. At present intensities are really not sufficient to obtain information away from the specular diffraction, and yet this contains important information on the in-plane configurations.

Atomic and molecular aspects of new materials is a subject that continues to evolve rapidly. More new compounds have been synthesised since 1980 than in all previous history. The variety of these materials, many of them tailor-made, is enormous, ranging from oxide ferroelectrics and superconductors to shape memory and permanent magnet alloys, and from novel hydrides and hydrates to self-assembling molecular materials. Underpinning all these new materials is a detailed understanding of their atomic and molecular structure. Neutron diffraction has been at the forefront of the characterisation and explanation of all the new developments in materials in the last two decades. Examples are the neutron work on high-T_c superconductors and the first definitive answers to the detailed structure of C_{60}.

The ability of neutrons to penetrate bulk materials leads to the advantage that materials may be investigated under realistic conditions of temperature and pressure that are necessary for their formation. Examples are the ageing of ceramics, and the discharge of long-life alkaline Zn-MnO_2 primary batteries. High pressures up to ~20 GPa can now be routinely used with neutron diffraction, but higher pressures will require the fluxes of the next-generation sources. Advances in optics, resolution, and source intensities gives the intriguing possibility that length scales from picometers to

fractions of a meter may be accessed by neutron diffraction experiments, and opens up a new horizon for the characterisation of complex materials.

Chemical reactions, catalysis and electrochemistry covers a vast range of different chemical reactions that are addressed by inelastic neutron scattering (INS). At least 90% of this utilisation relies on the different scattering cross sections of H and D.

The sensitivity to H and the simplification of the cross section have allowed molecular vibrational spectroscopy to become quantitative in the sense that both eigenvalues and eigenvectors can be obtained. When combined with the Q dependence this gives information on the shape of the chemical potential functions. These additional (i.e. as compared to optical techniques) features allow a much more rigorous test of theoretical models.

One of the main activities in this field is connected with catalysts. Such materials range from complex zeolite templates to relatively simple molecules such as the transition-metal sulphides. In all cases the key aspect of the catalytic activity concerns the residence time and place of a hydrocarbon molecule. In combination with NMR techniques, neutrons are alone in being so sensitive to the H vibrations. A good example in the report is the effort in discovering why the RuS_2 molecule is almost 10 times more efficient than MoS_2 hydrosulphurisation. In this study it is possible using INS to identify the different H species present on a catalyst, to determine their relative proportions, and to follow changes as a function of the catalyst treatment. For the future increased resolution (to compete with optical techniques ~1 cm^{-1} is required) and higher intensities (so that surface states, for example, can be studied) over a wide range of Q are needed. Polarisation analysis provides the option to suppress coherent scattering from both liquid and solid samples, and will become a valuable additional parameter when higher fluxes are available.

Earth sciences are a relatively new area for neutrons to address. The questions asked in earth science, like those in materials science, appear much simpler than those posed in the mainstream fields of condensed matter physics. However, the systems examined are much more complex. Often they are multiphase, and even with different compositions of the same material. A technique that has been particularly valuable has been powder diffraction with the Rietveld method capable of averaging over a large sample, and the ability to distinguish between materials with different hydrogen content. Averaging over a large sample is vital, for example, in determining the texture and preferred orientation of geological specimens.

Pressure experiments are obviously important to simulate conditions in the earth, and, although the majority of experiments, particularly those at the highest pressure, are being done with synchrotron X-rays, the importance of hydrogen in minerals, whether as part of a hydroxyl group or a water molecule, or as a free proton, makes the neutron experiment truly complementary. At present pressures up to ~20 GPa can

used in neutron experiments. Since the samples must by necessity be very small, the experiments would benefit greatly from increased flux.

Thermodynamic models for the earth rely on the knowledge of the Gruneisen parameters of its constituents. These are obtained from a variety of sources, but are most reliably obtained from the pressure dependence of the phonon dispersion curves. There have been some cases recently where the accepted values have been found to be seriously in error.

One of the major aims of the earth sciences is the prediction of earthquakes and volcanic eruptions. Given the complexity of the geology of the planet, models for such are very coarse approximations. They are improved by better information as a base for the computer codes. A good analogy is the prediction of the weather, which has improved dramatically over the last two decades, due both to the quality and quantity of the information available, as well as to the advance in computer simulations.

Materials science is concerned with property control by changing, or at least understanding, the microstructure. Such microstructure concerns point defects, dislocations, interphase boundaries and internal interfaces with microcracks, pores voids, bubbles, etc. Materials science is intimately related to processing methods, e.g. powder metallurgy, mechanical alloying, molecular beam epitaxy (MBE), sol-gel synthesis etc. Since this covers such a wide field of materials it is natural that the material scientist uses a vast array of analytical tools; neutrons being such a tool at the microscopic level is an important part of this arsenal. Two examples will demonstrate the variation in properties examined. In superconductors there are basic questions relating to vortex pinning that affect performance in the critical current that can be passed. Neutrons can image this vortex lattice and help to determine the best methods of fabrication for, for example, superconducting tapes. In the field of multilayers neutron reflectivity can be used to provide unique information about the extent of interfacial diffusion, and the direction and amplitude of the magnetic moments. These materials are also at the forefront of technology, especially since the discovery of the giant magnet-resistance effect. However, both these examples provide opportunities for further work. In the case of the superconductors, the possibility of determining the dynamic of the flux lattices, and in the multilayers the possibility of determining more information about the lateral dimensions, from off-specular reflectivity, represent new areas that are *just* possible with today's sources. Improvements in flux levels would of course benefit these studies enormously.

Reflectivity studies of single atomic layers are now possible with neutrons, and many new materials such as coatings etc., can be examined. An interesting example of the impact neutron reflectivity might have is on the problems of finding coatings for implant materials. The latter are normally made from cobalt or titanium based

materials and to prevent wear and adverse reactions special coatings containing hydrogenous materials are being developed. The high sensitivity to hydrogen in the presence of the underlying metals, would seem an ideal subject for neutron studies.

In the area of internal strains/stresses neutron diffraction is now being used extensively. Its advantage over x-rays is the high penetrating power of the neutron and the large scattering angles used, which allow a good definition of the "gauge" volume. At present the minimum gauge volume is about 1 mm^3. If this could be reduced to 50x50x50 μm^3, the technique would be of great interest in a range of problems where it cannot be now usefully applied. This is a reduction in volume of almost 10^4. Although some of this may be made by focusing techniques, there are clearly new horizons that can be reached only with a new source.

Engineering represents a field with totally different motivations from those discussed above. It is important to realise from the outset that it is not *curiosity* that drives engineering research; it is the need to fix problems as quickly and as cheaply as possible. Neutrons may provide the most elegant and complete knowledge of a certain materials science problem, but if the cost of neutrons is too high, and the time too long, they will not be competitive. Because important legal issues can often be at stake when components fail, there is a need for standards and documentation that might seem prosaic in basic research. Having said that, it is quite clear that the unique properties of neutrons are making an impact in engineering research, and there is considerable promise for the future.

One example is research on real colloids with a view to process control and stabilisation of complex colloids. SANS machines with $Q_{min} \sim 5x10^{-4}$ $Å^{-1}$ need to be available, and because of the use of H-containing polymers it would be of great advantage if polarisation analysis could be performed to separate the coherent from incoherent scattering. Of course, neutrons have the advantage over X-rays that the contrast can be changed by selective deuteration. This work has implications in the petroleum industry, for example, where one of the issues is the use of asphaltenes, the heaviest fractions of recovered production, and in efforts at enhanced oil recovery.

A second example concerns the non-destructive determination of the remaining lifetime in turbine blades. This is achieved by measuring in the real turbine blade the chemical coherency between the regions containing the γ phase, an fcc NiCr matrix, and cuboidal inclusions of the simple cubic Ni_3Al,Ti. The chemical coherency of these two phases is sensitive to strain, so that a relatively simple test provides important mechanical information. X-rays are not used because the bulk peaks are masked by the oxide contamination at the surface.

We have already mentioned in the Materials Science section the need to reduce the gauge volume, down to something like $(50\mu m)^3$ and, if possible, this would clearly have a large impact in the number of engineering problems that could be tackled.

Looking at rivets and welds is one. Work is presently done but often with insufficient information content to be directly commercially viable.

Further applications of neutrons

Finally, it should be realised that there are many fields of science that involve neutrons but not necessarily the scattering of beams, as discussed in the bulk of the report. Because such uses cover many different areas, as diverse as isotope production to boron-neutron capture therapy (BNCT), this Workshop did not have a group addressing these questions directly. However, for completeness we add a short section on these uses.

One obvious example is radiography and tomography. Another is transmutation doping of semiconductors, which is big business, for example, and requires a nuclear reactor, as do the production of many isotopes used in nuclear medicine. Boron neutron capture therapy (BNCT) is now becoming quite widespread in the treatment of certain tumours.

Neutron activation analysis is sensitive to 10^{-11} concentration of impurities, and is therefore one of the most sensitive techniques available for detection of impurities, especially in the semiconductor industry. Some 10^4 probes a year are analysed alone for environmental public services.

An exhaustive set of such possibilities is difficult to make, and the report makes no attempt to be all inclusive in this regard. In many cases the neutron flux needed for these applications may not be too great (radiography is often done with small Cf sources) but it should be realised that the development of new techniques in this field is often performed at a larger facility. These can then be scaled down to appropriate levels for the desired applications.

Particles and nuclei

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Introduction

Neutrons provide a useful tool to treat a number of questions from the domain of particle physics, nuclear physics, and of quantum and measurement theory. Further, several neutron-nuclear methods exist which are or may become helpful in the applied and industrial sciences. In contrast to the following surveys, the present article treats mainly (but not exclusively) the non-scattering experiments and techniques which are possible at existing and future neutron sources, and tries to explore the future potential of these methods. The article covers the following topics:

1. Particle physics
2. Nuclear physics
3. Neutron optics
4. Neutron related particle sources

1. Particle physics

Neutrons react to all known forces, except to the electrostatic force. This is fortunate (and unique for a long-lived particle), because, due to its long range, the electrostatic force is dominant in most processes and would mask many other more subtle effects. Therefore, neutrons are useful for a number of studies of the fundamental interactions and their symmetries.

Before going into any detail, let us recall some simple facts about neutron physics. Measurements in physics often rely on the sensitivity of the apparatus to small changes in energy, momentum, or polarisation of the particles involved. The possibilities of neutron physics here are remarkable, and have been improving steadily over the past years. They are likely to continue to do so as no saturation effects due to limitations of principle are in sight.

Shifts in neutron interaction energy of 10^{-21} electron volts are detectable today. This energy corresponds to a Bohr frequency of one cycle per month. For purposes of comparison, a typical atomic Bohr frequency is of order 10^{14} per second. Changes in neutron momentum corresponding to a lateral deviation in the neutron trajectory of several Ångstrom over a distance of ten meters can be resolved experimentally. And the direction of neutron polarisation can be controlled with an accuracy of less than 10^{-6} radians.

Table 1 lists a number of observables accessible to neutron particle physics, and also the scientific questions addressed by their measurement. In Table 1, the numbers in

parentheses indicate that the experiment:

1. is finished
2. is feasible with existing neutron sources
3. is being continued at existing sources, but would profit strongly from better sources
4. has been done and will be continued only if better sources are available
5. is feasible only with better neutron sources

Cases (2) and (3) describe the program of the next 10 years, while cases (4) and (5) point to the program beyond the year 2005.

Many of the topics listed in Table 1 came to life only during the eighties, and were by no means anticipated. Examples are: neutron-antineutron oscillations, which turned out to be allowed in the left-right symmetric grand unified theories; the axion as a possible solution to the strong CP-problem; three generation quark-mixing; the links between cosmology and neutron-particle physics, from which the total number of particle generations was deduced for the first time; the unexpectedly large parity violating (i.e. left-handed) amplitudes in various neutron optics and nuclear fission experiments; the question of the existence of right-handed weak currents in our left-handed world; and others. Therefore, by extrapolation, it is a rather safe prediction that in neutron-particle physics there will be new and unanticipated topics ahead.

In some cases more specific predictions can be made. The search for a neutron electric dipole moment, for example, has been going on for forty-five years, and the upper limit on this number is now at 10^{-25} e cm. A non-zero electric dipole moment would violate time reversal symmetry. The experiment has seen a gain in sensitivity of one order of magnitude every seven years. Several theories on the possible sources of time-reversal violation (which is known to exist in nature) have already been eliminated by this experiment. It is likely that progress in the search for a neutron electric dipole moment will continue at the same pace. Therefore, a further batch of very prominent theories will go the test bench of the neutron electric dipole moment within the twenty years ahead, among them the left-right symmetric grand unified theories. Also, the current explanation (provided by the late A. Sacharov as early as 1967) why, after the big bang, matter dominated antimatter - the so-called baryon-asymmetry problem of cosmology - will by then see a yes/no decision. These models require a neutron electric dipole moment of 10^{-27} e cm.

Another evident case is free neutron decay. In the past ten years, the accuracy in the measurement of neutron decay data has increased by more than one order of magnitude (from 7% to 0.2 %). Therefore, the question arises as to whether more neutron decay data are necessary. There are three main application of neutron decay data: Firstly, the verification of quark model predictions on the size of the effective weak quark-lepton coupling. These predictions, which are crucial for instance in the context

of the present "proton-spin crisis", are good to only several percent. Hence, at present, no better neutron data are needed in this sector. Secondly, neutron data today provide the only means to derive the weak cross-sections which determine, for instance, the abundancies of primordial elements, the temperature of the sun, solar neutrino fluxes, production of neutrino, $W^{\pm}$, Z^{0}, and other weak events in particle physics experiments. In these fields, for a long time the neutron data contributed the largest error to the pertinent calculations. Today, in the big-bang element abundancy calculations, the leading error is due to the imperfectly known baryon to photon ratio, but, still, the error from the neutron data is almost of the same size. So, here also, better neutron data are not of the highest importance today, but would be comforting. However, the field of cosmology keeps moving, and the observational distinction between the standard big-bang model and inflationary big-bang models would require a higher overall accuracy for the element abundancies than is presently available.

The third and today most important use of neutron data is for tests of the current standard model of particle physics. At the large accelerator centres, the standard model is intensely tested in the sector of the second and third particle generations. Neutron decay, on the other hand, involves all four particles of the first generation (down quark ' up quark + electron + antineutrino). In the Standard Model, only two parameters are needed to describe neutron decay. As there are many observables in free neutron decay, the problem is strongly overdetermined. Therefore, many tests of the standard model are possible, and these are listed in Table 1. These tests are generally more stringent than similar tests derived from high energy experiments, in particular the tests on the existence of right-handed currents, on the unitarity of quark mixing, and on flavour symmetry. They should be continued to the highest possible accuracy.

To this day, less than half of the possible neutron decay parameters have been addressed by experiment, and only a few of them with high precision. So it is another safe prediction that neutron decay experiments will be with us also during the decades to come.

The same is hoped for the neutron charge experiments. The standard model does not require charge quantization, i.e. does not require a zero neutron charge, while grand unified theories usually do. The question of a neutron charge (present limit: $<10^{-21}$e) should therefore be tested as stringently as possible. (If the neutrino should have a non-zero Dirac-mass, then a violation of charge quantization scaling with B-L should exist, with B = Baryon number, L = Lepton number. In this case, the hydrogen atom should be exactly neutral, while the neutron should not.)

Also, the beautiful parity violating neutron optics experiments are likely to continue, especially if they can be extended to liquid hydrogen or helium targets, where they promise unique information on the elementary quark-quark interaction.

Table 1

Observables in Neutron-Particle Physics Experiments and related Physics Questions

Observables with status numbers (3) to (5) need stronger sources.
(For details see text)
* Flagship experiments with new neutron source

Observables	Status	Physics Questions
Neutron particle properties		
Mass: m_n/m_p	(4)	Model independent value
$\hbar/m_n$	(4)	of electromagnetic interaction strength α
Charge	(4)	Charge quantization, Grand unified theories (GUTs)
Magnetic monopole moment	(4)	Grand unified theories
Magnetic dipole moment	(1)	Quark Models
* Electric dipole moment	(3)	Time-reversal violation, GUTs, baryon-antibaryon asymmetry of universe
Electric polarizability	(4)	Quark-confinement potential
Magnetic polarizability	(5)	
Neutron ß-decay		
Lifetime	(3)	Strength and structure of weak lepton-quark interactions, as input for: big bang cosmology, astrophysics and solar physics, quark models, and for tests of the Standard Model of particle physics on:
Correlation coefficients:		
ß-asymmetry	(3)	Right-handed currents
neutrino-asymmetry	(3)	Unitarity of quark mixing
ß-neutrino-correlation	(3)	Conservation of weak vector current
further correlation coefficients	(5)	Flavour symmetry
ß-helicity	(5)	Limits on scalar and tensor admixtures
triple neutron spin-correlations	(3)	GUTs, Time reversal violation,
triple electron spin-correlations	(2)	baryon asymmetry of universe
Energy spectra		
of electrons, protons,	(5)	Weak magnetism in electroweak interaction
of various correlation coefficients,	(5)	Second class currents
and of inner bremsstrahlung	(5)	Radiative corrections
* Neutron decay into hydrogen	(5)	Yes/no experiment on right-handed currents

Observables	Status	Physics Questions
Neutron interactions		
Scattering lengths:		
Neutron-electron	(4)	Neutron intrinsic charge distribution
Neutron-proton	(1)	Quark models
*Neutron-neutron	(5)	isospin invariance
Parity violating effects		
Spin rotation in non magnetic medium	(3)	
Neutron polarising action of nonmagnetic medium	(3)	
Neutron-proton γ-asymmetry	(4)	Quark-quark electroweak interaction
Neutron-proton γ-circular polarisation	(4)	
Asymmetry in nuclear fission	(3)	Mesoscopic manifestation of PNC
*** Time reversal violation in neutron optics**	(5)	GUTs, baryon asymmetry
Capture:		
Neutron-proton capture cross-section	(1)	Nucleon-nucleon interaction
Spin-dependence of neutron-proton capture	(2)	
Neutral current interactions of neutrinos		
Neutrino oscillations	(4)	Neutrino mass, GUTs, closure of universe
Searches for heavy neutrinos	(4)	
Neutrino helicity	(2)	Left-right symmetric GUTs
Neutrino cross-sections	(4)	Electroweak interaction
Other Rare processes		
Neutron-antineutron oscillations	(4)	Left-right symmetric GUTs
Axion searches	(1)	Strong CP problem, closure of universe
Searches for e^+e^- resonances	(1)	

Neutrino experiments nowadays are done mainly at accelerators. They will certainly profit from future high intensity spallation sources, but are unlikely to come back to the reactor neutron sources.

Four neutron-particle physics experiments have been selected as flagship experiments for future neutron sources, and have been marked (*) in Table 1. All of them are on crucial questions of particle physics or cosmology. Three of them are new proposals and are feasible only at a high current spallation neutron source. The expected event rates and the scientific impact of these experiments are discussed in the papers prepared for the scientific board of the European Spallation Source project.

2. Nuclear physics

Nuclear physics questions are addressed both at reactor neutron sources and at accelerator neutron sources. Mostly slow neutrons (< 1 eV) are used at reactors, while fast neutrons (up to many GeV) are used at accelerators.

At reactors, nuclear physicists possess a small number of highly sensitive and unique instruments, which have a broad spectrum of scientific applications. These instruments are in high demand, in spite of the fact that during the past decades many nuclear physicists have drifted away from low energy nuclear physics. This demand is due to the fact that these instruments and methods have been, and are still, improving at a high standard of sophistication.

Low energy nuclear physics essentially works on what could be called mesoscopic physics: the description of a quantum system with an intermediate number of interacting particles at low temperature. The theoretical problem is formidable, but the signals from this system, the nuclear radiation spectra, are copious and readily detectable. Therefore, many modern concepts like giant resonances or quantum chaos have first been developed in nuclear physics. The eighties have seen a rather unexpected revolution in nuclear physics: many of the often extremely complex nuclear energy spectra can now be fully described with rather simple algebraic formula, much like the Balmer formula for the atomic spectra. These formulae have emerged from bosonic and boson-fermion supersymmetric formulations of the nuclear dynamic problem. Many of the relevant measurements to check these formulas have been done at nuclear reactor instruments, because neutron capture spectra are more complete than those induced by other nuclear reaction, which latter usually impart much angular momentum to the system. With more sophisticated detector arrangements, more investigations in this field of principal scientific interest will be done in the future.

Studies on radioactive nuclei have boosted the interest of nuclear physics by extending the scope of the models to a very wide range of combinations of neutron and proton numbers N and Z. These short-lived nuclei are indeed real nuclei which cope fully with the nuclear interaction stability problem which is solved in an extremely short time, compared to the decay time. Intense neutron sources offer a unique possibility for producing high intensity, very neutron-rich fission products. Spallation produced radioactive nuclei cannot compete because they appear in a highly excited state which tends to decay by neutron evaporation.

Another field of science which profits greatly from these neutron-nuclear instruments is astrophysics. The heavier elements are synthesised by neutron capture both within the cores of red giants (slow process) and in supernova explosions (fast process). There are two types of nuclear instrument at reactors which together cover almost all unstable isotopes visited both during the fast path - these are the nuclear fission

instruments - and during the slow path - these are the in-pile neutron capture instruments. With them many details of the element production process can be deduced - the relevant temperatures, times, neutron and electron fluxes, and so on. But, especially the fast element production process is still largely unexplored, and more experiments on these questions will be done with new fission product sources currently under development.

The ultra-high resolution crystal spectrometers for gamma rays developed at research reactors have found applications in fields of science other than nuclear physics, such as particle, atomic, solid state and astrophysics. Their resolution could be further increased by cooling the in-pile target. Further, in the future, a high intensity cold neutron beam should be equipped with multidetector arrays for coincidence spectroscopy to study multiphonon excitations, scissors modes, pair breaking, Fermigas behaviour, and temperature effects in nuclei. Such an installation could also have a large potential for industrial applications.

The possibilities of medium energy neutron-nuclear physics are far-reaching and have been explored in a three volume LANL-study by A. Michaudon and collaborators (LA-UR-94-1320).

3. Neutron optics

Neutron optics and magneto optics deal with the study of transmission, reflection, refraction, diffraction and interference effects of neutron de Broglie or spin wave functions interacting with macroscopic materials and/or magnetic fields. Some topics of neutron optics are already included in Table 1. Table 2 gives a list of further topics addressed with neutron optics. About half of the topics listed have not yet been studied and would strongly profit from a better neutron source. No saturation can be seen in this very active field, and many exciting topics lie ahead. In recent years, some of the now classical neutron interferometry experiments have been repeated in the emerging field of atomic beam interferometry.

Table 2 does not include the many Bragg and inelastic scattering crystal optics methods that have been developed in condensed matter physics over the years. However, we want to mention a number of intriguing neutron optics methods for efficient beam tailoring which have been proposed in recent years and which may some day become interesting for condensed matter studies. For a pulsed neutron source, for instance, about one order of magnitude gain in monochromaticity can be obtained when travelling magnetic wave focusing is applied. An even higher gain is expected from a “monochromatizing machine”, which uses back-reflection from perfect crystals, magnetically gated crystals, and Zeeman energy transfer by neutron magnetic resonance irradiation. Further, new spatial and temporal Fourier spectrometers will allow measurement of the autocorrelation functions of the

wavefunction and the related neutron momentum and energy distribution functions. Another series of new high resolution neutron scattering methods, mostly using sophisticated spin precession schemes, has been developed and is listed towards the end of Table 2.

Table 2
Neutron optics and magnetooptics

Wave optics:	Squeezed states, classical and quantum vibrations, localisa tion in disordered media, chaotic billard, tunnelling times, phase topography, linearity and unitarity of quantum mechanics, in-crystal coherence phenomena, diffraction on macroscopic objects.
Spin optics:	4^1 symmetry of spinors, spin superposition, neutron Joseph son effect, neutrons with "$<\sigma_z> >>1$", spin bistability, anomalous Larmor precession, dressed neutrons.
Topology:	Aharonov Casher effect, scalar Aharonov Bohm effect, Berry phases.
Gravitation:	Phase shifts, tidal forces, Coriolis force, Michelson-Morley experiments, inertial vs. gravitational mass, negative effective neutron mass.
Quantum optics:	Zero-point fluctuation effects, quantum statistics phenomena, spontaneous polarisation.
Time optics vs. space optics:	Fresnel time lens, time analogue of Fourier Spectroscopy and of spin echo, beat optics.
Devices:	Crystal resonators, neutron accelerators, spin magnetometry, NRSE, NRSE-SANS, MIEZE, FOTOF, UCN-microscopy, supermirrors.

4. Sources

For existing neutron sources, a number of interesting proposals on neutron beam tailoring like bunching, cooling, focusing and storage have been made. Further, several concepts for better ultracold neutron (UCN) sources have been developed which play a decisive role in several neutron-particle physics experiments, as well as in some neutron optics projects. These concepts includes besides the existing UCN turbine, the superthermal UCN source, the thin-film source, the frozen deuterium source, and the rotating crystal source.

A new concept of a high-flux on-line positron source based on pair creation has been developed, which promises orders of magnitude higher positron fluxes than presently available. This source is to be used in solid state physics, surface science, atomic, particle and applied physics. - Extremely monochromatic gamma and electron sources are also of interest. Also, one can extract a high intensity beam of fission products from a neutron source. Plans for the postacceleration of such a beam are under discussion. They have been described in detail in a recent proposal by the PIAFE

collaboration*. There is not the space here to describe all these proposals. Table 3 gives a list of secondary beams that can be extracted from reactor or accelerator based neutron sources.

Table 3

Particle beams from reactor or accelerator based neutron sources

Neutrons	10^{-7} to 10^{+9} eV
Gammas	extremely monochromatic
Electrons	extremely monochromatic
Positrons	very high intensity
Neutrinos	4 kinds, separated in time
Muons	2 kinds, polarised
Pions	3 kinds
Fission Products	

* "PIAFE project - physics case", in print Lecture Notes in Physics, Springer Verlag

Magnetism and superconductivity

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The group of experts agreed that it should concentrate on assessing essentially three issues:

- Identification of key topics in the future of condensed matter physics
- Identify frontier experiments, i.e., aim at exploring the unpredictable
- Identify the necessary technical improvements with respect to neutron scattering

In order to achieve a reasonable assessment of these topics that are obviously centred around basic research, the group's discussion addressed four questions stated below. One additional question was related to the possible use of neutrons by industry in view of applications of magnetism and superconductivity.

- Review of previous accomplishments mainly including the last ten years
- Perspectives of the next 10 years?
- Longer term perspectives?
- Impact of alternative experimental techniques?
- What can neutron scattering offer to industry?

The group's discussions are summarised below.

1. Introduction and review of previous accomplishments

Due to the simple cross section for the scattering of thermal neutrons, experimental data can be interpreted very easily and compared directly with quantities obtained from theory. Both the Broglie-wavelength and the energy of thermal neutrons are matched to the length and energy scales in condensed matter and, therefore, not only the statics but also the dynamics may be studied in detail.

The basis for any further consideration of a magnetic material is the knowledge of the magnetic structure. Providing this information, even in complex systems, is the fundamental contribution of neutron diffraction to magnetism. In more general terms, the direct measurement of an order parameter and the accompanying fluctuations has made neutron diffraction a uniquely informative probe of magnetic phase transitions and related critical phenomena. Indeed, because magnetic materials provide among the best realisations of simple physical models, neutron scattering experiments laid the foundations for much of our present understanding of phase transitions and co-operative phenomena in condensed matter.

To understand the observed static properties on the basis of a microscopic concept of interaction and anisotropy energies determining the Hamilton operator, a direct measure of these energies is needed. Inelastic neutron scattering is the only method to provide, on a routine basis, this information very directly through the measurement of excitations, like magnons or crystal field excitations, in a wide range of frequency and momentum space. The corresponding excitations of the lattice, the phonons and their density of states are equally accessible.

The most recent *technical advances* may be summarised as follows. For the magnetic structure determination the use of *polarised* neutrons yields a qualitative step forward in the amount of information obtainable by neutron diffraction: the 3d- polarisation analysis, as realised by the CRYOPAD at the ILL/Grenoble, yields unequivocally magnetic structures including the moment direction even for complex systems. In many technologically relevant magnets, like Fe and Co, the excitation energies range beyond 100 meV and thus can be studied only if the usual range for inelastic neutron scattering is significantly extended. This has been achieved by the *hot source* at the ILL and, in particular, at ISIS with its *spallation neutrons*. At both facilities the high energy excitations in Fe and Co have been studied and the changeover from collective to single-particle excitations has been found. As a last example for the progress in neutron *techniques*, the invention of neutron *guides* and their recent improvement by *supermirrors* must be mentioned. These guides can transport neutrons over long distances from the end of the moderator to areas, where enough space is available for the instruments and where the background is very low. Without supermirrors, the neutron guides were only effective for long wavelength neutrons. Now this procedure is possible for 1 - Å neutrons and it will increase the flux available at the end of the guide.

The following recently achieved scientific highlights will sharpen the more general comments given above. The important contribution of neutron scattering to the understanding of the **high temperature superconductors (HTSC)** ranges from the structure to the dynamics of these systems. The determination of the average structure by neutrons has not only served as a basis of all considerations about the mechanism of HTSC but has led to the production of better quality samples. The relation between superconductivity and magnetism in cuprates has been investigated and led to phase diagrams again fundamental for any explanation of HTSC. The unique possibilities of neutron scattering have enabled a detailed study of the lattice- and spin dynamics. This has yielded very important information about the electron-phonon coupling, the extraordinary large energy scale of the spin fluctuations and about the characteristics of the superconducting state via the investigation of the spin gap in the normal and the superconducting state. The observed disappearance of the flux lattice in high magnetic fields at $T << T_c$ might have important consequences for possible technological applications of the HTSC (see also Materials Science section).

Neutron scattering has been important in studies of the space- and time-dependent correlations in **correlated electron systems**. Again, the simple cross section is essential for the interpretation of neutron scattering data. Outstanding results are the proof of the importance of correlations for the spin dynamics and the antiferromagnetic character of the spin correlations. If these correlations lead to static magnetic order, neutron scattering has shown that this order is often characterised by very small ordered moments. The superconductivity present in some of these systems is of exotic character. This has been proven, e.g., by a study of the flux lattice in UPt_3.

Since many years, a classical field of neutron scattering has been the study of **model systems for statistical physics in 3 and lower dimensions (2 and 1 dimension).** Recently, the differences between classical and quantum ground states in one dimensional chains without long range order have been in the centre of neutron studies. The existence of a special disordered quantum ground state in integer-spin 1d- Heisenberg antiferromagnets has been demonstrated, in agreement with a prediction made by Haldane. The properties of the predicted Haldane gap have been verified by polarized neutron scattering experiments in $CsNiCl_3$ and NENP. In corresponding S = 1/2-systems no gap in the excitation spectrum is expected and the excitations are not single magnons as in classical systems. All these predictions have been verified in $KCuF_3$. In higher dimensions, the highly frustrated antiferromagnets in 2 dimensions have been found to be disordered, too. The spin dynamics appears to be of spin-liquid type, quite similar to the behaviour of Haldane systems. For a particularly exciting example of such a transition in $CuGeO_3$, neutron studies of the transition have helped to clarify the underlying mechanisms.

In the last few years, neutrons have also become an invaluable new tool for the investigation of very small samples. Polarised neutron reflectometry is well suited to determine the magnetic ordering and the moment direction in **thin films and magnetic multilayers**. The fact that neutrons do penetrate deeply into matter allows the study of interfaces and their influence on the magnetic behaviour, providing information very important for any technological application of multilayers.

Another exciting recent development has been that high energy neutrons are now available with sufficient flux at spallation sources like ISIS to make detailed experiments in the limit where the impulse approximation is valid. In this limit, neutrons measure the momentum distribution n(p), a quantity, which should allow to measure for example the superfluid fraction in ^4He by a determination of the amount of atoms in the n(0) state. Such experiments on **quantum liquids** have begun to yield reliable data in recent years, but no definite results for n(0) have been obtained yet.

This review of some highlights of recent neutron scattering experiment is incomplete without mentioning the experiments probing the **ordering of the nuclear spins** in Cu and Ag, fcc antiferromagnets at temperatures below 70 nK and 500 pK,

respectively. These frontier experiments, previously thought to be impossible, show that the potential of neutron scattering in conjunction with extreme conditions has, by far, not been explored to the limits. Nuclear ordering is a consequence of the weakest interactions in a solid. Its observation is one small step towards answering the question what the ultimate ground state of electronically non-magnetic metals might be.

2. Primary research topics in the next 10 years

It is needless to say that outlooks on hot topics in research over a period of 10 years must be speculative at best. Nevertheless, the present situation in magnetism and superconductivity allows for the following layout of ideas.

2.1. The beginning of a revolution: novel conductors

It is becoming clear that the peculiar "normal" state properties of the cuprate superconductors (e.g. $\rho \approx T$) are not restricted to this class of materials alone. There are now several systems (e.g., Cerium and Uranium compounds, some d-metal incipient magnets and spin density wave systems) which exhibit similar behaviour with the apparent common feature of being close to a critical point at zero temperature.

This has recently been linked with the behaviour of $\chi''(q,w)$ and its limiting behaviour as $\omega \rightarrow 0$:

$$\chi''(q,\omega) \approx \frac{\omega^{\alpha}}{q^{\beta}}$$

where $\alpha = \beta = 1$ corresponds to Fermi liquid behaviour. Because the experimentally observed exponents do not necessarily fulfill the latter requirement, these materials are termed "non-Fermi liquids". In the case of the cuprates, it is found that

$$\chi''(q,\omega) \approx \frac{\omega}{Tq^{0}}$$

so $\alpha = 1$ and $\beta = 0$. Neutrons play a significant role in uncovering both this behaviour and the nature of any new phases "nucleated" in the neighbourhood of the critical point. In the cuprates and some heavy-electron compounds, superconductivity of an unconventional nature is nucleated whereas, in some other materials, the character of the new phases has not yet been identified.

In connection with these phenomena in fermion systems, it is conceivable that "bosonic" analogues may exist in structural transitions at zero temperature: The phonons should become a "marginal" Bose liquid and the lifetime $\tau(q)$ should behave in an unusual manner.

For this type of experiments the following developments and improvements of the experimental infrastructure are essential. *New polarisation filters* will be of great help

in measuring the extended spectra to accurately measure the power laws allowing for the identification of the particular type of non-Fermi liquid.

High magnetic fields would allow to drive exotic superconductors with a relatively low upper critical field $H_{c2}(T = 0)$ into the normal state at sufficiently low temperature. This would give access to study this particular zero-temperature critical point. *High - pressure cells*, compatible with the requirements of neutron scattering would allow to probe the zero-temperature critical point in simple Peierls systems such as Iodine (unbinding of the I_2 molecules) or metal-insulator systems such as Xenon, which is believed to be a simple "band-crossing" transition.

2.2. A new frontier: the ultra-low temperature "phase diagram" of the periodic table

With the new possibility of performing neutron scattering experiments at extremely low temperatures, an as yet untackled question may be asked: What is the ground state of the pure metallic elements? How are these ground states grouped in the periodic table?

Materials at low temperatures may be magnetically ordered or have adopted a superconducting state. However, there are general arguments that, if nothing else intervenes, they either become superconducting due to the Kohn mechanism which states that even a purely repulsive interparticle interaction has attractive regions somewhere in the Brillouin Zone, or they adopt a state which is different from that of Fermi liquid. In an ideal system this may occur due to interactions with the transverse parts of the electromagnetic field - the photons.

However, it is most likely that coupling to the nuclear spins will intervene or, indeed, the pure dipolar interaction of the electrons' spins may dominate, for instance, if the nuclear spins are zero. The former may lead to nuclear magnetic ordering or to nuclear Kondo effects, perhaps with effective masses of the order of 10^5 bare electron masses, with all the complications that the latter promises.

Since it is now possible to reach 100 μK or lower for neutron scattering and so many new possibilities are opened up, the principal requirement for this type of investigations will be, of course, the quality of the samples that are being studied. Part of these experiments may safely be classified as "new frontiers" experiments.

2.3. Statistical physics: investigating magnetic model systems

In some non-conducting materials there is no magnetic ordering at low temperatures although there are magnetic moments present. This basic reason for the lack of magnetic order in insulators is either a low dimensionality of a "frustrated" lattice, or both.

In the first case, there are interesting questions as to the crossover to higher dimensional behaviour at very low temperatures. For instance, weakly coupled antiferromagnetic Heisenberg spin-1/2 chains which order three dimensionally at sufficiently low temperatures. The spin waves in such a system will look like unbound spinons on a short length scale and ordinary spin waves on a larger length scale. Hence, the form factor should be highly anomalous. Doping one-dimensional integer spin chains is already producing interesting results. Here one wishes to test whether, by analogy with the cuprates, doping all spin liquids produces a superconductor. The exploration of three-dimensional coherence at low temperatures will be interesting.

In the category of frustrated systems, the main efforts will be in trying to find low-spin, extremely frustrated lattices (like Kagome or pyrochlore) and in discovering new ground states for both the quantum and classical limits.

2.4. Major intellectual challenge: understanding the metal-insulator transition

The recent work on the cuprates has initiated a re-examination of previously known oxide systems such as V_2O_3 and also, at least implicitly, has lead to the discovery of new materials such as the giant magneto-resistance La manganates. This trend will continue in the short term in classifying the puzzling diversity of "generalised Kondo systems" which include La-Mn-O, EuS, and the Nickel/Cobalt analogues of La_2CuO_4. In the longer term, a very promising direction would be to synthesise and investigate oxide heterostructures where the dopants reside in different layers than the oxide, where the carriers would reside. This strategy to maximise the mean free path in semiconductor heterostructures has lead to the discovery of the fractional quantum Hall effect. We may therefore expect some surprises.

2.5. Quantum liquids and solids

^{3}He is considered to be the simplest Fermi liquid since there is no crystal lattice. However, there are no measurements of the discontinuity of $< n_k >$ at k_F, which would be a crucial test of the validity of the Fermi liquid theory. At low temperatures ^{3}He is the classic unconventional superfluid. Experiments that check certain detailed features of the normal state still need to be made; the same is certainly also true for the superfluid phase.

In solid Helium-4, a long-standing theoretical prediction is that impurity motion, both vacancies and ^{3}He, in ^{4}He will be coherent quantum mechanically. This would be an exciting new experimental area.

2.6. Miscellaneous

The previous five subsections describe some possible future directions in condensed matter physics that are related with magnetism and superconductivity. Other relevant areas of interest are listed below.

1. Technologically and scientifically the phenomena related with *flux lattice* or *glass* or *liquid* in extreme type II superconductors like the cuprates, are of current interest. Both the mapping of the [H,T]-phase diagram and investigations of phase boundaries in this diagram are being studied very actively with a big contribution from neutrons. Better data with higher resolutions with muons as well as neutrons are needed, however, and we may thus expect studies of the dynamics of the lattice.

2. *Driven/non-equilibrium systems*
Spatial effects are not easily visible without neutrons.
Possible experiments might be: (i) monitoring the equilibration of $T < 0$ nuclear spin systems, concentrating on the q-dependence, (ii) studies of driven spin-wave systems and "spin wave turbulence".

3. *Current fluctuations* at T_c in superconductors or at $T = 0$ in incipient superconductors, by examining the diamagnetic fluctuations.

3. Longer term perspectives of neutron scattering

In comparison with our suggestions regarding major contributions of neutron scattering to contemporary condensed matter physics, any prognosis for the longer term future is necessarily even more speculative. Nevertheless we have made a list of prototype experiments that appear as attractive possibilities and we identified the absolute need for neutrons to become a feasible *local probe* and to allow new experiments on *ultrashort time* scales. This latter requirement is dictated by general trends in basic and applied research in physics of condensed matter and chemistry and the advances that have recently been made in the use of other investigative tools, in particular synchrotron radiation and scanning microscopic methods, opening new possibilities on nanometer scales and picosecond time periods.

At the end of this subsection we list the technical requirements that seem necessary to envisage these speculative proposals.

3.1. Prototype experiments

- Measure $S(q,\omega)$ of quantum Hall states
- Verify a Wigner crystallisation in doped semiconductors, search for the state of a Fermi glass
- Study the dynamics of the flux lattice with high resolution in type II superconductors
- Spectroscopy of bound states in flux line cores
- Spectroscopy in ω and q of energy gaps of superconductors
- Mapping of the Fermi surface of new, chemically complicated materials
- Time resolved experiments probing the kinetics of phase transitions or observe the switching of magnetic domains in small systems
- Studies of lifetime effects of electronic excitations, S(q,t) in metals
- Dynamics of systems out of equilibrium in general (e.g., ferrofluids)

Needless to say, this list cannot be regarded as exhaustive.

3.2. Neutrons as a local probe

Here we see the following developments that should be continued or initiated.

• directly image a neutron beam on a small 50x50 μm^2 spot and combine it with a scanning device. This could provide a near field neutron microscope as a bulk probe.
- Use this new tool for a local imaging of magnetic structures (random field problem in antiferromagnets)
- Search for correlations between structural and magnetic defects
- Study magnetic order and corresponding excitations in small particles

• Develop the possibility of neutron scattering with phase information
- Use in studies of incommensurably modulated structures

• Develop a local imaging via NMR or ESR-type experiments as a function of frequency and space co-ordinate via scattering in large magnetic field gradients and combine with SANS for gaining information in q space
- Use as a probe for bulk inhomogeneities in chemical composition of materials with high quality requirements

3.3. Future technical requirements and developments

Essentially all these proposals require higher neutron fluxes at the location of the samples to be investigated than is commonly available at present. This may, of course, be accomplished by the construction of a new and more powerful neutron source, without which the field of neutron scattering will fail to attract the talent required to exhaust its potential We believe, however, that in parallel, more sophisticated solutions for the technical infrastructure should be sought at existing neutron sources without delay. This includes *new neutron moderators* that should and can be developed and we also see potential for further improvements in *neutron mirrors*. What is definitely needed are *high intensity* beams of *polarised* neutrons and we suggest that developments of more efficient *polarises* and *transmission filters* are encouraged and supported.

Any plan for a new source should definitely allow for *time structured neutron beams* (pulses) of high intensity. Devices for neutron *focusing* and *beam scanning* ought to get high priority in future development programs. Equally important are new *high resolution position sensitive detectors*. As an ultimate goal one might set the detection of *single* neutrons with clever SQUID arrangements. This, of course, would require an experimental environment of extremely low background, naturally also beneficial for many other applications. Parallel to these advancements in direct experimental infrastructure, more *sophisticated software* for data acquisition and analysis should be high on the agenda of future development programs. Already under the present circumstances, *more information per neutron* is probably available. In addition to all this, endeavours to adapt extreme experimental conditions like high magnetic fields,

high pressure, very low or high temperatures etc, to neutron scattering instrumentation, are required to allow the advantages of neutron scattering to be exploited in future pioneering investigations of condensed matter and physics in general.

4. The role of neutrons in magnetism and superconductivity

(Comparison with other Experimental Tools)

Studies of magnetic properties of solids require the observation of bulk properties on a macroscopic scale and the measurement of magnetic couplings and correlations at a microscopic level. The determination of the macroscopic bulk properties is important because it provides an estimation of the relevant energy scales through an averaged value of the dynamical response $\chi''(q,\omega)$ and excitation spectrum. Furthermore, such measurements can be performed easily and quickly on any sample with a very high accuracy. A first and simple comparison can be made with model calculations yielding estimates for the dynamical response of magnetic systems and magnetic contributions to thermodynamic properties such as the specific heat and magnetic susceptibility. Similarly, comparisons with some macroscopic quantities like the thermal expansion, magnetostriction and transport properties are essential. However, a complete understanding of the magnetic properties implies the experimental characterisation of $\chi''(q,\omega)$ over a wide range in q and ω. This can only be achieved through the use of microscopic probes.

We can distinguish several types of local probes for the study of microscopic properties:

- local probes (NMR, EPR, Mössbauer, X-ray absorption)
- real space probes (scanning tunneling spectroscopy, topography)
- sophisticated techniques like quantum oscillation methods (de Haas van Alphen)
- scattering techniques (neutrons, X-ray, visible light).

The neutron and X-ray scattering techniques are the only ones to cover some range in q and ω and are the probes of choice to investigate static and dynamic correlations. Visible light scattering is too limited in q space. The NMR method gives a q-averaged value of $\chi''(q,\omega)$ in the limit $\omega \approx 0$. Other methods like spin dependent X-ray absorption and magnetic X-ray dichroism are efficiently used to probe magnetic properties (electronic band structure determinations, observation of magnetic moments) but are rather restricted to thin samples.

Today, it can be said that neutron scattering is the only scattering probe that allows a full determination of $\chi''(q,\omega)$ over a range in q and ω that is of interest for magnetism in solids.

Nevertheless, the static part can now be studied using synchrotron X-ray sources (magnetic X-ray scattering, spin-dependent X-ray absorption and dichroism).

Resonant magnetic X-ray scattering and dichroism provide access to details in the electronic band structure (orbital momentum versus spin, exchange splitting, density of states at the Fermi level) that cannot be obtained from neutron experiments. Magnetic X-ray scattering is advantageous when studying small samples, surfaces or when high q-resolution is needed to analyse critical phenomena. Up to now, no real ab-initio determination of magnetic structures has been made with X-rays, however. It is fair to say that neutron diffraction (with and without polarised neutrons) will remain the probe of choice for magnetic structure determination for about 5 to 10 years. It is likely that by then, the X-ray methods will have developed to a state where they can be competitive for general magnetic structure determination. X-rays are inherently more surface sensitive and can be used to investigate micro-crystals. Certainly, these two methods (neutrons and X-rays) have to be combined to study static microscopic magnetic properties. Similarly, neutron topography is an excellent imaging method to investigate magnetic domains in bulk samples but is to be complemented with synchrotron X-ray topography. However, neutrons remain and will remain the only probe to study spin dynamics and magnetic fluctuations as a function of q and ω in the μeV to μeV range, which is of interest to the physics of magnetism. Finally, we repeat that most neutron experiments that can be performed in a wide variety of extreme conditions (very low temperature, high pressure, high magnetic fields) are, as a major advantage, easy to interpret because of the simple coupling between neutrons and magnetisation densities.

5. Industrial applications of neutrons in magnetism and superconductivity

We expect that the special subgroup evaluating the situation of Neutron Scattering and Industry has covered this topic in detail in their report and therefore we keep this sub-section short. Our proposals for the use of neutrons for industrial applications follow directly from our discussion of future technical developments mentioned above.

The industrial use of neutrons in magnetism and superconductivity has tended to deal with problems related to basic knowledge of involved mechanisms and structures, including microstructure, rather than dealing with product development and process optimisation. If more direct involvement of industry is to be developed, we believe that quick turn-around services in areas of key industrial interests need to be established.

Examples of the use of neutrons are:

- Neutron depolarisation characterisation of magnetic and superconducting films.
- Magnetic stiffness and anisotropy from measurements of spin wave excitations and the corresponding evaluation of parameters J and Æ.

- Determination of magnetically ordered structures, field induced polarisation patterns, particularly on small scales.
- Studies in view of optimisation processes for hard magnets, superconducting wires, local magnetic structures for recording devices, magnetoresistive and magnetostrictive devices etc.

Areas that could be further developed for industrial use in the near term future are real space imaging, alone and in combination with spectroscopy (neutron absorption or activation). The focus should be on real space imaging of bulk samples because synchrotron radiation is superior for applications involving surfaces.

More sophisticated experimental techniques in radiography and tomography would widen the industrial use in thin film characterisation. What is further needed are detectors, software and system set ups suited for high productivity that matches the industrial needs for cost effectiveness.

Real time resolution in millisecond or less time frames would allow on line studies of domain reversals and domain boundary dynamics both in magnetic and superconducting devices. Industrial usage could also come from the development of the near field neutron spectromicroscopy using the suggested focusing devices in combination with effective high resolution detectors. For this, high intensity primary neutron sources are indispensable. Finally we expect that also the MR-type imaging with neutrons mentioned in section 3.2. would be of interest for innovative industries.

Amorphous materials and liquids

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1. Introduction

A knowledge of atomic structure and dynamics is an important prerequisite in understanding the properties of amorphous materials and liquids for pure science. The need to determine the microscopic interactions among the constituents particles in a condensed system, and the understanding of the connection between the microscopic properties and the interaction itself, is of central importance. In particular, in the liquid state the interaction must be known at all ranges, which makes the determination more difficult. The understanding of the connection between forces, structure and dynamics in the liquid state is also important for understanding the role of these properties in the determination of the macroscopic behaviour, and of relevant questions such as the physics of the liquid-solid phase transition, of the glass transition, of supercooled liquids, and of the metal - non metal phase transition and therefore also in determining solid-state properties.

Neutron scattering has been, and will remain, one of the most important tools for these studies. In comparison with other probes and techniques (i.e. X-rays (diffraction, EXAFS and XANES, XPS,...) and electrons) neutrons have several unique properties that make it ideal for the study of amorphous materials and liquids:

- The neutron interacts with the atomic nucleous which is very small compared with thermal neutron wavelengths (~ 1Å). As a consequence the scattering is isotropic and well described using the Born approximation.
- Typical neutron scattering cross-sections are such that the penetration depth of the neutron into the material is measured in centimetres. It is therefore an ideal tool for studying materials in bulk.
- Different isotopes of the same element have different neutron scattering lengths in magnitude and sign. This means that it is frequently possible to optimise neutron scattering experiments by the use of isotopically substituted samples to produce excellent contrasts between the constituent parts of the sample, but also to determine the individual pair distribution functions by varying the isotopic composition of chemical identical samples.
- The ability of neutrons to detect light atoms, (particularly hydrogen) in the presence of heavy atoms, e.g. in a heavy-atom hydride.
- The neutron has a magnetic moment which interacts with magnetic moments in the sample. Neutrons are ideal for studying magnetic correlations in materials.
- Thermal neutrons have the appropriate energy and sufficiently large scattering cross-section to facilitate the measurement of inelastic and quasielastic scattering. This

allows phonons, magnons and diffusion to be studied in condensed matter.
• Diffraction experiments are easily normalised to absolute cross-sections (i.e. using vanadium as a reference).
• A key feature of neutron scattering techniques is their ability to probe directly the Fourier transforms of the van Hove correlation functions G(r,t).
• The range of characteristic times and lengths covered by neutron scattering overlaps extensively with those covered by computer simulations.

The fact that neutron scattering is the direct way in which we can probe the microscopic structure and dynamics, and that neutron scattering results can be compared directly with those of simulation, make neutron scattering the complementary technique that underlies macroscopic observations for amorphous materials and liquids.

2. Significant past achievements

Studies of liquids underpin an enormous range of scientific and technological areas ranging, for example, from understanding the fundamental interactions between atoms in terms of interatomic potentials, to understanding the basic interaction between molecules and ions in relation to the highly complex materials found in the earth sciences or biology. Industrial applications such as fibre-optics, amorphous silicon (in large displays), or amorphous magnetic recording tapes illustrate the importance of today's technology.

The single most important feature of the application of neutron scattering techniques to the study of liquid and amorphous solids is the large range of different kinds of topics that have been studied. These have included molecular liquids, molten salts, water and aqueous solutions, glasses, condensed gases, collective and individual motions in simple liquids and alloys, mixtures (noble gas, alloys, composite systems), modelisation and simulation, quantum liquids, amorphous metals, liquid and amorphous semiconductors, molten semiconductors, liquid interfaces, quasicrystals, clusters and colloids (as model systems), porous media, sol-gels, polymers, fast ion conductors, new ceramics.

Whereas neutron scattering is acknowledged to have made distinctive contributions to the study of every type of material or scientific field listed above, it is nevertheless possible to identify and highlight some cases for which the contributions of neutron scattering studies have been fundamental.

2.1. The determination of the precise form of the microscopic interaction

among the elementary constituents of a condensed liquid phase is of basic interest for the understanding of the microscopic static and dynamical properties of these systems. Neutrons give the possibility of measuring quantities which are directly connected to the space-time microscopic distribution, i.e. the dynamic structure factor $S(Q,\omega)$ and its moments, in particular the zeroth frequency moment S(Q).

In the case of S(Q) precise measurements are needed in order to connect the structure factor with the details of microscopic interaction because approximately 80% of the significant part of the S(Q) is due to the excluded volume effect , i.e. are well reproduced by only considering hard-spheres interaction potential models. Therefore only approximately 20% of the measured quantity is related to the intermediate and long-range portion of the microscopic interaction, which is relevant to determine the properties in the liquid and dense phase properties. Recently, precise experiments and calculations on classical systems like argon and krypton have elucidated the role of the pair microscopic interaction in these systems. From this point of view also simple quantum systems like D_2 have been studied, and comparison between experiments and quantum mechanical path integral Monte-Carlo calculations have shown classical behaviour. This illustrates that only a few % may be attributed to many body interactions, which at present are unknown. S(Q) is therefore a sensitive measure of the microscopic interaction in dense fluids; however, higher precision measurements must be pushed; the order of 0.5% must be achieved.

Recently, new studies of the $S(Q,\omega)$ in simple fluids have been performed at small angles allowing a measure of the properties of dilute and dense gases in the small Q-region for the first time by means of new instrumentation. This gives the possibility of studying in more details a new (Q,ω) region with a more direct link to the microscopic properties, particularly the role of the microscopic interaction in determining the dynamic and transport properties in a simple model system.

2.2. The study of static and dynamic structures of various kind of liquids

For liquid metals, liquid semiconductors and glasses, the availability of high-quality neutron-scattering data has been a stimulus for theoretical calculations. These have included ab-initio calculations of liquid structure and more recently the Car-Parinello method has been applied to calculate the structures of a range of liquids.

Extensive experimentation has also led both to the validation of theoretical approaches, singling out the universal features of the transitions to glassy states, and to the unravelling of the microscopic details of the low-energy spectrum of these systems in a significant number of cases.

2.3. The study of aqueous solutions has steadily developed from the original work on simple ions in solution (although there are many questions still to be resolved here) to systems of interest to physicists, chemists, biologists and geologists. The technique of isotopic substitution remains the key to these studies as it allows the structure around specific atomic sites in the liquid to be probed directly without recourse to models. Some examples include ionic co-ordination in polyelectrolytes (of significance in new materials for batteries), water conformation around hydrophobic molecules and DNA in solution (both of biological importance).

2.4. The study of liquid helium 3 and 4 is also an exciting and high-quality field where a significant series of recent experiments is that on (normal) liquid helium-3. The reasons for this are twofold. First, liquid ^{3}He is the only readily accessible Fermi liquid; experiments on stellar matter is rather difficult, whereas the electrons in a metal are much affected by the periodic potential of the ionic cores. Second, the immense absorption cross-section for thermal neutrons (of order 10,000 barns) makes these measurements an experimental tour-de-force. Nevertheless, detailed information is now available on the elementary excitation spectrum of liquid ^{3}He (spin fluctuations, zero-sound collective mode, quasiparticle-quasihole continuum) at saturated vapour pressure, under applied pressures up to 20 bars, and when diluted with ^{4}He atoms. This was truly an international effort with experiments at ANL and ILL carried out by scientists from France, Germany, Sweden, UK, USA.

Another significant experiment is to observe a direct "signature" of Bose-condensation in superfluid ^{4}He at large momentum transfer Q. Final-state effects, combined with the unavoidable impact of instrumental resolution, make it impossible to see a clear Bose-Einstein "spike", superimposed on the normal fluid scattering.

However, theoretical advances allow a deconvolution of the experimentally observed S(Q) at large Q into its constituent parts. New elegant systematic experiments have shown the power of these analytical techniques applied to excellent new data of high precision. It is now accepted that there is a Bose-condensate in pure ^{4}He with a value of about 9% (+/-1%) at low temperatures (<<1K). This is an important result for condensed matter physics and is indeed a triumph for neutron inelastic scattering.

As a conclusion we have to note **the close interplay between neutron diffraction experiments and theories for the structures of liquids**. This has been a long-established feature of the important Liquid and Amorphous Solids series of International Conference and **traditionally a field where European scientists have played a major role.**

3. Contribution of other techniques

Many experimental techniques contribute to the study of liquids and amorphous materials. Notable among these are very high-precision specific-heat measurements, torsional oscillator measurements, light scattering, x-ray diffraction studies of S(Q), thermal conductivity and other transport properties, quantum evaporation and NMR. All of these contribute to particular aspects, but neutron scattering addresses the underlying structures and elementary excitations. There is no reason why the current situation should change, in which different techniques support and complement each other.

A good example of complementarity can be done with the emergence of inelastic scattering of X-rays. Once it is widely available (or at least to the same degree as

neutron inelastic scattering!) it will open a new horizon in which small molecular systems, for example, will be contemplated experimentally through the response of the nuclei (via neutron scattering) and through that of the electrons (via photon scattering). In small molecular systems, it is tempting to envisage, for example, challenging experiments on the breakdown of the Born-Oppenheimer approximation.

Nevertheless, neutron scattering will continue to be a technique of central importance, especially as new and refined techniques (much finer instrumental resolution, sophisticated polarisation methods) become available.

4. Future scientific prospects for liquid and amorphous materials

Four kinds of improvements in the current provisions for neutron scattering experiments, have been identified by the Group as being both desirable and feasible with relatively modest injections of funds over the next 10 years. These improvements can be made at the existing neutron facilities and in many cases will involve extensions of programmes of improvement which are already underway. They are :

4.1) the continued need for neutron data of better statistical accuracy
4.2) the extension of neutron scattering experiments to more complex liquid and amorphous systems,
4.3) the study of small samples and small volume elements,
4.4) the development of neutron experiments with more complex geometry and sample environment.

The division between these headings is somewhat arbitrary and there is correspondingly some degree of overlap.

4.1. The need for neutron data of better accuracy

The search for neutron data of better quality has been the driving force in the subject since its earliest days. The quality of neutron data determines the confidence with which comparisons can be made between experiment and theory. The quality and extent of the neutron data also influences the progress of theoretical advances. The need for neutron data of better statistical quality is felt most strongly in the following areas :

- Precise measurements of S(Q) leading to the interatomic pair potentials $\phi(r)$.
- Statics and dynamics of quantum fluids.
- Systems composed of small molecules.
- MD calculations on 10,000 atom arrays also, ab-initio calculations of liquid structures by parallel computing methods and the combination of diffraction, RMC and MD.

4.2. The extension of neutron scattering experiments to more complex systems of liquid and amorphous materials

Neutron data of better statistical quality is obtained by having higher neutron count rates and lower background levels. Such improvements can lead to measurements of better quality on simple systems but they also extend the range of more complex systems which can be effectively addressed by neutron experiments. These include:

- Hydrogen containing materials e.g. metallic (batteries) and biological (membranes)
- Heavy ions in water, contact with Earth Sciences group.
- Multi-component fast ion conductors.
- Multi-component glasses and metallic glasses
- Complex fluids.

4.3. Small samples and small volume elements

The traditional need for large samples in neutron scattering, (at least in comparison with X-ray and electron diffraction techniques) has always been seen to be a disadvantage of neutron methods. However the use of focussing monochromators and efficient multidetector arrays has meant that this perceived problem has been greatly reduced in recent years. This is particularly true in small-angle-scattering and in reflectometry, where milligram samples can now be measured routinely. There is a need to extend this advantage to the following fields:

- Structures and dynamics of liquids and glasses in restricted media.
- Composite crystalline and amorphous systems
- Solid state amorphisation in the regime of small volume fractions.

4.4. More complex sample environment

As discussed above, the low absorption of neutrons by matter expedites the development of complex sample environment. This has led to the growth of real time in-situ neutron experiments and there is considerable scope for development in the future. Measurements will be made of the changes produced by external agencies including stress, electric and magnetic fields and optical stimulation. In the case of pulsed neutron scattering, there is an additional advantage, because these can be applied to the sample in phase with the neutron pulses. Chemical reactions can also be studied as they take place, by exposure of the samples to the appropriate liquid and gaseous reactants, exploiting the advantages of neutron scattering methods summarised above.

At present, experiments involving chemical reactions are often limited by the time scales of the reactions (within available temperature ranges) in comparison with the characteristic times for data acquisition on existing neutron instruments. The advent of the “next generation” neutron sources will therefore significantly increase the

range and scope of these real-time experiments which can be undertaken. In future many more scientific, technological and industrial processes will be studied by in-situ neutron experiments. Some examples can be given:

- Study of binary alloys, multicomponent systems or molecular systems as a function of extended regimes of pressure, temperature, magnetic and electric field.
- Polarisation analysis for the study of magnetism.
- Polarisation analysis for the separation of the coherent and incoherent scattering cross-sections.
- Structural studies of anisotropy in planar samples.
- Glass transition and laser melting.

5. Prospects for neutron scattering techniques on liquid and amorphous materials

Sections 2 and 4 above have illustrated that neutron scattering has contributed, and will contribute, substantially to the study of an exceptionally wide range of amorphous and liquid materials. There is every indication that this process will continue both in the short and longer terms. There is a large and experienced user community in Europe, in the field of liquid and amorphous materials, including world leading groups in many of the specialist areas.

The first requirement for the future health of this field of study is the access to neutron instruments which can be optimised for the study of liquid and amorphous materials. Note that this does not necessarily imply that all of these neutron instruments should be devoted exclusively to the study of liquid and amorphous materials, but that they should be capable of being optimised for this purpose.

The unique feature of the experiments on liquid and amorphous materials is that they normally involve an absolute measurement of intensity, rather than of relative intensities. This determines what constitutes an optimised instrument for the measurement of liquid and amorphous materials. The existing neutron instruments for the study of liquid and amorphous samples must therefore incorporate in the near future the appropriate features as listed below:

- higher neutron flux on the sample
- a low level of background scattering at small values of scattering vector Q
- low background scattering levels generally, in order that complex equipment for extreme sample environment can be used effectively, e.g. high temperature, high stability furnaces which may have sophisticated systems of internal heat shields, high pressure, high electric fields...
- high temporal stability for experiments with long counting times in which small differences in scattering from different samples are measured, e.g. as in isotopic substitution.

• the development of multidetectors and position-sensitive detectors to permit individual measurements of great precision to be made on few samples or alternatively series of shorter, but statistically reliable, measurements as function of sample composition, temperature, pressure or applied field.
• simultaneous development of data acquisition electronics and programs for data analysis to keep pace with the expected improvements in instrument design.

The group has then identified the following areas in neutron scattering, as being sufficiently important to be the focus of development: both in the short and long-term beyond 2005.

5.1. The continued development of polarisation analysis for both steady-state and pulsed neutron sources to alleviate the current poor provision of polarised neutron beams for the study of liquid and amorphous solids.

5.2. The application of neutron spin-echo as a small-angle neutron scattering instrument (using DC magnetic field) leads to the measurement of the real-space correlation function for systems with large correlation lengths, and may enable one to measure time-dependent effects in correlation lengths with a time resolution of a few seconds.

5.3. Neutron Brillouin scattering: at low Q the maximum energy transfer is limited by the incident neutron velocity. If this velocity is lower than that of certain excitations in the material (i.e. the sound velocity), then important information is missed. Typically this missing information falls in a region where the behaviour is intermediate between that described by local microscopic theories and that described by macroscopic continuum theories (i.e. hydrodynamics). Our understanding of this region is poor. It is not well probed by other experimental techniques and is currently at the limit of what can be achieved with computer simulations. Neutron Brillouin scattering will provide complementary information to that available from light-scattering methods.

5.4. Neutron reflectometry, focussing optics, high intensity, large Q range: great progress has been made recently in the study of liquid metal surfaces by X-ray reflectometry at synchrotron sources. Neutron reflectometry offers considerable advantages in the study of surface segregation in liquid metal alloys, but the range of scattering vectors which can be covered with existing instruments is too small for the neutron method to be competitive with X-ray measurements. It will be necessary to develop high-intensity neutron reflectometers with focusing optics, or instruments for simultaneous X-ray and neutron measurements for this work, and these will have application in many areas of study of thin-film samples.

5.5. Mesoscopic physics, large structures, slow dynamics: the study of clusters is identified as a growth area in the scientific plans of many of the EC partners, and represents a link between the study of liquid, amorphous and nanocrystalline materials, as well as the one with molecular physics. Special high-flux neutron instruments will be needed to study the structures and properties of free clusters in beams. The ability to make "neutron invisible" substrates will be exploited in the study of deposited clusters, where the total sample volume will be significantly below the present practical minimum levels.

6. Industrial perspectives

The following list of topics in the field of liquid and amorphous materials were discussed by the group as being of potential industrial interest

- optical fibres doping, coating
- thin film sensors, non-linear optics
- ionic conductors
- amorphous semiconductors
- polymer electrolytes, rubber electrolytes for batteries
- metallic glasses
- ultra easy glass formers - superplastic materials aerospace applications
- hydrogen absorbers, batteries
- metallic glasses as precursors of nano-crystalline materials, hard and soft magnetic materials
- in-situ studies of processing in ceramics, mixed crystalline/amorphous systems
- SiN for coatings
- amorphisation of crystalline materials under heavy doses of radiation
- studies of stability and leaching in glasses for storage of radioactive materials
- replacement of hostile liquids, CFC replacement
- neutron radiography, transport of liquids inside porous media.

7. Conclusion

The group has highlighted several areas of the science of liquids and amorphous materials.

The main problem for us is to determine the microscopic interaction among the constituent particles in a condensed system, and the understanding of the connection between the microscopic properties and the interaction itself. Usually this requires investigations over a wider range of parameters than is common at present, including extreme conditions. The information will be obtained from the derivatives of S(Q) and S(Q,ω) with respect to these parameters (concentration, temperature, volume and pressure, electric field, magnetic field.)

This demand for information, produced by this trend towards complexity in the amorphous materials and liquids field, will not be met by any single experimental technique, but

neutron scattering will be an INDISPENSIBLE PART of a series of complementary techniques and in certain cases could be THE most appropriate technique.
This requirement has to be satisfied by :
• more, or improved, instrumentation on existing sources (in the future up to 2005)
• new, more intense neutron sources with specially optimised instrumentations (beyond 2005).

Polymers and soft matter

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General Overview

Soft matter encompasses a very large class of molecular materials such as polymers, thermotropic liquid crystals, micellar solutions and lyotropic mesophases of amphiphilic molecules microemulsions and colloidal suspensions. As materials or complex fluids they have wide applications related to macroscopic properties such as viscoelasticity, surface tension ... which control many practical phenomena such as rubber elasticity, detergency, adhesion or lubrication.

In trying to relate these macroscopic properties to the chemical and microscopic structure, it has become progressively clear that these various systems share a number of underlying similarities such as a large number of degrees of freedom, weak interactions between structural units, delicate balance of enthalpy and entropy, large thermal fluctuations, macroscopic softness, sensitivity of the phase diagrams to external constraints.

Static and dynamic neutron scattering have been key techniques in studying these basic properties and revealing in model systems some of their universal structures and scaling laws. The unique role of neutron elastic or dynamic structure factor results not only from the adequacy of the momentum and energy transfer to the characteristic lengths of these systems and to the characteristic time of their fluctuations but also, and often mainly, from the manipulation of the contrast by specific deuteration of one component, a fraction of one component or a part of one molecule. This unique feature which permits to distinguish one molecule or one component among the others, through the determination of partial structure factors , has no equivalent in other techniques for organic systems containing no heavy element. This will appear more and more as a specific advantage, considering that the optimisation of the systems for practical use is not only related to the fine tuning of the chemical structure of one component but also to an increasing number of components including additives in their formulation. Ultimately there is a need for analysing the systems under mechanical and thermal constraints close to that of actual processing conditions.

Even in the few simple systems where the contrast is sufficient for X-rays to compete (polymer solutions, periodic structures) neutrons keep the decisive advantage of negligible multiple scattering, and simplicity of absolute intensities determination. In experiments under constraint, the high penetration allows the use of complicated cell geometries.

While the principle of deuterium labelling opens the way to a parallel use of deuterium quadrupolar NMR for selective dynamical measurements, it only provides information on local motions analogous to incoherent scattering, whereas the large scale motions require the time space correlation of coherent scattering. The specific role of neutrons in the present and future studies on polymers and soft matter is detailed below for characteristic systems and situations.

Polymers

Conformations and interactions: Small Angle Neutron Scattering (SANS) has been the basis of the verification of the validity of the universal scaling law approach to polymer solutions from dilute to concentrated. It remains the privileged method of characterisation of the dependence of the characteristic length scales with the chemical variability. The interplay of electrostatic interactions and conformations in salt free solutions of flexible polyelectrolytes remains poorly understood and needs careful separation of the different partial structure factors.

Molecular rheology deals with the microscopic understanding of viscoelastic properties in term of a distribution of q dependent relaxation times in the linear viscoelastic regime as well as chain deformation in the non newtonian regime. Among recent successes is the observation of reptation from spin echo experiments (1, below)

1. Neutron spin echo and reptation

One of the basic problems in the dynamics of soft matter concerns the importance of geometrical or topological interactions which are directly related to the large scale molecular and supra molecular structures. In polymer dynamics e.g. they manifest themselves as “entanglements”, while in the case of amphiphilic structures they show as large scale fluctuations induced steric interactions. In this respect one of the recent large successes concerning the dynamics of dense polymer systems was the microscopic observation of topological constraints in polymer melts and concentrated solutions by neutron spin echo (NSE) spectroscopy.

Depending on the time scale of observation, the dynamics of polymer melts is governed either by elastic behaviour or viscous flow. This viscoelasticity relates to the topological constraints which are imposed by the mutually interpenetrating chains. In the famous reptation model these entanglement constraints are pictured in terms of a tube of localisation following the averaged chain profile and confining the chain motion to the curve linear tube. Studying the dynamic structure factor of a single labelled chain in a polymer melt by means of NSE recently, it became possible to observe directly these tube constraints : They cause the time dependent dynamic structure factor not to decay continuously but after an initial fast decay, corresponding to wiggling

motion in the tube, to exhibit a temporal plateau signifying the spatial limits of motion. From the dependence of this relaxational arrest on the momentum transfer the distance between entanglements can be directly deduced. These distances observed on a molecular scale agree very well with those tube diameters derived from dynamical mechanical measurements on the basis of the reptation model, proving thereby the basic assumption of this Nobel-Prize winning model.

Now that the first observations of such topological interactions on a molecular level in polymer melts have been made, the route is open to microscopical clarification of the molecular nature of an entanglement as well as to an exploration of its impact on rubber elasticity.

and of non affine deformation of chain in stretched elastomeric networks (2, below).

2. Chain labeling and rubber elasticity

Similar to staining in microscopy hydrogen-deuterium exchange provides the unique possibility on a molecular level to label and to observe a single chain molecule among equals. More than 20 years ago, by this technique a neutron small angle scattering experiment proved the Gaussian coil structure of long chain polymers in the melt and the amorphous state. After this basic and decisive experiment which chose among many different theoretical approaches, and in particular showed that the idea of screened excluded volume interaction in the melt was correct, this technique nowadays is routinely employed to obtain information on chain conformations in dense systems often under the influence of external fields like e.g. in fibres during spinning, in strained elastomers or in polymer systems under shear.

The experiments on labelled chains in an elastomer matrix aim at a molecular understanding of rubber elasticity. They facilitate the detailed observation of the microscopic deformation of network chains under external strain. Recently the effect of topological constraints, which give rise to the viscoelasticity in melts, on rubber elasticity have been addressed. Scattering curves parallel and perpendicular to the elongation contain in a subtle way the microscopic degree the affinity of deformation and in this way also information on the presence of topological constraints. It turns out that those constraints are deformed subaffinely following a square root power law of the microscopic strain.

Neutron scattering offers a molecular view of the deformation processes in networks which are important for the design of new materials. On the other hand, the discovered correlation of topological hindrance and deformability of rubbers is also a highlight of basic research bringing forward a better understanding of elasticity.

Of more conceptual and practical importance is the deformation and relaxation of polymer melts in elongational flows close to processing conditions in non linear regimes. It is now observed in quenched partially relaxed systems but should be observed in real time experiments (3, below).

3. The response of polymer melts and suspensions to shear and stress

The microscopic response of macromolecular materials and suspensions to external fields like stress and shear is presently only poorly understood. This situation exists, despite the fact that polymeric materials are typically exposed to both major stress and shear during the manufacturing processes and when used in the final product.

Macroscopic information establishes that both mechanical and optical properties of polymeric materials are critically sensitive to such fields. By experience, various methods have been introduced in manufacturing, including, for example, oscillatory pressures in injection moulding. It is also well known, and widely utilised, that the properties are improved by specific control of the orientation of the polymer chains and many products use highly oriented polymers for improved performance.

Shear and stresses may influence both the macromolecular conformation, the molecular crystallinity and the compatibility in polymers. The latter may relate to both different polymers within a blend, or to compatibility between amorphous and crystalline domains within the same polymer. It is also known from studies on model systems, that both shear and uniaxial stress may align crystalline mesophases into a mono-domain material with major changes in the rheological properties. The crystallinity is highly dependent on molecular alignment, which may be induced by uniaxial stress. The impact of such properties on commercial products is, however, still unexplored.

In the coming years we foresee that there will be great demand for scattering experiments in situ with for example shear, stress or pressure. This includes both studies of model systems with well defined sample and sample environment like simple shear obtained either in an oscillatory mode between two parallel plates, or in Couette cells. But also in-situ studies while the polymer is flowing through extruders and other tools used in industry probably will be needed in the future and might have significant impact on the manufacturing process.

Blending becomes a standard strategy of tuning properties, comparable to alloying in metal. The control of the phase dispersion through added block copolymers, the influence of shear on phase decomposition are presently under study with neutrons. Particularly interesting would be the possibility to observe the competition between spinodal decomposition and interfacial reactions to stabilise the morphology for further processing. The new techniques of living radical polymerisation should give

multiblock copolymers of industrial importance and call for study of their microheterogeneity at rest and under shear.

Polymeric glasses : Many of the structural polymers are used in the glassy state. Ageing is critically related to secondary relaxations whose features in polymer have still to be seriously compared to ordinary supercooled liquids (4, below).

4. Secondary relaxation processes in polymers

Besides the main segmental relaxation (a-relaxation) which is directly related to the glass-transition, polymers show additional relaxations on various faster times scales, which are called secondary relaxation processes. These processes are mainly observed at temperatures that are below the glass-transition (sub-glass region) where general segmental motions (a-relaxation) are frozen out. There are two general characteristics of the dynamics of all sub-glass secondary relaxations. The first is the Arrhenius temperature dependence of the dominant or central relaxation time. The second is that such processes are extremely broad in time/frequency domain, likely to involve a wide distribution of relaxation times. The first, and usually most prominent, secondary relaxation process is known as b relaxation (it is now often referred to as the Johary and Goldstein-b-relaxation) and appears to be present in all kind of glass forming systems, i.e., being an universal feature of the glassy state.

From a practical point of view, secondary relaxation is of utmost importance because it determines the mechanical properties of glassy polymers of technological interest like engineering thermoplastics and related materials. One typical example is the well known ductibility of polycarbonate, which is directly related to the rich dynamics displayed by such a polymer in the sub-glass solid region.

The secondary relaxation processes in polymers have been investigated for more than 40 years by relaxation techniques like dielectric or mechanical spectroscopy. However, the nature of the molecular motions involved in such processes remains obscure. An important piece of information missing is the geometry of the molecular rearrangements. This information can only be obtained by quasielastic neutron scattering, which observes atomic motions in their natural length and time scales. Recently, in a pioneering neutron spin echo experiment, it became possible to investigate the dynamic structure factor resulting from the secondary relaxations in 1.4 polybutadiene and thus shedding some light on the conformational changes underlying the β-relaxation process. This experiment has now opened the way for more systematic studies of secondary relaxation processes in other polymers with the opportunity for unravelling the molecular motion on which mechanical processes such as ductibility of polymeric solids are based.

Self assembling Systems and surfactants

The soap like water-surfactant phase diagrams, from micellar solutions to lyotropic mesophases, were first described by X-ray scattering. Neutrons have been unique in unravelling the internal structure of micelles, or the complicated arrangement of water and bilayers in bicontinuous mesophases.

Among the forces which stabilise the lamellar phases, correlated undulations are assumed to play a role. The dynamics of these fluctuations have been studied by measuring the coherent dynamic structure factor, which can be observed in the presence of polymers in the water separating the bilayers.

The domain of existence of microemulsions and inverse microemulsions in the brine, oil, surfactant system is of major importance in secondary oil recovery. The contrast variation method has been unique in analysing the zone of inversion in model system (5, below).

5. Curvature inversion in microemulsions

Microemulsions are dispersions of two immiscible liquids-water and oil-thermodynamically stabilised by an interfacial film of amphiphilic molecules-surfactant and cosurfactant. Most commonly they are made of spherical droplets of one liquid dispersed in the other. However, in certain phase diagrams, oil in water and water in oil droplets can be observed at the two extremes of the concentration range with a continuous transition from one situation to the other, which implies a change of the topology of the dispersion.

The evolution of the organisation of the film in the intermediate zone was the matter of many conjectures and neutron scattering studies, applying the contrast variation method, provided a decisive element for its description by showing that the mean curvature of the film changes its sign midway between the two dilute zones.

The basic physical argument is that a local fluctuation of the volume fraction of one liquid implies a local fluctuation of the volume fraction of film proportional to the curvature of the film, as the curvature of a surface corresponds to a gradient of area for parallel surfaces.

Thus the two volume fraction fluctuations are correlated in a manner proportional to the curvature and the determination of the cross-structure factor at vanishing scattering vector, which cannot be measured directly, but must be extracted from a series of contrast variation experiments, gives access to it.

This is an unambiguous indication that the curvature of the film vanishes on average for equal volume fractions of water and oil in microemulsions. This supports the model of random minimal surfaces to describe the organisation of the film in the intermediate zone.

Introduction of reactive components in the organised water surfactant structures and inverse microemulsions leads to methods of production of new materials :
polymerisation or synthesis of inorganic nanocrystals in inverse microemulsions, formation of porous inorganic materials by carrying sol gel reactions in bicontinuous phases. The location of the reactants that control both the reactivity and the stability during the reaction can be carried out through selective deuteration.

Associating polymers are growing in importance as thickeners, particularly in the paint industry. Their associative and rheological properties are very dependent upon the size and placement of hydrophobic sequences in the normally water soluble chains. Using again the variable contrast in H_2O-D_2O mixtures, the size and structure of the hydrophobic domains, in the presence or absence of added surfactants, at rest and under shear, will be the basis for understanding their widely different rheological properties that underpin their applications.

Colloids and interfaces

Stabilisation and flocculation of colloids and particles in suspension by addition of polymers and/or surfactants is a practical process. The scattering from the adsorbed layer can be separated by phase contrast. Its thickness and concentration profile can be measured in a unique way for layer thickness', which are not negligible with respect to the particle size, by SANS.

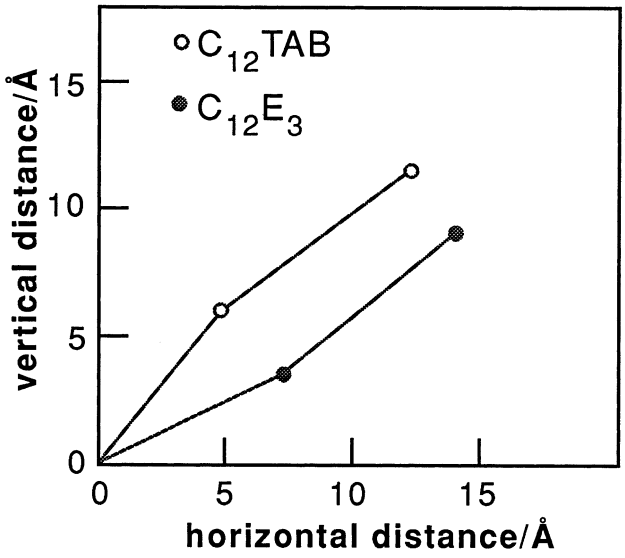
The characterisation of thin layers, as well as more subtle details such as the distribution of chain ends, is more easily carried out when working on layers adsorbed or grafted on flat interfaces by neutron reflectometry. Specular reflection provides the density profile, off-specular reflection gives information on the disorder, and hopefully with increasing fluxes the dynamics, in the layer. Two examples are given in items 6 and 7. Other situations for future investigations are the process of polymer-polymer interdiffusion and additive diffusion during the formation of adhesive interlayers, and the modification of a surface layer under a liquid flow, in relation to lubrication processes (6 and 7, below).

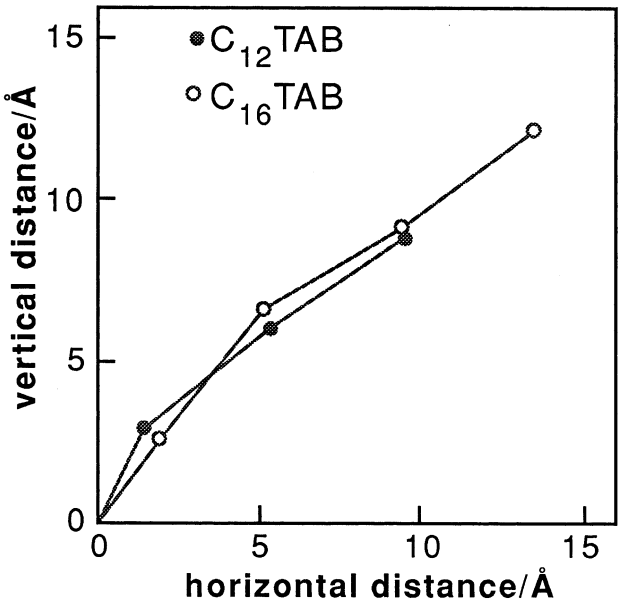
6. Neutron Reflection from the Air Water Interface

Neutron specular reflection probes the structure of an interface along the direction normal to the interface. By the use of isotopic labelling with deuterium the technique can be made specific to a layer of adsorbed material or to fragments of such a layer, which makes it uniquely powerful for the determination of structure at wet interfaces. The two diagrams show examples of the determination of the chain conformation of soluble surfactants adsorbed at the air/water interface. The upper diagram compares the chain conformation of a twelve atom carbon chain attached to different head groups. In both cases the chain is strongly tilted away from the surface normal,

but for the one with the ethylene glycol head group the tilt is much greater. The lower diagram compares the conformation of two chains of different length but with the same head group and shows that the shorter chain behaves similarly to the equivalent part of the longer chain. In both examples the chains are not on average fully extended. No other experimental technique is yet able to give structural information about soluble surfactant layers at this resolution.

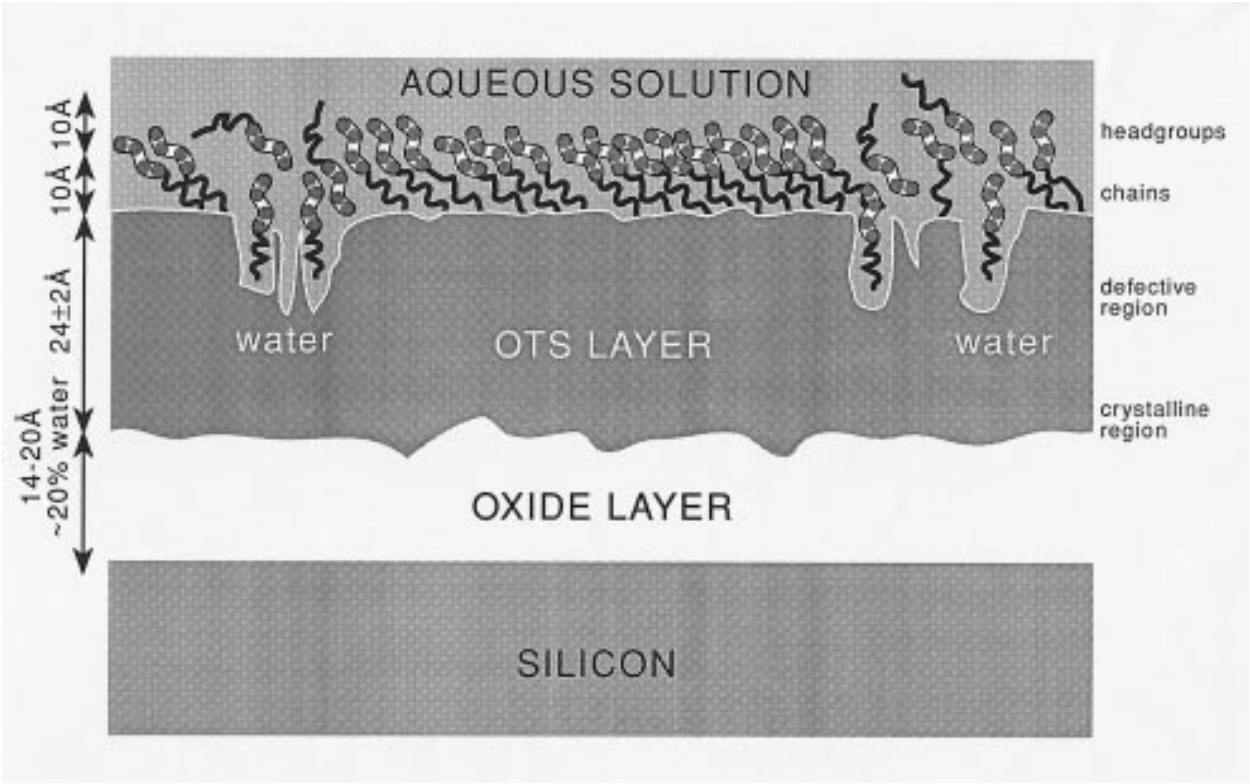
Chain conformation: 3 (Alkyl chains)





7. Structure of complex interfaces

The use of isotopic abelling makes it possible for neutrons to probe surfaces of complex composition and structure. Each part of the surface may be examined separately by judicious labelling and, more importantly, the distance along the normal direction between labelled fragments can be measured directly from the cross interference. The diagram also illustrates that, because of the transparency of many crystalline solids to neutrons, neutron reflection may be used to probe the structure of buried interfaces. In the structure shown neutron reflection has been able to determine the thickness and composition of each of the layers comprising the silicon/aqueous solution interface ; the neutral oxide layer, a self-assembled hydrophobic monolayer (OTS), and the heads and chains of an adsorbed surfactant layer. The structure shown demonstrates what is already possible with the technique but there is considerable scope for extending such studies to the types of complex interface that occurs in many technological systems.



It is clear that in situations with complex molecular conformations, interactions between the constituents and with the surfaces compete to control the final macroscopic properties. This is the case for the flow of complex fluids in porous media (8, below).

8. Porous media

Complex fluids are multicomponent liquids or macromolecular solutions characterised by length scales that span the atomic and macroscopic (roughly 1-10^4 nm) ranges. Typical examples of complex fluids include polymer and colloidal solutions and liquids containing self-assembling components such as surfactants or diblock copolymers. One of the most exciting specific challenges is in the study of such complex fluids in porous (complex) media.

It is known that many of the most important industrial products are connected with porous materials, with the behaviour of contained fluid being a critical feature. So it is with oil-bearing rock, water-saturated soils, separation materials, heterogeneous chemical materials such as silicas and zeolites, as well as an enormous range of foodstuffs, cleaning powders and pastes, building materials and even cosmetics. The confinement in, and/or movement through, a network of interfaces having length scales comparable to that of the complex fluid, has profound effects on the thermodynamics and phase behaviour, dynamics, and transport properties of constrained complex fluid. The alteration of such properties therefore can greatly modify the industrial methodology needed to perform or control tasks, ranging from enhanced oil recovery within oil baring rocks and shales to the penetration of cosmetic oils through lipophilic layers of epidermal tissue. The unique ability of neutrons to contrast match the scattering length densities of passive solid matrices to that of the liquids filling the pores allows the study of the behaviour of specific components of the complex fluid in the porous medium.

The need to predict the phase behaviour, kinetics and rheological properties of mixtures of surfactant/oil, polymer/surfactants ; polymer/protein and protein surfactants in microenvironments must become a reality, if effective control of the desired industrial need is to be fulfilled.

Whereas the science of determining macroscopic structure is well developed, many of the chemically-important structural rearrangements occur over distances from 10-100 Å. SANS is one of the few techniques capable of yielding information on this length scale and has the advantage of being able to do so in-situ.

Industrial applications

It is clear that the physics of polymers and soft matter is directly connected and very often inspired by the understanding and optimisation of industrial applications. Industry will benefit not only from the conceptual developments arising from the study of simple model systems, but also from the study of actual complex situations and processes, ultimately in the conditions of industrial processing. The study of complex multicomponent systems with additives, i.e. a "formulated" product should be carried out in parallel with numerical simulations of the thermodynamics and dynamics of these systems.

Technical improvements

Among the required technical improvements in neutron scattering, the most important deal with

- polarisation analysis for separation of coherent and incoherent scattering
- decreasing Q_{min} available in SANS by another order of magnitude, giving access to structures in the order of several hundred to several thousands nanometers
- synchronisation of time acquisition with application of a controlled sinusoidal or pulsed external field, allowing measurement of the amplitude and phase of the response or kinetic studies
- ultra high resolution spin-echo methods like zero-field neutron spin echo with bootstrapping and traditional NSE with highly collimated beams
- the combination, in a time of flight instrument of the intensity of the time focusing IN6 instrument at ILL with the clean resolution and signal to noise ratio of a multichopper machine like IN5
- focusing of the neutron beam, particularly for surface analysis
- inelastic or quasielastic experiments in the domain of specular or off-specular reflectometry.

Most of these developments will require higher flux, and some are well suited to a spallation source. The required effort on instrumentation should not only be launched for future sources, but also as a continuous contribution to the improvement of existing facilities.

Future directions of research

The main question to be addressed, with the progressive implementation of the technical improvements, deals with the mesoscopic structure of multicomponent - multiphase systems, with a general emphasis on interfacial layers. At our present level of understanding and modelisation, the prediction of phase separation and phase dispersion relies on integrated thermodynamic quantities such as bulk cohesive energies and interfacial tension of the pure constituents. At the mesoscopic scale, it

becomes necessary to use direct intermolecular forces. Static and dynamic neutron scattering will be unique in providing the reciprocal space imaging of composition distributions to compare to numerical simulations for the development of efficient algorithms. There is then also the hope to understand the pathways for phase transformation under external changes such as temperature, pressure, shear or external fields for systems which very often do not go to a complete new thermodynamic equilibrium, but remain in metastable states. Examples are in processed multiphasic polymer blends, adhesive layers, artificially deposited multilayers, membranes.

Biology

T.M. Bayerl, G. Büldt, S. Cusack, E. Sackmann, J. Smith, P. Timmins, G. Zaccai

The uniqueness of biology among the sciences represented at this workshop consists of the fact that much of its interest lies in diversity. That is to say differences between the functional mechanisms of different biological systems are as intriguing as similarities. Therefore, one can broadly classify biophysical experiments with neutrons into two types. The first is experiments aimed at understanding **general principles** of the physical chemistry of macromolecules. Examples of this would be the interplay between the different factors responsible for folding a protein into its functional native state or the general characteristics of forces and internal motions in macromolecules or macromolecular assemblies such as model membranes. The second type is experiments with the aim of understanding the mode of functioning of **specific** biological systems. Examples would be the light-driven proton pump protein, bacteriorhodopsin, atomic descriptions of the catalytic mechanism of particular enzymes or the mode of interaction of the chaperonin GroEl with its substrate partially folded proteins.

Future developments with neutrons should be aimed partly at experiments that can furnish new types of information on the physical characteristics of biomolecules, and partly on ways of opening up access of present techniques to the wide range of diverse biological systems whose structure, dynamics and function could be better understood with the aid of neutron scattering. The human genome project is scheduled for completion in about 10 years. The result of the genome project will be a large number of protein sequences, each coding for a protein with a distinct function. An understanding of the principles leading from sequence to structure and from structure to dynamics and function will require the use of an arsenal of physical techniques. The present question is what role can neutron scattering play in this grand adventure.

Past achievements with neutrons

- Neutron scattering studies, that fall under the field of biology, are part of **Structural Biology**, although not all experiments are directly on structure.
- Structural biology is an important part of biology, and neutrons have in the past provided some key information, complementing that obtained by more widely available structural biology techniques. Examples are as follows:

Enzyme function

Much structural work using neutrons relies on the ability of neutrons to detect hydrogen and distinguish its isotopes ^{1}H and $^{2}H(D)$. High (atomic) resolution crystallography with neutrons is useful for determining the positions of hydrogen

atoms in biomolecular systems. An example of the use of this has been the determination of the water hydrogen bonding networks in crystals of vitamin B12 (Savage) and in cyclodextrins (Saenger).

Similarly, structural hydration properties of myoglobin have been determined (Schoenborn). The location of a particularly important hydrogen atom in the catalytic triad of trypsin has been determined (Kossiakof). H/D exchange has been used to determine the accessibility of labile hydrogens in different parts of the protein lysozyme (Mason, Bentley) and trypsin (Kossiakof). Advances in modern molecular biological techniques allowing cloned proteins to be produced in perdeuterated forms would significantly increase signal to noise and should lead to an increase in the number of proteins amenable to such studies.

Protein - nucleic acid and protein-protein complexes

Small angle neutron scattering (SANS) has frequently been used to obtain low-resolution structural information on biological systems in solution. The use of H_2O/D_2O contrast variation allows particularly clean spectra to be obtained in which only one component of the system dominates the scattering. This technique has allowed several structural questions to be answered. For example, contrast variation in SANS and also low resolution crystallography have been used to determine the protein-DNA distribution in the nucleosome (Worcester and Pardon; Finch and Bentley), the RNA, protein and lipid distribution in spherical viruses (Schneider and Zulauf; Jacrot, Timmins and Cusack). The combination of contrast variation with triangulation has allowed the positioning of all the 21 proteins in the 30S subunit of the ribosome of *E. coli* (Engelman, Moore) as well as the general arrangement of protein relative to RNA. SANS has also provided information on functional states of RNA polymerase (Heumann), aminoacyl-tRNA synthetase/tRNA interactions (Dessen), GroEl-GroEs (May and Heumann) and on the configurational distribution of a strongly denatured protein (Calmettes). Contrast variation can be extended to low resolution crystallography with the advantage of providing true three dimensional information. Several of the protein-nucleic acid complexes mentioned above have also been studied by this technique, notably the nucleosome (Finch and Bentley), small spherical viruses (Bentley, Timmins, Witz) and the ribosome (Yonath, Pebay-Peyroula, Roth).

The macromolecular-solvent interface

This important aspect of structural biology is difficult to study because of static and dynamic disorder. By using contrast variation in SANS and low resolution crystallography, neutrons have provided unique information on solvent interactions in tRNA and halophilic proteins (Zaccai) and detergent interactions with membrane proteins (Roth, Timmins).

Protein dynamics

Inelastic neutron scattering is a unique tool for probing the internal dynamics of biological macromolecules on the picosecond time scale and Ångstrom length scale. In the 1980s incoherent scattering experiments were combined with computer simulations to characterize large-amplitude internal motions in small proteins and to investigate their vibrational frequency distribution (Smith, Cusack). A dynamical transition resembling the liquid-glass transition was characterized in myoglobin (Doster, Cusack) and a similar transition was found to be correlated with function in bacteriorhodopsin (Ferrand, Zaccai). Molecular dynamics simulations have been used to interpret the diffusive, quasi-elastic component of the incoherent scattering (Smith).

Model membranes

Without the neutron scattering technique, our present day knowledge about the structure and dynamics of model membranes would be rather poor, particularly for the widely used saturated lipid bilayer and monolayer systems. The early work of Worcester and Büldt et al. demonstrated the advantages of selective deuteration for the determination of phospholipid multilayer structure. This and other work showed that extremely high resolution can be achieved for well defined model systems. Moreover, SANS proved to be a unique tool for the elucidation of the mixing behaviour of lipids in model membranes and particularly for an assessment of critical mixing behaviour (Knoll and Sackmann).

Quasi-elastic neutron scattering (QENS) recently allowed the detailed study of the rotational and translational motional processes in the bilayer (both phospholipids and the surrounding water) in the GHz - THz frequency range, which is largely inaccessible by other techniques like NMR, fluorescence or ESR and provided a basis for our present view of the bilayer as a dynamically rough and extremely soft surface (König, Bayerl and Sackmann). Using the unique feature of measuring either coherent or incoherent QENS, a distinction between collective membrane motion and individual lipid dynamics was achieved.

Neutron reflection, the latest neutron technique that has been applied to model membrane research, is exceptional for its extreme sensitivity and the correspondingly very low sample quantity requirements (Bayerl, Lösche and Sackmann). Only a few micrograms of lipids or proteins can give reflectivities of supported bilayers or monolayers down to 10^{-6} and allow to analyse the data in terms of layer thickness and density for a variety of different scattering contrasts via selective or full deuteration of membrane components. Besides this, the power of this method lies in its ability to monitor the structural changes of the membrane upon the interaction with foreign molecules like amphiphiles, peptides or proteins (Bayerl, Lösche, Möhwald and Als-Nielsen).

Natural lipids, membranes and membrane proteins

Contrast variation has also been used in low-resolution crystallography. Examples of this are the determination of the protein-detergent distribution in membrane protein crystals (Roth, Pebay-Peyroula, Timmins) and the localisation of lipid in a lipoprotein (Timmins).

The purple membrane of the *Halobacterium salinarium* contains a protein, bacteriorhodopsin, that acts as a light-driven proton pump. The purple membrane is at present the only known natural membrane amenable to structural studies with X-rays and neutrons. Much information on the structure of purple membrane has been determined using neutron diffraction, particularly by Engelman, Zaccai, Büldt and co-workers. This has included information on the hydration properties of purple membranes, the use of H/D labelling to localise the retinal chromophore in bacteriorhodopsin and to determine the position of specific a-helices, and information on the structure of trapped intermediates in the bacteriorhodopsin photocycle.

Biological tissues

Diffraction studies have also been used to study biological tissues. For example, the mineral in calcified Turkey tendon was located (White and Miller) and the orientation of hydroxyapatite crystals in bone was determined (Bacon).

Important experiments for the near or medium future

In this section we discuss problems in structural biology where the use of neutrons could contribute significantly.

Enzyme mechanisms

Enzyme catalysis does not follow a general mechanism: each enzyme works in a different way. In many cases, however, active site hydrogen atoms are involved. Neutron crystallography can be used to determine hydrogen bonding geometries involving functional amino-acid residues or water molecules in hydration or active sites. Localisation of hydrogens in new biological systems would be feasible by exploiting new instrumentation (e.g., quasi-Laue crystallographic techniques) in combination with advances in molecular biology involving cloning and expression of perdeuterated material. The flux limitations of present sources mean that these studies will still be limited to relatively small globular proteins (less than about 30-50 kD) similar to NMR studies. Indeed the development of isotopic labeling methods is a common interest between NMR and neutron scattering. The localisation of protons in functional reaction intermediates of small proteins may be feasible. Present quasi-Laue experiments can be combined with X-ray crystallography to obtain a comprehensive description of the time-averaged structure of a small protein and its

hydration shell. Indeed combined refinement of a model against X-ray and neutron data might lead to considerably better models; this has already been tried in a few cases.

Protein-protein interactions and protein-solvent interactions involved in protein folding

The problem of protein folding i.e., the principle by which a protein with a given amino-acid sequence obtains its native, three-dimensional architecture, remains one of the most important in biology. Recently there has been much interest in finding pathways of protein folding and in characterising trapped intermediates. Small angle scattering of X-rays has proven to be of much use in the low-resolution characterisation of these states. Complementary SANS studies are desirable for the variety of partly folded intermediate and end states (including the denatured state) presently under examination. It is especially powerful in determining protein-solvent interactions under different conditions e.g. in high concentrations of denaturants. In the cell, chaperonins are often involved in assisting protein folding. The mode of action of chaperonins such as GroEl-GroEs is an inherently dynamic phenomenon which will benefit from SANS studies using contrast variation to for instance locate the partially folded substrate.

Dynamics

Inelastic neutron scattering experiments on biological macromolecules have been largely confined to determining general characteristics of dynamics. There is a need now to examine a wider range of proteins and other macromolecules so as to determine if a diversity in internal motions might accompany the diversity of biological structures. These experiments might be on thermophilic or halophilic proteins, on mutant proteins, partially folded proteins and on proteins with substrate or inhibitors bound. The dynamical response to pressure changes would also be of interest. Now that X-ray crystallography has solved the structures of several membrane proteins, a characterisation of their dynamics is also required. Exploratory coherent inelastic scattering and spin-echo experiments are also desirable. Specific deuterium labelling, which has been used extensively for diffraction work is now being applied to dynamic studies, to highlight for instance the dynamics of active site regions rather than global dynamics.

Macromolecular complexes

Cellular processes depend on interactions between large numbers of macromolecules. These complexes range from (i) “simple” complexes involving only two partners (e.g. aminoacyl-tRNA synthetase-tRNA, nucleosome, transcription factor-DNA) to (ii) large

stable complexes with many components (e.g. the ribosome, viruses, signal recognition particle,) and (iii) large, less well-defined, labile complexes with many components (e.g. spliceosome, transcription complexes, chromatin, nuclear pore, multi-synthetase complex). Determing the structure of such complexes, their assembly and organising forces is a major, challenging problem in structural biology and of increasing importance.

This is not a simple problem. A wide spectrum of structural methods is required (X-ray diffraction, electron microscopy, NMR, X-ray microscopy?). How can neutron scattering contribute in this area?

- (i) "Simple" stable complexes are becoming more and more amenable to high resolution X-ray crystallography but complementary solution studies by SANS remain not only useful for cases that do not crystallise but also to detect conformational changes upon complexation, to explore stoichiometry under different solvent conditions and to study kinetics.
- (ii) Large stable complexes may be crystallised (e.g. ribosome, viruses) but solving such structures by crystallography is not straightforward. Low resolution structural information (e.g. quarternary structure) using neutrons, contrast variation, triangulation (using specific deuteration) will provide a useful stepping stone to higher resolution studies (e.g. ribosome triangulation will help ribosome crystallography). One promising approach is to put together known high resolution structures of components or subunits (found by NMR or X-rays) into a model for the complete complex using low resolution information (e.g. SANS, EM).
- (iii) Labile complexes are more difficult but the same comments hold as for (ii). Such projects on complexes require a very big investment in biochemistry (production and deuteration of subunits, reassembly of complex, homogeneous preparations). The results have to be obtained in a timely fashion, otherwise biology moves to other methods.

To perform these kinds of studies, existing instruments are generally adequate but the amount of access is often inadequate, although of course more flux gets things done more quickly.

A concrete example: The signal recognition particle is an important complex for targeting of nascent protein chains to the endoplasmic reticulum membrane in eukaryotic cells. It consists of 6 proteins and 1 RNA. The 6 proteins have been cloned and expressed (but not always in large amounts and not deuterated). Full re-constitution has yet to be achieved from cloned subunits. SANS with triangulation on this complex would give useful structural information about the overall shape (compact or elongated), the arrangement of the subunits and about potential conformational changes which might occur e.g. upon signal peptide binding, whereas X-ray crystallography is being used to determine atomic structures of individual components.

Model membranes

In the near future, model membrane research will increasingly concentrate on the molecular interaction mechanisms between membranes and proteins in order to narrow the gap between the relatively simple model membranes and the highly complex biological membranes.

One of the most challenging tasks in model membrane research is the reconstitution of functional proteins into bilayers. This gives the unique opportunity to study the structural and dynamical aspects of the interaction mechanism between protein and lipids and thus to learn about the relationship between protein function and membrane environment. One particularly interesting group of proteins with respect to their membrane interaction is the cytoskelton proteins.

Another highly interesting question is why natural membranes consist of a wide variety of different lipids (headgroups and tails) and what is the function of cholesterol and of other steroids in the membrane. Finally, as lipid bilayers seem to become useful as carriers for drug delivery and for the biocompatibilisation of anorganic surfaces (e.g. in transplants), knowledge of the interaction of bilayers with cell surfaces and with anorganic surfaces on a molecular scale is required.

For neutron scattering, the applications will concentrate on diffraction, SANS, QENS and reflectivity. A prerequisite is the availability of selectively deuterated lipids and proteins. For neutron reflectivity, the next important step will be the simultaneous measurements of specular and off-specular reflection arising from bilayers in order to facilitate the data analysis. Regarding protein-lipid interaction, the applicability of this method to distinguish between partial membrane penetration or adsorption of the proteins will be of special interest. Future QENS measurements on model membranes will focus on the study of oriented stacks of bilayers with and without proteins. While experiments on plain bilayers will concentrate on cholestrol and lipid dynamics, fluid domains and collective membrane motions (undulations), the membranes with proteins will provide insight into the dynamical effects of the proteins on the bilayer and vice versa. A very interesting prospect is the comparison between results using QENS and molecular dynamics simulations. The latter can be extended over almost the same time window as QENS and provides even the EISF and the linewidth similar to the experiment. This opens up new opportunities for a refinement of the force field used in the simulations and for a better interpretation of the experimental data. A recent and very promising development in this field is neutron reflectivity at single bilayers supported by silicon crystals since such systems are capable of mimicking a membrane surface more realistically than the lipid monolayers used so far in most reflectivity work.

Natural membranes and membrane proteins

Future studies on membrane proteins could include studies of systems such as the light harvesting complexes, which, when solubilised with detergent, retain some natural lipid bound.

Future experiments at high flux

Crystallography

Neutrons would complement the X-ray work in that localisation of hydrogens is possible and so, for example, critical hydrogen bonding interactions could be characterised that are not presently accessible with X-rays. One question is what flux would be necessary to enable neutrons to work on the same systems as X-rays can now. Recent measurements of an 8 mm^3 tetragonal lysozyme crystal (with unit cell of about 80 x 40 x 40 $Å^3$) on the prototype quasi-Laue machine at ILL took 1 - 2 weeks for a 2Å data set. If we wish to do measurements on a crystal volume 64 times smaller (0,5 x 0,5 x 0,5 mm^3, quite large still by current X-ray standards) and 5 times bigger unit cell volume then we need at least 320 times more flux! Higher brilliance would also be necessary to help in the resolution of closely-spaced diffraction spots. The speed of the data collection would allow experiments that are now exotic to become routine.

Small angle neutron scattering

It is obvious that high flux neutron sources will extend the observation of faster structural relaxation processes with SANS up to the millisecond time domain. In combination with contrast variation techniques and specific deuteration this would allow to follow up conformational changes in different parts of a protein or a macromolecular complex.

Inelastic scattering

Higher flux would open new application fields for neutrons in membrane research like the use of ultracold neutrons for studying membrane dynamics. So far the feasibility of the application of ultracold neutrons for membrane studies is hampered by the acquisition time required to obtain reasonable statistics. Similarly, for QENS a significantly enhanced flux would allow the study of more delicate reconstituted systems. This would be of high importance since QENS is the only method that provides simultaneously both spatial and temporal correlation functions in the GHz-THz frequency range. Moreover, coherent QENS measurements of highly oriented bilayer stacks at different hydrations may shed some light on the question why such stacks do not swell indefinitely under maximum hydration and thus provide some clues about the basic intermolecular forces acting between membranes.

Increased flux would allow the study of the dynamics of parts of a macromolecule by using specific deuteration, with conventional time-of-flight inelastic experiments. X-ray diffuse scattering from protein crystals gives information on correlated displacements in and between protein molecules. Neutrons hold the possibility of being able to energy analyse the coherent diffuse scattering and to obtain information on the length and timescales of correlated motions, either between different unit cells (thermal diffuse scattering) or within proteins (very diffuse scattering). Coherent inelastic scattering using spin echo machines would allow the determination of the ns timescale motions of different parts of macromolecules in solution.

Reflectivity

At present reflectivity can be used to determine the density profile across a lipid membrane in the presence of adsorbed proteins. Neutron reflection is sufficiently sensitive to allow measurements with micrograms of substance within 1 - 2 hours, a time range that seems reasonable considering the fast degradation of many proteins under measuring conditions. With very high flux one could envisage examining the lateral arrangement of proteins adsorbed on the surface by observing Bragg scattering in the bilayer plane. In contrast to X-rays these applications benefit from contrast variation.

Competing and complementary techniques

Structure

The field of high resolution structure is dominated by X-ray crystallography with significant contributions from NMR for smaller proteins (< 30 KDa). For low-resolution studies, electron microscopy is a competing and complementary technique. In the field of low and high resolution structural work fast kinetic processes are better studied using synchrotron X-ray radiation. In all cases, the complementary advantage of neutrons arises from deuterium labelling, contrast variation and the possibility of using a wide range of solvent conditions. For neutron reflectivity, the synchrotron reflection methods are clearly most competitive. The clear advantage of the latter is the higher flux allowing the measurements of reflectivities over a considerably wider q-range in a shorter time than for neutrons and thus facilitating the model fitting of the data. Besides this, in-plane scattering is already well established for the X-ray methods. On the other hand, neutron reflection offers the unique advantage of contrast variation by deuteration and the lower probability of sample radiation damage. A very new technique that will complement both the neutron and the X-ray method in the field of lipid monolayer studies is the infrared reflection absorption spectroscopy (IRRAS). While the former methods give information about monolayer thickness and density, the IRRAS can provide orientational order parameters, infor-

mation about lipids phase state and about the orientation and secondary structure of embedded proteins.

Dynamics

Functional dynamics in biomolecules span a wide range of time and length scales (fs - s and Å - 100 Å) and thus require a battery of experimental techniques. Neutron scattering complements best with spectroscopic and the X-ray methods. For QENS, the two-dimensional exchange NMR and the quasi-elastic light scattering methods are the best choice for increasing the width of the time window for the observation of dynamical processes in membranes. All three methods provide simultaneous spatial and temporal correlation functions but their time and spatial resolution is very different. While QENS covers the region of GHz-THz, quasi-elastic light scattering is best in the KHz-MHz region and the NMR method is sensitive in the Hz-KHz region. Thus, by combining the three methods, the experimenter can study selectively dynamical membrane processes over more than 10 orders of magnitude. Thus, neither NMR nor light scattering should be considered as competing techniques but rather as complementary ones. Fluorescence and Moessbauer spectroscopies also provide ns-time scale information on dynamics in globular proteins. Infrared and Raman spectroscopy give fs information on local vibrations. In the future, quasi-elastic X-ray scattering (QEXS) may become useful after the development of high flux coherent X-ray sources. As a coherent method it could complement neutron spin echo and incoherent inelastic systems. Computer simulation is complementary to both the structural and dynamical neutron experiments. As computing power and methodology improve, modelling and molecular dynamics simulations are increasing in reliability and will aid in the interpretation of those neutron experiments that can access atomic detail information.

Spectroscopic techniques as a whole represent the probably most important pillar in experimental model membrane research. X-ray diffraction methods are equally important as they provide essential structural information on most of the lipids that occur in membranes and on the membrane structure. Microscopic techniques, particularly optical and electron microscopy are well established in this field and the new scanning techniques (STM and AFM) gained more attention recently for their resolution on a molecular scale and their potential to measure molecular forces on membranes. Langmuir-Blodgett techniques helped to study monomolecular films of lipids by a variety of - mostly spectroscopic - methods. Various techniques for measuring forces down to 10^{-14} N allow to study the interaction forces between membranes.

Industrial applications

The various structural methods described above have potential applications in a wide range of industrial domains. High and low resolution structures are of interest to the pharmaceutical, agricultural and biotechnology industries. Structure-based protein and drug design require high precision structures with the location of hydrogens and water molecules. Neutron reflectivity and scattering methods might obtain more direct industrial applications in characterising systems like

- biofunctionalised solids,
- supported membranes or polymer films as for biosensors,
- polymer films on titanium implantates,
- biocompatible materials,
- drug delivery by vesicles or micelles.

Atomic and molecular aspects of new materials

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The contribution of neutron scattering to structural physics and chemistry

1. Introduction

Neutron scattering has played a principal role in our understanding of almost every area of modern structural physics and chemistry. Research topics ranging from catalysis to magnetism and from battery materials to superconductivity have been profoundly advanced as a result of the detailed structural insights brought by neutron diffraction. Topically, the immense research efforts over the past decade in the area of high-temperature superconductivity have been underpinned by the initial structure determination and subsequent detailed structural investigation of these materials by neutron diffraction methods. Almost all that we know about structural magnetism has been discovered through neutron diffraction. Neutrons pervade our understanding of solid and liquid materials.

This chapter will summarise the contribution of neutrons to our understanding of the structure of crystalline materials, indicating the breadth of work that covers all the major scientific and engineering disciplines. The chapter will also address the growing impact of synchrotrons on many traditional areas of strength in neutron scattering and will conclude that the two techniques will continue to be complementary. The presence of third generation synchrotron sources such as the ESRF in Grenoble, France, rather than hastening the demise of neutrons, suggests an urgency in developing existing major neutron sources and constructing a new third generation European *neutron* source to match the known potential gains of neutron scattering with the strengths already beginning to be realised at third generation synchrotron sources.

2. Principal techniques

Single-crystal neutron diffraction

It is an inalienable fact that the results obtained from a neutron diffraction experiment are fundamentally distinct from an X-ray or electron diffraction measurement. Neutrons scatter from the atomic nucleus and thus details about atomic position and movement are uncomplicated by the convoluted structure of the electron distribution. As a result, single-crystal neutron diffraction in general provides the most precise and reliable structural information that may be obtained. This is particularly true (i) for the location of hydrogen atoms and (ii) for the most precise studies of electron density distributions by combining X-ray and neutron diffraction data. Much

information concerning the bonding in chemical systems can be found in the electron-density distribution. These charge distributions, obtained by experiment and supported by quantum chemical calculations, are essential for understanding some of the most subtle but profound details of a crystal structure (for example, the effects of charge transfer, magnetostriction and the onset of superconductivity) and will be of increasing use in the derivation of electrostatic parameters for the ab-initio study of molecular and supramolecular materials.

Neutron powder diffraction

Most significantly, neutron powder diffraction consistently provides accurate and reliable results that are largely free from systematic errors. The introduction of the Rietveld method in the late 1960s has been one of the most important developments in neutron diffraction since the vast majority of materials are most easily synthesised and most often developed in polycrystalline form as powders or ceramics. Despite the advent of third generation X-ray synchrotron sources, the most accurate, reliable and complete powder diffraction measurements are still obtained using neutrons. X-rays, however, are usually the technique of choice for structure solution where a few heavy atoms may dominate the diffraction pattern; neutrons are preferred for structure refinement since (i) all atoms scatter with roughly equal power and are thus equally visible and (ii) systematic errors are smaller because samples are generally larger. With the new high-resolution powder diffractometers, increasingly complicated structures have been investigated; the host/guest configurations in the framework structures of zeolites are a good example of this complementarity that is of technological importance (because they are molecular sieves that behave as solid-state acid catalysts). The framework structure is generally initially determined and refined from X-ray work; neutron powder diffraction is then used to locate the small hydrocarbon guest molecules within the framework channels. This combination of neutron and X-ray measurements is essential; X-rays provide the initial framework details; neutrons give direct location of the active acid site (i.e. the proton position), the location, ordering, condensation processes and dynamics of sorbate molecules inside the channels and cavities and the topology of Al/Si or Ga/P segregation of the tetrahedral atoms which are the reactive centres in the zeolitic framework.

3. The achievements of neutron diffraction in structural physics and chemistry

Investigating materials under realistic operating conditions

Two of the principal goals at the frontiers of synthetic chemistry and materials science in both academic and industrial laboratories are the creation of new materials by rational design and the monitoring of the life of a material under realistic operating conditions. For a complete understanding of the performance of a material, one needs not only to know the crystal structure but also how it is made, how it

performs under operating conditions and how its performance eventually deteriorates; the birth, life and death of a material.

With the development of high-intensity neutron sources such as ILL and ISIS, powder diffraction measurements can be as short as a minute allowing time-resolved studies to be performed. Given the high penetrating power of the neutron, the full life of a material can be investigated under *realistic operating conditions*. Specific examples of topical interest include (i) the formation of high-temperature superconductors under hot-zoning conditions, where a video movie of the hot zone is correlated with the formation of 2-, 3- and 4-layer superconductors, (ii) the in-situ ageing of Mg-stabilised zirconia ceramics in which the fracture strength of the material is correlated with the formation of different zirconia polymorphs at different ageing temperatures and times, and (iii) the in-situ discharge of "long-life" alkaline Zn-MnO_2 primary batteries. This latter case is a landmark example of the application of neutron diffraction to solid-state chemistry. Many electrochemical reactions of relevance to fuel-cell and battery applications simultaneously involve electron transfer and proton insertion within the lattice of a crystalline solid. In the particular case of long-life batteries, the voltage is obtained by the reduction of manganese dioxide (MnO_2) to manganese oxy-hydroxide (MnOOH). In-situ neutron diffraction measurements probed the irreversible discharge of this electrode under realistic operating conditions. The simple reaction γ-$MnO_2 + H^+ + e^- \rightarrow MnOOH$ hides a series of phenomena that were determined by the neutron diffraction experiment. Most importantly, the in-situ measurements gave very different answers to previous ex-situ X-ray results. The simple two-step discharge model that was proposed gave a full understanding of the kinetics of out-of-equilibrium effects that are relevant to battery operation. The generic extension of this in-situ bulk probing of material processes to other areas such as fuel cells and catalysts is obvious.

Investigating materials under extreme conditions

In the previous section, the high penetrating power of the neutron was shown to be invaluable in the study of bulk samples under realistic operating conditions. All sample environments benefit from this high penetrating power; the use of a vanadium- or aluminium-tailed cryofurnace or a very-high temperature mirror furnace presents no problems for data collection. Many of these sample environments have been established for over two decades at reactor-based facilities. However, over the past decade, the emergence of spallation sources has offered further advantages; a full diffraction pattern may be collected at a single detector angle allowing very confined environments such as catalytic reactors or high-pressure cells to be used without difficulty producing diffraction patterns free from sample environment contamination.

Magnetism

Historically nearly all that is known about magnetic structure is based upon neutron diffraction data. The demonstration of the Néel model, the discovery that magnetic electrons in metals are spatially localised, the unimagined variety of incommensurate magnetic structures that include spirals, fans and cycloids all result from neutron-diffraction studies. The investigation of the ferromagnetic elements, the paramagnetic transition metals, the ground state wave-functions in rare earth alloys, the spin and orbital magnetisation in the actinides, the magnetisation distribution in the NO free radical, the diamagnetism of bismuth and graphite, covalency in nickel oxide and the asymmetric magnetisation in antiferromagnetic K_2IrCl_6 are landmark experiments in magnetism obtained by neutron-diffraction measurements. The contributions from magnetic neutron diffraction are being complemented by synchrotron X-ray radiation, which is providing insights into magnetism through magnetic dichroism, resonant magnetic scattering, extreme Q-resolution and the separation of orbital and spin contributions to the magnetic moment. Indeed, many of the new insights into the structural physics of magnetism are likely to come from X-ray synchrotron experiments. However, the weakness of non-resonant scattering, and the absence of suitable resonances in the 3d-transitional elements means that neutrons still have an important, if perhaps no longer unique, role to play. Magnetic single-crystal neutron diffraction will still offer the best approach for the initial structure determination of a new magnetic structure. Furthermore, magnetic neutron *powder* diffraction is, and will continue to be in spite of the advances in magnetic X-ray diffraction, the primary technique and the simpler tool for obtaining information about the arrangement of magnetic moments in crystalline solids.

New magnetic materials are often no longer simple binary alloys but generally complicated multicomponent systems with complex chemical and magnetic structures. Good resolution at both short (for chemical structure) and long (for magnetic structure) d-spacings is needed. These two requirements are difficult to realise in a single constant wavelength (CW) diffractometer. The time-of-flight (TOF) technique has more potential capability which makes TOF powder diffraction with cold neutrons an absolute priority for future developments. TOF diffractometers can access extremely long d-spacings (10-50 Å) with a resolution that is impossible to obtain on conventional diffractometers with, in principle, full neutron polarisation. A good example of the power of the time-of-flight technique is the recent study using cold neutron powder diffraction at ISIS of the magnetisation distribution in a Mn_{12} complex in $[Mn_{12}O_{12}(CD_3COO)_{16}(D_2O)_4].2CD_3COOD.4D_2O$. Neutron-diffraction patterns were measured on IRIS in the paramagnetic phase in a large magnetic field and at zero field. The difference revealed unusual molecular magnetic properties despite the large unit cell (3589$Å^3$), short run times (8 hours) and unoptimised detector configuration (a factor of 200 increase will be available with the commissioning of OSIRIS in 1997). There is much potential for development.

The study of molecular compounds

Diffraction has played a major role in the elucidation of the structures of organic molecules. Although, at present, it has to share that position with NMR and IR-spectroscopy, it still provides the most definitive answers to structural problems. Its role became even more pronounced with the advent of supra-molecular chemistry where the host/guest molecular bonding is mainly electrostatic in character and includes highly important hydrogen bonds. Although the bulk of molecular crystallography will continue to be performed by laboratory X-ray techniques, there are substantial areas of research where neutrons make a unique and continuing impact because of their ability to determine hydrogen positions and the fact the chemical atom is a point scatterer (the nucleus) of neutrons. Neutron reflectometry, for example, provides unique insights in the area of sensors where supra-molecular compounds are applied in thin layers. Neutron diffraction is essential in a number of areas that include: (i) the measurement of accurate positional parameters of all atoms (hydrogen and non-hydrogen) for the determination of parameters for computational chemistry, (ii) the accurate determination of thermal motion; in X-ray diffraction, in contrast to neutron scattering, the atomic deformation by covalent bonding is too much intertwined with thermal motion to permit unambiguous analysis and (iii) the investigation of materials in which hydrogen bonding plays a major role; reliable information concerning this type of bonding is essential in areas that include hydrides and hydrates, ferroelectrics, and molecular and supramolecular chemistry and biology.

Oxide ceramics: high-temperature superconductivity - a case study

Oxide ceramics are, without doubt, the broadest range of materials studied today by inorganic solid state chemists and materials scientists. The diversity of mixed metal oxides is enormous; the structures of tens of thousands of these materials have been characterised. The richness of this diversity is also reflected in materials properties ranging through magnetism and magneto-resistance, ferroelectricity and ferroelasticity, intercalates and inclusion compounds, battery cathodes and electrolytes, molecular sieves, clays and catalysts, superionic-conductors and superconductors. Almost without exception, the important structural components are determined by the location and topology of the oxygen positions. Neutron diffraction is particularly sensitive to oxygen and is, as a result, pre-eminent in the determination of the detailed structures of these materials. We illustrate the neutron contribution to oxide ceramic studies with the example of high-temperature superconductors.

Superconductivity underlines the thesis that materials are becoming increasing complex. In the early 1970s, the highest temperature superconductors were Nb_3Ge-based alloys, simple binary systems. The discovery of superconductivity by Bednorz and Müller in 1986 in the doped-La_2CuO_4 ternary copper oxide led to an unprecedented search for higher temperature superconductors of increasingly complex chemical composition. The quaternary copper oxide, $YBa_2Cu_3O_{7-x}$, discovered

less than a year later, was the first material to superconduct above the boiling point of liquid nitrogen. The current "record holder" is a quinary system, $HgBa_2Ca_2Cu_3O_{8+\delta}$, with a superconducting temperature of 133K at atmospheric pressure. Neutron scattering has played an important role in all stages of the development of the field of high-temperature superconductivity. In 1987, neutron powder diffraction became the obvious choice of many different laboratories for the first determination of the structures of these new materials. Subsequently, important results were obtained about their properties and crystal chemistry by the same technique. Neutron powder diffraction was, for example, used to demonstrate the charge transfer concept of hole-doping with oxidation, and that the superconducting temperature was related to the evolution of structural order. Site-specific oxygen compositions are commonly obtained to accuracies of under one per cent. In all these measurements, the unparalleled precision and accuracy of subtle structural details were crucial to the final conclusions about physical properties.

4. Expanding opportunities for existing sources and the development of new sources

One of the few predictable aspects of materials research is that major advances will generally be unpredictable! It is impossible to foresee new scientific developments in detail but broad generalisations can be inferred:

- new materials are becoming more complex: subtle solid-solutions are created to enable oxide ceramics to have particular optimised properties, self-assembling molecular structures with sophisticated topologies are generating much interest, heterogeneous nano-scale structures are being developed with attractive technological properties;
- structural analysis is becoming more complex: with improved instrumental resolution, subtle structural distortions may be parameterised as a function of temperature or pressure; the difference between local and average structure may be analysed by both total and elastic diffuse scattering; detailed microstructural information may be obtained in conjunction with average crystal structure; fundamental systems such as quasicrystal and incommensurate structures may be more fully investigated;
- the ability to work with smaller samples is increasingly demanded - the list is long: a compound may be synthesised in milligram quantities through exotic conditions, the single crystal may be substantially sub-millimetre in size, the component of interest may be present in only dilute amounts, the surface of the structure may be the region of primary interest, the sample conditions, for example the achievement of 100 GPa pressures, may demand the use of tiny sample volumes, or intrinsic sample inhomogeneity (e.g. concentration gradients in a chemical cell) may require a millimetre by millimetre spatial pixellation of the sample;

• there is an increasing emphasis on the technological impact of material properties. This is well-exemplified by the development of surface studies by neutron reflectometry. With higher intensity sources, new surface properties may be studied. Combined reflectometry and surface diffraction may be tenable that would deepen our understanding of the structure of surfaces and interfaces. Two particular areas that would benefit would be the magnetic properties of thin films, multilayers, surfaces and interfaces and the role of the proton/hydrogen atom at chemical interfaces such as the study of bonding interactions in adhesives and paints and the investigation of chemical activity at electrode and metal catalyst surfaces;
• underpinning all these new avenues of research is the historical observation that neutron scattering has played a pivotal role in most of the new developments in materials research. High-temperature superconductivity, fullerenes and most recently the giant magnetoresistance materials have all benefited from the unique insights provided by neutron scattering studies.

Instrument development

Although structural physics and chemistry are concerned with the relationship between structure and property, the determination of structure and measurement of a given property are usually performed separately, often not in-situ (e.g. study of quenched specimens or use of ambient structural data to interpret properties under extreme conditions), and usually with different specimens. There is great opportunity for generalised instruments that provide the opportunity for simultaneous and in-situ determination of structure as a function of temperature, pressure or atmosphere in conjunction with simultaneous determination of electrical, thermal or magnetic behaviour. Neutrons are particularly appropriate for this dual measurement because the dimensions of an experiment make the development of complex multi-purpose sample environments relatively straightforward. There is a significant technological impact in the development of more sophisticated sample environments for studies of product synthesis, operation and processing.

Recent developments in neutron optic and detector technologies indicate that substantial gains on existing sources may be envisaged. Detector solid angles may be increased by factors of five on machines such as D19 and D4 at the ILL. The imminently operational D20 diffractometer will have a count-rate at least an order of magnitude higher than the existing D1B machine. Supermirror guide and detector developments at ISIS mean that the count-rate of OSIRIS, a spectrometer to be commissioned in 1997, will be 4 (guide) × 50 (detector solid-angle) = 200 times more intense than the current diffraction capability of IRIS. The GEM diffractometer at ISIS due to be operational in 1999 will have an order of magnitude more count-rate than POLARIS. Funds permitting, with new area-detector developments, it is possible to envisage a single-crystal time-of-flight machine at ISIS with at least 20 times the SXD count-rate.

High-flux sources such as the ILL and ISIS have been pre-eminent in the development of rapid real-time measurements. However, the trend towards more complex materials combined with the synthesis of smaller samples (by, for example, combined high-temperature/high-pressure techniques) reveals the limits of what is currently possible.

New instrumentation and new sources will be essential to exploit the unique advantages of the neutron in the study of dimensionally smaller and more complex systems. New sources are also required to extend the scope of current diffraction techniques - an excellent example is the study of materials at high pressure. With present sources, pressures are limited to around 20 GPa; a next generation source would allow the smaller sample volumes needed to approach pressures of 100 GPa and very substantially widen the opportunities for solid-state high-pressure research. Pressures far in excess of this are achieved at synchrotron sources, but neutrons are frequently required to detect positions of light atoms. Synchrotrons can best measure lattice parameters and angles as a function of pressure.

Finally, the combination of advances in neutron optics and detectors together with a next generation source offers the possibility of closing the gap between the time-scale of a real-time diffraction measurement and the time-scale derived from an inelastic scattering measurement and between the length-scale measured by neutron microscopy and that derived from a small-angle scattering experiment. The exciting possibility with a next generation source of covering all length scales from fractions of an Ångstrom to fractions of a meter and all time-scales from picoseconds to days offers tremendous potential for the development of many new types of experiments of both industrial and academic relevance.

Chemical reactions, catalysis and electrochemistry

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1. Introduction

Chemical reactions, catalysis and electrochemistry present a challenge to advanced neutron scattering methods because there are problems of both a conceptual and fundamental kind which could be solved by foreseeable advances in the method in the next ten years. These subjects are also important because of their relevance to industrial processes. At the fundamental level, phenomena such as the cage effect in liquids, fast proton transfer in solids and liquids, catalyst synthesis and active site identification as well as interfacial structure and dynamics all pose questions about short and long range structures and speed at which they fluctuate.

The Q, ω space accessible to neutrons and the real space and time conjugates of this (0.1 Å to 1000Å; 10^{-15} sec to 10^{-8} sec) allow relevant picosecond phenomena occurring on the atomic scale to be followed. This with isotopic contrast, the neutron's magnetic interaction and its penetration of samples provide a useful complementarity to X-ray, nuclear magnetic resonance and optical spectroscopic methods which are also indispensable for the fields covered here.

This report illustrates the types of problem accessible to neutrons. Important *complementary methods* are marked in the text by *simple italics* and realisability of major issues on the ***five year*** and the **ten year** time scales by ***bold italic*** or **plain text** respectively.

The seven broad areas are:

- **Solid State Reactions**
  (Advantages of combined diffraction and spectroscopy)
- **Molecular Vibrational Spectroscopy**
  (Reassignment of optical spectra, new protonic species, free H^+)
- **Proton Transfer and Ion Conducting**
  (Fast ion conductors)
- **Liquid State Structure, Dynamics and Reactions**
  (Complementarity, Simulation)
- **Zeolite synthesis and Properties**
  (Nucleation and Growth, site structure and dynamics)
- **Catalytic Sites and Reactivity**
  (Identity of active species)
- **Electrochemical Reactions**
  (spatial distribution of electroactive films)

2. Solid state reactions

The kinetics of many solid state reactions may now be conveniently followed over a wide range of temperature and pressure using high resolution neutron diffraction. The absorption of gaseous ammonia by alkali metal-graphite intercalation compounds is one such case and occurs because of the strong exothermic reaction as the ammonia is co-ordinated with the intercalated alkali metal ions. Ultimately the system forms a two dimensional alkali metal -ammonia solution. Absorption isotherm measurements are bland and reveal only a steady uptake of gas with time as the reaction proceeds. Such reactions do not produce enough crystalline order to allow the local structure of the complexed alkali ions to be determined, but with time of flight neutron scattering, simultaneous measurement of the high resolution diffraction pattern (at a resolution of about 1 x $10^{-4} = {}^{\Delta d}/_{d}$) and the inelastic scattering (at a resolution of a few microelectron volts) from the ammoniated clusters allows both local and long range aspects of the process to be followed. Since optical techniques are not applicable for such opaque materials, the neutron methods are unique.

The inelastic scattering thus reflects the local structure, the diffraction, the long range order along the c-axis. These experiments open a number of new possibilities. **Furthermore, in real time considerable greater flux experiments may reveal further important details of the reactions.**

3. Molecular vibrational spectroscopy

(Reassignment of Optical Spectra, New Protonic Species, Free H+)

Although vibrational spectra are commonly used to finger-print molecular groups for analytical purposes or process-control, these spectra also contain important information on the vibrational dynamics. These are governed by forces, or potentials, due to many interactions between atoms and molecules. ***The great increases in neutron intensities, in spectrometer design, in data processing and in computer simulation and fitting of spectra have now made incoherent neutron scattering a powerful method. Coupled with the use of coherent inelastic neutron scattering from single crystals for analysing the consequences of the intermolecular part of the potential it will now be used routinely to study localised molecular dynamics.***

The major advantages of INS are related to the properties of calculable intensities, contrast and momentum transfer. For optical techniques, intensities are related either to derivatives of the dipole moment in the infrared or to components of the polarisability tensor in Raman. With INS, the neutron scattering process is entirely attributable to nuclear interactions and transition moments can be calculated accurately.

Contrast arises because the cross section of the proton is about 10 times greater than that for any other atom. Therefore, proton dynamics can be studied in many different

non-hydrogenous environments. This proton selectivity can be further exploited because the deuterium atom (^{2}H or D) has a much smaller cross section than the proton.

Thirdly, INS spectroscopy uniquely allows vibrational spectra to be measured over a broad range of energy and kinetic momentum transfer (Q). The full scattering function, S(Q,ω), contains spatial information on the wave functions for the corresponding vibrations. ***We can then use the Q dependence of the intensity to obtain the shape of the potential functions and the effective oscillator mass for the various vibrations. The Q dependence provides a straightforward distinction between single and double minimum potentials (tunnelling).***

Fundamental problems and prospects

Force-fields

For an isolated non-linear molecule containing N atoms, there are 3N-6 internal degrees of freedom corresponding to internal vibrations of the molecule. Eigen vectors related to the effective oscillator masses and spectral intensities in optical spectra remain largely unknown. There are many examples of different force-fields having been proposed for the same molecule (e.g., at least 6 different force-fields for the benzene molecule). All of them are in accord with observations. INS provides access to these eigen vectors.

Localised modes

In some cases, the usual valence bond force field approach fails completely. This is the case for many hydrogen bonded systems: carbonates $MHCO_3$ (M = Na, K, Rb, Cs), disulfates $M_3H(SO_4)_2$ (M = K, Rb), trifluoroacetates $MH(CF_3COO)_2$ (M = K, Cs), N-methylacetamide (NMA, $CD_3CONHCD_3$), polyglycines (PG) $(COCD_2NH)_n$. In every case, irrespective of the ionic or molecular nature of the systems, the dynamics of the protons involved in hydrogen bonds are almost totally decoupled from the dynamics of the other atoms and must be described in terms of localised modes, rather than normal modes. This is clear from the S(Q,ω) maps of intensity. ***These dynamics could not be anticipated from optical data and at present, such dynamics are beyond the capabilities of quantum chemistry. It is worthwhile to stress that this decoupling does not occur for much weaker hydrogen bonds such as in ice.***

New Assignment Schemes

In the case of the NMA molecule the INS , shows the hydrogen modes clearly and the intensities reveal that previous assignments based on optical data are largely in error. The previous estimate for the vibrational frequency of the proton (NH stretching) at ca 3000 cm^{-1} is almost a factor of 2 too high. New assignment schemes must be proposed for infrared and Raman spectra. Consequently, a new view of hydrogen

bonding in peptides emerges: the covalent bond between the N and H atoms is actually considerably weaker than was thought previously, and the ionic model ($N^{\delta-}$...H^{+}...$O^{\delta-}$) appears to be more realistic. Again, these results emphasise the limitations of quantum chemistry.

Proton transfer in amides and polypeptides

One of the recent highlights of INS in vibrational spectroscopy hasbeen the study of N- methylacetamide ($CH_3CONHCH_3$) and polyglycine $(COCH_2NH)_n$, and their partially deuterated analogues.

The $S(Q,\omega)$ map of the tunnelling transition of the stretching mode has been measured for PGII. It is located at ~ 40 cm^{-1}. The double minimum potential is symmetrical with a distance between the two minima of 0.5 Å. A totally new picture emerges for polyglycines: hydrogen bonds form a network with the protons being delocalised between two equivalent sites. The structure of the peptide unit is strictly intermediate between the amide-like (OCNH) and the imidol-like (HOCN) structures, which cannot be distinguished. Therefore, proton transfer, an essential process in biology, is achieved naturally as a result of the hydrogen bond.

Single crystals

A MARI type spectrometer offers a unique opportunity to visualise vibrational wave function in space. For this purpose, $S(Q_x,Q_y,Q_z,\omega)$ maps of intensity must be obtained for different orientations of single crystals. Such maps provide the most detailed information on the vibrational dynamics ever obtained. Long-standing problems like vibrational coupling, Fermi resonance, coherent tunnelling, etc., can be resolved. However, the necessary theoretical framework is not yet totally developed.

New protonic species

For γ-MnO_2, it has been speculated that charge compensating $(H^+)4$ entities should be located near by Mn^{4+} vacancies. INS reveals that these entities effectively exist. ***A complete characterisation of these entities should be provided by the $S(Q,\omega)$ map of intensity. This is a unique opportunity to observe rather unusual mixing of tunnelling and rotational wave functions. Again, this would require very good statistics.***

Tetrahedral oxonium ions on H_3O^+

In hydrated protonic conductors, mobile entities are proton hydrated species: H_3O^+, $H_5O_2^+$, etc. Optical spectra are dominated by signals due to the matrix stabilising these species. For proton-free matrices, INS is the best technique to observe and characterise the mobile entities. This is the case for β-alumina. The INS spectrum of β-alumina can be interpreted in terms of tetrahedral H_3O^+ entities rather than the trigonal symmetry supposed so far. ***The remarkable capability of INS to reveal new protonic species in proton conductors is a very strong incentive for more studies. Because the concentration of some mobile charge carriers can be very small, their identification requires intense flux and excellent statistics.***

Insertion and intercalation compounds

The assembly of ions or molecules in solid materials through ion exchange or intercalation reactions continues to excite much interest as one strategy in the optimisation of the physicochemical properties of materials. The concept of such host structures as templates allows reactions including proton or electron transfer, aggregation and *in situ* polymerisation. Inorganic acid salts of two dimensional character, microporous pillared layered solids and zeolites, mesoporous zeolites of the MCM-41 type all provide suitable hosts (see below). ***Here INS is the vibrational spectroscopic technique of choice, since it is sensitive only to those modes involving large amplitude displacements of hydrogen and provides, for practical purposes, a 'guest-specific' spectroscopic method.***

Rotational tunnelling spectroscopy

Rotational tunnelling of small molecules, molecular groups and ions like CH_4, NH_3, CH_3 and NH_4^+ in solids at low temperature have been studied extensively with INS. This has been used also to study the physisorption potentials for small molecules (CH_4, NH_3) adsorbed on surfaces (graphite, MgO), or isolated in cryogenic "inert" matrices. ***There is no other technique to observe such tunnelling frequencies. In this respect, INS provides crucial evidences for fundamental aspects of quantum mechanics.***

Coupled rotors

Experiments with spectrometers of better resolving power have revealed more complex energy level schemes attributable to coupling between rotors. Rotational dynamics in infinite chains of coupled rotors have been used for the 4-methylpyridine crystal (C_5H_4N-CH_3 or γ-picoline) and for the 2,6- dimethylpyridine crystal (C_5H_3N-$(CH_3)_2$ or lutidine). The quantum sine-Gordon has been proposed.

New areas

Significant developments in the areas of matrix isolation high pressure and the use of the increasing momentum transfer range and energy resolution of spectrometers are foreseen. Matrix isolation is an important field which could be extended with an increased flux. So far, INS spectra of matrix isolated species have been obtained essentially for quantum rotational tunnelling of small molecules (CH_4, NH_3). An increased flux by a factor of 30 should allow the internal molecular vibrations of non hydrogenous or fully deuterated systems to be tackled. Current measurements with MARI on non hydrogenous systems (C_{60}, graphite, glass...) demonstrate that such measurements would be feasible and a TFXA-like spectrometer with a detected flux ~100 times greater would be a powerful adjunct. There are some examples of INS spectra for samples under hydrostatic pressure, typically below ~ 10 kbar. These rather moderate pressures are useful for phase transition phenomena, but insufficient to observe significant changes of forces between atoms or molecules. Very high pressure effects can be obtained only with anvil cells, but the amount of sample is divided by a factor ~ 10^4.

4. Proton transfer and ion conducting solids

Current theory accepts two types of mechanism for proton transfer, both of which involve attachment of the proton to the associated base at some stage in the transfer process. These mechanisms are the so-called Grotthus mechanism, operative in both liquids and solids, and the vehicle mechanism, probably most important in solid acids. The first implies proton jump and molecular reorientation and so involves processes of rotation and transfer (translation). The vehicle mechanism has no proton transfer step, and translational diffusion of a proton carrying entity is the essential process. Characterisation of the decisive proton transfer step, when the proton is freed from one entity and passed to another, is a key problem in this area. ***With the availability of INS data over spectral ranges comparable to those in optical (infrared and Raman) spectroscopies, the methods have become truly complementary, and the combination of the information they provide is particularly suited to the identification of the nature of protonic entities in protonic conducting solids.***

In the case of proton insertion in transition metal oxide frameworks, ion exchange processes can also occur in addition to the redox reaction. *Here, other probe spectroscopic techniques, such as X-ray absorption near edge structure spectroscopy, (XANES) which allow change in the oxidation state of the metal ion to be followed, are essential complements to INS.*

5. Liquid state structure, dynamics and reactions

(Complementarity, computer simulation)

Neutron and x-ray diffraction methods have been successfully combined with modern computer simulation methods (molecular dynamics etc) to describe the structure of simple fluids. **The extent to which simulation methods and neutron inelastic scattering from such fluids has provided a basis for understanding the liquid state is the point of departure for an attempt to understand proton transfer and proton transfer reactions in disordered solids and in the liquid state where most chemistry occurs.**

Typically, it is always postulated for liquid state chemical reactions that in passing from the reagents to the products, the atom or atoms transferred must pass through some activated state of higher free energy than either. In the liquid state, this will require the relaxation of surrounding solvent molecules and possibly involve both translational and rotational displacements. The inability of the solvent to so relax for some systems is called the "cage effect" and in those cases, leads to particular types of reaction pathway.

Clearly a detailed knowledge of the local structure of ionic and aqueous solutions and of the molecular rotational and translational dynamics over distances of a few Angstroms and timescales of a few picoseconds is of fundamental importance

to an understanding of fluid state chemical reactions at an atomic level. Quasi-elastic and inelastic neutron scattering with the possibility of contrast variation, provide an avenue to do this as long as there is enough flux and resolution to make the necessary detailed measurements. There are strong indications that for many proton transfer reactions the rates are very high and at the Q-dependence of the scattering could allow differentiation of the scattering from chemical fluctuations from that of the host fluid.

Solution structure and dynamics

On the structural side, recent experiments at ISIS by Soper, Finney and colleagues on dimethyl sulphoxide-water solutions have produced maps showing the nearest neighbour water distribution at defined distances from the dimethyl sulphoxide molecule at the origin. Clustering around the methyl groups and the strong dipole of the sulphoxide group is apparent and differs from the, as expected, tetrahedral clustering of water around a central water molecule in the same solutions.

Chemical fluctuations

Recent QENS experiments on sulfuric acid solutions of various concentrations have provided evidence of a weak quasielastic component for those solutions of maximum specific conductivity which can, perhaps, be associated with high proton diffusivity. These results can be tested against those from NMR or tracer techniques. **The future availability of polarisation analysis for neutron quasi-elastic/inelastic scattering will add an important dimension to such work by providing access to a wider range of momentum transfer without the interference which currently arises from coherent elastic scattering.**

6. Zeolite synthesis and properties

(Nucleation and growth, site structure and dynamics)

An unusual chemical reaction, and one of great industrial importance, is the template induced synthesis of zeolites. An understanding of such template directed self assembly and of the nucleation and growth mechanism is central to the design and synthesis of new and useful zeolitic materials. These materials are the most widely used catalysts in the petroleum industry for cracking and reforming crude oil and in their various forms can act as solid acids, shape-selective micro-reactors and as support structures for a variety of transition metal ionic and cluster catalysts. Most recently, the molecular sieving properties of these materials have been greatly extended by the production of silicate, aluminosilicate and other mesoporous structures by the use of liquid crystal templates.

Small angle neutron scattering coupled with x-ray small angle scattering and NMR is becoming the method of choice for studying the kinetics of the hydrothermal reactions involved. The size range accessible by the method (10Å to ca.1000Å) is ideal

and the ability to change the state of deuteration of the template molecule or the solution so as to produce contrast as the zeolite nucleates is a key aspect. ***The case of template induced nucleation of ZSM-5 was the first of its kind and the methods have now been extended to the new mesoporous class of MCM-41 and related structures where the pore sizes are of the order of 41Å.***

"Aging" is a preliminary step which many of the patents specify as part of the synthesis. The nature and yield of the products formed in many preparations strongly depend upon the period between mixing reagents and the onset of heating to the reaction temperature. Neutron contrast variation methods have been used successfully to define the kinetics of nucleus growth and template incorporation there. ***Nuclei whose size increase from about a few unit cells to about 100Å have been observed in growth during in situ experiments and their scattering length densities have been measured. There could be major applications of these ideas in the next five to ten years.***

7. Dynamics of molecules in zeolites- NMR and neutrons

(Hydroxy groups and water molecules in aluminosilicate sodalites)

^{1}H MAS NMR and quasielastic neutron scattering
Aluminosilicate sodalites are characterised by a microporous framework composed of a perfectly periodic array of all-space filling [$4^6 6^8$] polyhedra ("sodalite cages") which are formed by an alternating network of corner-sharing SiO_4 and AlO_4 tetrahedra. The sodalite cages may accommodate various guest species, which in this study are represented by hydrogen dihydroxide anions (sample a), hydroxy groups (sample b), or water (sample c), and Na^+ cations. *The dynamics of the protonic guest species were studied by ^{1}H MAS NMR spectroscopy and quasielastic neutron scattering (QENS). It is shown that complementary information on different dynamic processes can be derived from the two techniques owing to their distinct characteristic time scales.*

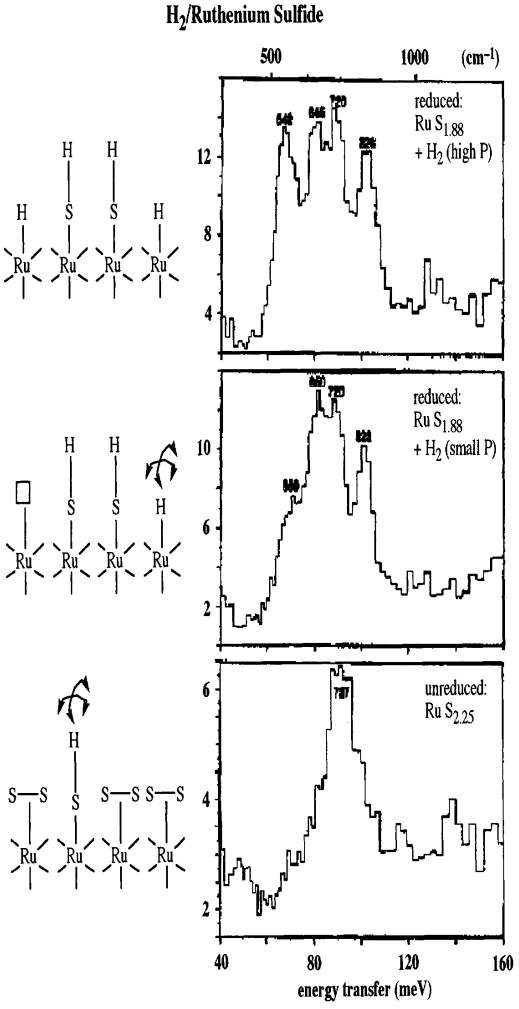
8. Catalytic sites and reactivity

(Identification of active species)
Transition metal sulphides, e.g. MoS_2 are efficient catalysts to remove sulphur compounds from crude petroleum. EU environmental legislation will require ever decreaing levels of sulphur and therefore improved catalyst performance. Such improvements depend on rational catalyst design based on an understanding of how the catalysts function.

It has been found that ruthenium sulphide RuS_2 is ~10 times more active than MoS_2 in hydrodesulphurisation and hydrogenation reactions. This could be due to the larger adsorption capacity of ruthenium sulphide or to the presence of different hydrogen species. INS, which is a sensitive technique to detect hydrogen, has been used to study the adsorption of H_2 on RuS_2 by changing the degree of reduction and the experimental conditions.

Since the integrated intensities of the bands are a direct measure of the populations of the various species, it appears that the reduction of the catalyst creates new SH groups: their intensity is three times larger in Figure 1(b) than in Figure 1(a). The shift to lower frequency observed for the SH modes after reduction, from 737 to ~ 683 cm^{-1}, indicates that the Brönsted acidity of the catalyst increases. The intensity of the 542 cm^{-1} peak correlates directly with the catalytic activity of the system.

It is therefore possible, using INS, to identify the different hydrogen species present on a catalyst, to determine their relative proportion and to follow changes according to the catalyst treatment. It is this weakly chemisorbed hydrogen which is the active species in catalytic reactions since its intensity in the INS spectrum directly correlates with the catalytic activity as measured in bulk specimens. *For other types of catalytic acive site EXAFS and combined EXAFS/SAXS/HIGH ANGLE diffraction methods have great value in characterisation and following the kinetics.*



ure 1: Incoherent neutron inelastic scattering at ious stages of the hydrogenation of a RuS_2 ydrosulphurisation catalyst

9. Electrochemical reactions

(Electrochemical principles, growth and structure of electroactive films)

The general philosophy of the work in electrochemistry is to make measurements under realistic circumstances, i.e. not compromising the electrochemical experiment when incorporating the neutron environment. The high penetration of neutrons makes this a realistic prospect, but more sophisticated design of electrochemical cells and of neutron delivery/detection at the electrode will be required. Issues of substance include making measurements *in situ* with the electrode under potential control and exposed to technologically relevant conditions (e.g. temperature and pressure).

Neutron and X-ray methods could contribute significantly in ways that complement, rather than compete with, existing approaches. It is worth noting that electrochemical methods are generally used to ask the question "*how much?*" (reactant consumption, via charge passed) and spectroscopic methods to ask "*what?*" (intermediate / product identification). ***An extremely important, but largely unaddressed, question is "where?". This might, for example, concern the spatial distribution of electroactive sites in a surface-confined film. Neutron reflectivity is ideally suited to answering such a question.***

2D & 3D Electrochemistry

One recent development at the electrochemical/surface science interface has been to study single crystal surfaces. Obvious areas for exploration include "buried" interfaces (for example in polymer or electroplated metal multilayer structures), distribution of electrocatalyst sites in polymeric or metal oxide matrices, characterisation of composites, penetration of intercalants (for example, Li^+ insertion into metal oxides in batteries).

Neutron reflectivity is presently providing extremely interesting data with high resolution perpendicular to the interface. Looking ahead, many opportunities would be presented by a technique able to provide data about the distribution in the electrode plane. **The opportunities involve features from tens of microns down to the molecular level, so one could envisage a continuum of interesting questions to be solved as instrumental improvements occur. Neutron off-specular reflectivity will be important here, and the combination of X-ray and neutron reflectivity.**

10. Spectrometers: INS spectrometers and neutron sources

An ideal spectrometer or spectrometer set for molecular spectroscopy should cover the whole energy-transfer range of diffusive and vibrational modes (at least from 10^{-6} to 500 meV). The instruments should continuously cover a large momentum transfer range in order to measure, for example, the maxima of intensity for oscillators with heavy and light masses. Extremely good statistics are required in order to measure simultaneously vibrations due to protons and other atoms. This

requires a dynamical range greater than ~ 100 and, therefore, statistical errors, background definition to be smaller than ~ 10^{-4}. **At the same time, high energy resolution better than ~ 1 cm^{-1}, at high energy transfers, is necessary to achieve reliable spectral profile analyses in condensed matter. Such spectrometry is not available at present and is not expected to be in the foreseeable future. However, any step in this direction should shed new light on vibrational dynamics.**

Advanced pulsed neutron sources providing intense fluxes of epithermal neutrons are well suited to vibrational spectroscopy at high energy transfer. **However, these spectrometers are limited by their detected fluxes and it is worthwhile to increase flux/statistics/resolution in order to obtain even better views of the various types of dynamics.**

To examine the Q dependence, spectrometers like the present MARI instrument at ISIS should be developed. MARI suffers from rather long counting times to obtain $S(Q,\omega)$ maps with statistics and resolution allowing for detailed profile analyses. Detected fluxes should be significantly increased with an increased number of detectors and attention to providing a wide range of resolution in energy and momentum space so that the spectrometer characteristics can be "tuned" to the problem, thereby gaining signal to noise. **There should be provision for polarisation analysis as a routine option to suppress coherent scattering from both liquids and solids samples and to provide new contrast options in diffraction and scattering, small angle scattering and reflectometry.**

Earth sciences

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Neutron scattering in the earth sciences

1. An overview

Neutron scattering has been developing into an important technique in the study of earth materials for a number of reasons:

• The cross-section for coherent scattering from hydrogen is in the same range as for the coherent scattering from other nuclei, whereas the scattering of X-rays from hydrogen is extremely weak. Since hydrogen is important in many minerals, it is essential that there is a diffraction technique that can detect hydrogen.

• The cross-section for incoherent scattering of neutrons by hydrogen is much larger than the coherent or incoherent cross sections for scattering from other nuclei. Incoherent scattering provides basic geometric and dynamic information about individual atoms. Thus incoherent neutron scattering is a tool that can be used to study the motions of hydrogen atoms or bare protons inside minerals. The types of motions include vibrational, rotational, or diffusion. Neutron scattering allows studies over length scales (of the order of nm) and time scales (of the order of ps) that are presently not available with other techniques.

• The fact that the scattering cross section for neutron scattering does not change with scattering vector, whereas with X-ray scattering it falls off with scattering vector more-or-less as the inverse of the atomic radius, means that it is possible to collect diffraction data to large scattering vector. This is useful for a number of reasons. First, for complicated crystal structures, such as many minerals, it allows a significant increase in the amount of information available in a diffraction pattern. Second, for information about thermal motion a wide coverage of scattering vector is essential. Third, to extract information about site occupancies, and to decouple this information from the thermal motion, it is again essential to have data over a wide range of scattering vectors.

• The fact that the scattering cross section does not simply scale with the atomic number (or number of electrons) as it does with X-ray scattering is extremely useful for studies involving cation ordering. In many minerals the important cations are isoelectronic, e.g. Mg^{2+}, Al^{3+} and Si^{4+}. Untangling the ordering of these cations by X-rays can only be achieved indirectly by the analysis of bond lengths, but these are not definitive since bond lengths are affected by factors other than the specific site occupancy. Neutron diffraction allows for the direct determination of site occupancies for these frequently coexisting cations in minerals. In the future this traditional

advantage may suffer the competition of anomalous X-ray scattering from synchrotron sources.

• The same fundamental property, makes neutrons extremely useful for studies involving atoms of very different atomic number. A problem with X-ray diffraction is that the scattering can be dominated by a few heavy atoms, and in these cases it can be extremely difficult to determine the positions of light atoms such as hydrogen, and even oxygen. Neutron scattering is frequently used to overcome this problem.

• Because neutrons have a magnetic dipole moment they can be scattered by magnetic ions. In physics this has probably been the most significant aspect of neutron scattering since the development of the technique. Neutron scattering will therefore always provide a tool for the study of magnetically ordered minerals or minerals with a spin-flip phase transition.

• Neutrons have often had an advantage over X-rays in that they are scattered by the bulk of a sample, whereas because X-rays are strongly absorbed they are basically scattered by the part of the sample near the surface. For example, in the study of phase transitions it has been found that the scattering from the surface can give significantly different results than from the bulk which has meant that the only meaningful results have come from neutron scattering. It is important to note, though, that with high energy X-rays from synchrotron sources this particular advantage of neutrons is not as significant as it once was.

• Neutrons are sensitive to both the length scales and time scales of atomic motions. One of the traditional tools of neutron scattering has been to investigate the dependence of vibrational frequencies on wave vector. With conventional X-ray sources it is not possible to obtain adequate energy resolution, and with spectroscopy using light it is not possible to obtain data over a range of scattering vectors. However, with synchrotron X-rays it is possible to improve the energy resolution so that inelastic spectroscopy with synchrotron X-rays may become a routine tool in the future.

2. Past and present

Complementarity of X-rays and neutrons

Because of the difference in the scattering cross-section and form factors, X-ray and neutron diffractions are traditionally regarded to be complementary in the structural studies of matter. Electronic versus nuclear interaction is the basis to evaluate charge bonding effects in crystal structures by X-N difference maps, and there is also general consensus that one cannot resolve fine vibrational effects such as anharmonic site motion using X-rays, because of scattering from the whole charge volume. Neutrons are therefore much more accurate when detailed studies of the crystal structure are needed, especially when seeking the temperature (and pressure) dependence of

structural parameters. Present high temperature X-ray studies commonly suffer from considerable inaccuracies in position and atomic displacement parameters. Important non-quenchable mineral structures can only be studied *in-situ* by neutron high-temperature diffraction because of fundamental and experimental impracticalities associated with the use of X-rays. Furthermore, X-rays can provide complementary information when detecting (n+1) ions over n sites.

Although very penetrating, when compared with X-rays, neutron beams are weak, hence the need for rather large samples (from a few tenths of a gram to several grams) whereas X-ray samples can now be as small as micrograms or even nanograms. This can be a great advantage for example in very high-pressure studies with the disadvantage, however, of not much "averaging".

Basic crystal-structural studies and cation ordering

The neutron nuclear cross-section and the angle independent scattering lengths of chemical elements made neutron diffraction the optimal choice of radiation in a number of structural studies beyond the limits posed by X-ray diffraction. The basic areas where neutrons have traditionally been strongly needed in the past are: the characterisation of light atoms in the presence of high Z elements (i.e. mostly H in H-bond studies, but also Li, Be, B ...), the characterisation of elements with similar Z (i.e. Si-Al, Fe-Mn, ...), studies of charge density distribution by X-N methods, and the characterisation of magnetic structures through the use of polarised neutron beams.

The low neutron absorption coefficients of many elements and the subsequent flexibility in the experimental geometry made it also possible to perform diffraction experiments in highly controlled environments (i.e. temperature, pressure, oxygen fugacity, etc.) while maintaining adequate resolution in a wide Q range. These peculiarities have been especially exploited in high-temperature and high-pressure powder studies using pulsed neutron beams. Areas of interest in the Earth Sciences are: equilibrium studies at high temperature or high pressure of intrasite cation partitioning (as the recent studies on olivine at high temperature have demonstrated), measurement of thermal expansion and compressibility coefficients, accurate measurement of site vibrational properties, including enharmonic components.

Phase transitions with temperature

i) High-resolution neutron diffraction

A phase transition invariably involves small changes in the crystal structure as a result of small symmetry-breaking displacements or atomic ordering. These can be studied with good accuracy by high-resolution neutron powder diffraction and the use of the Rietveld method. Recent examples include the displacive phase transitions in cristobalite and leucite. The simultaneous measurement of the crystal structure (atomic coordinates etc.) and lattice parameters allow for an accurate determination of the coupling between the phase transition and the lattice strain. Neutron powder

diffraction measurements of the structural changes occurring at phase transitions are presently the most accurate measurements possible.

Another type of phase transition involves changes in the chemical composition, and in the Earth Sciences one of the important changes is the dehydration process. Actually the fact that hydrogen has a large incoherent cross section can be exploited in dehydration studies, since the incoherent background in a powder diffraction experiment will give a direct measurement of the water content which can be correlated with the structural changes that occur during dehydration. This approach has been used in studies of dehydration of clays and analcime.

ii) Inelastic scattering

The vibrational properties of a mineral at a phase transition can be strongly dependent on temperature, not least because displacive phase transitions will involve a soft phonon whose frequency falls to zero at, or around, the transition temperature. There has been some work on minerals in this respect, most notably on quartz, but also on leucite, but rather more could be done. However, this is not a trivial exercise, as discussed below, and will require significantly more neutron beam intensity to make this a routine approach.

Aside from the soft mode, a phase transition can have other effects on the vibrational spectra. Recently some very new features were observed in calcite on heating towards the high-temperature order-disorder phase transition, which may be implicated in a coupling to a high-pressure phase transition.

Synthesis

Minerals are synthesised in order to better understand earth processes. Most natural rock-forming minerals (e.g. pyroxenes, micas, amphiboles, olivines, feldspars, and garnets) are solid solutions with complicated chemical compositions. In addition, natural phases have experienced complicated and poorly known geologic histories. There exists a need for compositionally simple, laboratory produced phases whose pressure-temperature histories are well known.

Mineral synthesis is necessary because for structural and chemical investigations earth scientists normally only have access to those minerals and rocks originating in the crust or uppermost mantle. In order to better understand deep earth processes, high pressure and temperature experiments must be undertaken or ultrahigh pressure materials must be synthesised for later study at room pressure. One of the largest obstacles in the application of neutrons to high pressure synthetic phases is in obtaining sufficient amounts of material for study or, conversely, high enough beam fluxes to perform the experiment on small amounts of material. The amount of material which can be obtained is inversely proportional to the synthesis pressures and for pressures above about 5 GPa normally only several tens of milligrams can be produced in a single experiment.

Phase transitions with pressure

Five years ago, neutron scattering data could be obtained only over a limited pressure range, 2-3 GPa at most, in practice. This is insufficient to explore the conditions of the earth's mantle. At present, neutron scattering methods, both elastic and inelastic can be used well above 10 GPa and, in the next few years, pressures above 30 GPa will be accessible.

Neutron scattering studies of constituents of the earth under high pressure adequately complement X-ray studies, and in a number of cases, offer unique possibilities which are not accessible with X-rays.

Since hydrogen is found in large quantities in the crust and mantle, an obvious target for high pressure neutron studies are the hydrous phases. The presence of H in the mantle's constituents profoundly modifies their properties, since it varies their melting points, their plastic properties and viscosity, and their structural properties through phase transitions, diffusion, transport, etc.. Only neutron scattering methods, preferably on deuterated samples, can provide precise information on the OH radical and its role in these physical and chemical modifications, through the study of the H(D) atoms location in minerals under adequate conditions of pressure and temperature.

Texture on monomineralic compounds

Texture is defined as orientation distribution of crystallites in polycrystalline material. Polycrystalline rocks constitute most of the crust and the mantle of the earth. The texture of geological material originates from complex physical processes during and after crystallisation, and it is caused by recrystallisation and deformations on a very large time scale. In looking backwards, texture is a fingerprint of the history of the material, which needs to be documented; looking forward, texture gives rise to anisotropies of physical properties to be correlated with geophysical phenomena.

Texture analysis of geological material is concerned with bulk material. Neutrons guarantee high grain statistics for reliable results also on coarse grained material. Complete pole figures are obtained by sample scanning in transmission geometry without the need of severe absorption corrections.

The application of neutron diffraction for texture investigations on geological material is increasing rapidly. During the past ten years the feasibility of quantitative neutron diffraction texture analysis has been demonstrated. Pioneering experiments have been performed to test and optimise pole figure scanning and data collection and to reduce measuring times by using position-sensitive detectors at steady-state reactor sources and to apply angle-dispersive time-of-flight techniques at pulsed sources. Dedicated texture instruments are operated in Dubna (IBR-2), Jülich (FRJ-2) and Geesthacht (FRG-2). The ROTAX-instrument at ISIS is just being reconstructed for pole figure measurements.

Past and present neutron diffraction texture studies on geological material, so far, are mainly confined to monomineralic systems: e.g. pyrite, chalcopyrite, quartzite, haematite, calcite and anorthosite. Studies are concerned with the documentation and understanding of natural deformation processes by comparing texture formations on the same minerals originating from different locations. Another approach consists of texture studies on originally undeformed samples, which are experimentally deformed in the laboratory under well defined conditions; resultant textures are compared to those of naturally deformed samples of the same mineral.

Vibrational spectroscopy

Within the Earth Sciences a concerted effort is being spent in obtaining a complete and quantitative data base for the thermodynamic properties (enthalpies of formation, third-law entropies, volumes) of rock-forming silicate minerals. This is necessary because many processes within the Earth can be explained or modelled using equilibrium thermodynamics. Vibrational spectroscopy offers the possibility to characterise the structural state and thermodynamic properties of a phase. Most thermodynamic data is derived from calorimetric and phase equilibrium experiments and relatively little vibrational spectroscopic measurements have been made on Earth Science materials. The field is, however, of great interest (see Reviews in Mineralogy vol. 18, Spectroscopic Methods, 1988) and is ripe for study.

i) Phonon dispersion curves

Measurements of phonon dispersion curves are critical in the study of interatomic forces in minerals as they contain significant information about the second derivative of the potential energy. Most empirical models of the interatomic potentials are derived from structure and elastic properties, which probe the first derivatives of the potential and the compressional force constants alone. Recent phonon dispersion curve data has been reported for quartz, corundum, forsterite, enstatite, leucite, calcite and pyrope. With complex systems, such as many minerals, these measurements are difficult since the neutron scattering is distributed amongst many vibrational modes, which causes the signal from any one phonon to be weak and also overlapping with that from other phonons. Accordingly some of these studies are rather incomplete, and other studies have focused only on measurements of the acoustic modes. It is unlikey with present sources and instruments that better data will be achieved.

ii) Phonon density of states

The phonon density of states contains rather less detailed information than measurements of dispersion curves, but there are cases when the information from a measurement of the density of states can be adequate. Examples are when the density of states is to be used for thermodynamic modelling, or when looking for changes in the vibrational spectra as a result of changes in the structure. An example of the latter is the dramatic demonstration of the large number of low-frequency modes in the high-temperature phase of cristobalite.

The ubiquitous occurrence of hydrogen in minerals, whether as part of a hydroxyl group or a water molecule, or as a free proton, allows for the measurement of the hydrogen component of the phonon density of states by incoherent neutron scattering. Recent work has been carried out on a number of minerals, including gypsum, bassinite, hydrated cordierite, and analcime. The spectra show considerable structure, and may be temperature dependent. At the present time there is no established theoretical method to analyse the data, but by comparing data obtained at different temperatures it is possible to draw definite conclusions about the formations of hydrogen bonds.

This work will be greatly helped by the development of a new spectrometer at ISIS, presently suggested as the 'MODES' concept. The MODES spectrometer will provide better resolution, that allows band-origins to be seen better at higher energy transfer which is important for measurements of high-frequency water vibrations and measurements in samples with only partial hydration.

iii) Low-energy spectroscopy by incoherent scattering

High-resolution low-energy measurements of the incoherent scattering from water molecules inside structural cavities provide information about the slow rotational dynamics. Two demonstration experiments have been carried out on analcime and cordierite, from which it was possible to deduce activation energies for reorientational motions. Unfortunately there is not yet the instrumentation for this to be a routine tool.

3. Immediate future

Diffuse scattering and total scattering

Conventional diffraction gives information about the average crystal structure, or equivalently the component of the crystal structure that has long-range order. In many cases the short-range order can be significantly different from that suggested by the long-range order. For example, defects can modulate a structure, and dynamic disorder can give rise to large fluctuating displacements of the atoms from their mean positions. The short-range order will give rise to diffuse scattering, which can be measured by single crystal diffraction, and in some cases can give rise to a significant background in a powder diffraction experiment. In the latter case, a measurement of the total scattering, S(Q), containing both the Bragg scattering and the diffuse scattering properly integrated over all energies, can be analysed to give detailed information about the short-range order. This work is very new in the Earth Sciences, although it has been applied to studies of highly-disordered ionic conducting oxides. Given the potential of this approach, it is likely to find many applications in studies in Earth Sciences. The most promising route to the analysis of S(Q) is the "Reverse Monte Carlo" method, although it is probable that considerable development is still necessary.

High pressure - high temperature studies

SiO_4 tetrahedra in silicates frequently exhibit subtle modifications under high pressure which involve slight rotations, which are best studied by neutron scattering. This is mostly true for complex structures where Rietveld refinement procedures must be applied. At the present time, earth scientists do not sufficiently take advantage of neutron scattering methods especially as regards the evolution under pressure of individual bond lengths which can be probed most effectively by neutron scattering. The chemical activity of minerals can be understood only if the bond lengths (Si-O, O-H, etc.) are known under pressure conditions representative of the various geological environments.

This will gather even more importance when high pressure-high temperature scattering becomes routinely available. The advantage of neutron methods in that field is that temperature may, in principle, be measured directly under pressure by introducing an adequate temperature calibrant, that is a heavy element (Hf, W, Ta) with suitable resonant absorption, the width of which is proportional to the absolute temperature and almost independent of pressure. This will be a unique opportunity of separately measuring pressure (NaCl calibrant) and temperature (resonant absorption) without resorting to thermocouples which are the weakest part of high pressure/high temperature set-ups.

Texture on multiphase systems

Neutron texture analysis of geological material can draw on the instrumental achievements and methodical developments of recent years. Substantial progress is to be expected for "real" geological systems, which are characterised by multiphase material of different mineral constituents of low structural symmetry. Aims of geological texture analysis are: (1) systematic investigations to study the development of different textures in different phases of natural geological material; (2) investigations on magnetic ores, e.g. haematite, magnetite and rare earth containing minerals, to study probable differences between magnetic and crystallographic textures; magnetisation relevant parameters can be obtained additionally from the depolarisation analysis of monochromatic neutrons penetrating ferromagnetic material; (3) conclusions from textures on finite strains when being referred to kinematics relevant features of the rocks like foliation and lineation; special textures are indications of tectonic transportation in the crust; (4) correlation between textures and anisotropy of physical properties, e.g. compressional and shear-wave sound velocities. The knowledge of the anisotropy of the different crust constituents is helpful for the simulation of synthetic seismograms, the calculation of thermal conductivity and the research of natural resources.

Study of melts

The approach outlined earlier on is effectively the same as that which has been used

for many years to study the atomic structures of glasses and fluids, whereby measurements of S(Q) are transformed to the pair distribution function g(r). It is worth noting that very little work, if any, has so far been carried out on measurements of S(Q) for silicate melts. The neutron instrumentation exists for this work, although the technology associated with the high temperatures necessary may not be current.

The current emphasis placed on understanding the physical, chemical and dynamical properties of silicate melts can be shown by the two recent short courses sponsored by the Mineralogical Society of America in 1994 and 1995 on these topics. Whereas many previous experiments have been undertaken on quenched glasses, investigations are being and will be directed in the future towards making experiments *in-situ* at high temperatures and at high pressures. One important issue will be the structure of the melt in the vicinity of a molecule of a "volatile component" such as water or CO_2. This is a very challenging prospect, and one that we believe is not possible with present sources and instrumentation. The role of neutrons, although hardly applied by earth scientists to address other fundamental questions (*e.g.* short-range structure, dynamic properties, diffusion) about melts, will be of great value. Total scattering experiments will certainly find many applications in the study of geologically important silicate melts although up to now little has been done.

For example, the determination of density and bulk modulus and its pressure derivatives for mantle phases and silicate melts is critical for the interpretation of seismic velocity profiles measured in the Earth by geophysicists. They are used in models which attempt to understand early Earth differentiation and Earth structure with depth. It has been shown in laboratory measurements that some silicate melts are more compressible than their equivalent crystalline materials and that at some elevated pressure a cross over point occurs such that melts will have a negative buoyancy and crystals will float. A rigorous microscopic explanation for this phenomenological observation has not been given.

Silicate melts are only found at temperatures above about 1100 C at 1atm. They are also chemically aggressive and it is necessary to enclose them in inert and robust containers. Neutrons, because of their great penetrating power, offer the possibility of studying the structure and dynamics of melts in environments that can be controlled with respect to thermodynamic conditions (T, f_{o2}, etc.). All of these aspects point to the need for *in situ* experiments at extreme P and T conditions. It would be possible, for example, to construct high pressure multianvil devices on neutron beam lines as already has been done at synchrotron sources.

Hydrous minerals

The role of hydroxyl groups in determining the structural properties and stability of hydrous silicates is of great interest for the understanding of large and small scale geological processes. Neutron scattering experiments offer the most logical

experimental tool because of the relatively large cross section afforded by hydrogen. Most structural work undertaken to date on these phases has been obtained from X-ray studies and a clear need exists for undertaking more neutron studies.

Specifically, a number of dense hydrous magnesium silicates (DHMS), which have to date only been synthesised in the laboratory, could, in addition, to natural phases such as pumpellyite, talc, mica, and amphibole, be important carriers of "water" within subduction zones into the mantle. The structures and more importantly the role of OH groups in the stability of these DHMS phases have not been elucidated. One problem facing such investigations lies in obtaining enough synthetic material for study. With regard to the study of all OH containing phases, synthetic material will also be required in order to obtain phases that are enriched in deuterium.

Further developments in this field of application are discussed in the sections on high pressure studies.

Mode Grüneisen gammas of minerals at HT-HP

Thermodynamic models of the Earth rely on the knowledge of the Grüneisen parameters of its constituents. Depending on the assumptions which are made, and on the object of the calculation, various definitions are adopted for this quantity which may be the Debye gamma, the Mie-Grüneisen gamma, the Debye-Brillouin, or Slater gammas, to cite only a few. This confusion may be removed by measuring the true mode gammas $\gamma i = \partial \ln \omega i / \partial \ln v$ for individual branches of the dispersion diagram of a given solid. This implies performing inelastic neutron scattering measurements on the relevant phonon branches under high pressure. This has recently been shown to be entirely feasible up to 10 GPa or more. In addition, it will be equally feasible to measure the full set of mode gammas at variable pressures and temperatures.

Recent experiments on the pressure-driven first order phase transition in Ge yield variations of the Grüneisen of 50% or more at a pre-transition value of pressure. This behaviour may be present in minerals exhibiting phase transitions with pressure therefore greatly modifying thermodynamic models of the Earth which utilise ambient (low) pressure values of γ.

4. More into the future: towards and beyond the year 2005

Hydrogen in nominally anhydrous minerals

Within the field of mineralogy much work has been done within the last five years on the incorporation of OH in anhydrous rock-forming minerals of the Earth's mantle (pyroxenes, garnets, olivines). Using newly developed single crystal FTIR spectroscopic methods, OH has been detected in many natural high pressure mantle minerals which were previously considered to be "water" free. The amounts are very small ranging from 1 to 1000 ppm, but when integrated over the whole mantle, they

are important within the water budget of the Earth and in influencing all properties of the mantle such as: the elastic and rheological properties (earthquakes, subduction, convection), the thermodynamic properties (melting, phase transitions), and also geochemical processes owing to the solvent-catalyst-aggressive properties of H_2O.

Much speculation is now centred on how many "oceans of water" are stored in such phases. Estimates vary greatly because the amounts and structural locations of OH in such minerals are simply not known. No neutron work along these lines has been carried out in spite of the important geologic implications, because present beam fluxes are too weak to obtain reliable results. Little is known, moreover, about the effect of pressure and temperature (20GPa, 1300K) on the stability or the equilibrium amounts of "water" incorporated in these phases. This is presently possible but the low H content of such minerals precludes neutron diffraction experiments with existing sources. A gain of 10 in flux and a further gain of 5 to 10 with improved instruments (diffractometers, detectors, data processing) will make it possible.

Quasielastic scattering

As mentioned above, the first experiments using quasielastic neutron scattering from the motions of water molecules in minerals have shown the potential for this method, but have also highlighted the shortcomings in the available neutron instrumentation. Whilst it would be possible to overcome these problems in the short-term for studies of hydrous minerals, for the study of the motions of water or hydroxyl molecules in nominally anhydrous minerals, or in samples (such as the high-density hydrated magnesium silicate phases) that cannot be synthesised in large quantities, a considerable increase in neutron beam flux and detected intensity is necessary. Moreover, quasielastic neutron scattering can also be used for the study of translational diffusion of hydrogen, particularly the proton. We have in mind the possibility of direct measurements of the proton diffusion in nominally anhydrous phases, where it is known that trace quantities of hydrogen can significantly alter the mechanical and other physical properties of a mineral. Indeed, neutron scattering will provide the most direct probe of proton diffusion, and with neutron scattering there is the possibility of *in-situ* studies.

In order to follow this ambitious route, it will be essential to have a considerable increase in the number of incident and detected neutrons.

Dynamic studies

Dynamic diffraction studies of phase transitions and reaction kinetics are nowadays almost totally performed with X-rays. Present neutron fluxes are much too weak to allow sufficient time discrimination in most cases. Only slow transformations can be addressed with neutron diffraction (sampling time of the order of seconds), whereas synchrotron X-rays already allow phase transitions to be easily studied with sampling times in the range of 10^{-2} - 10^{2} sec.

The field of non-equilibrium studies will therefore be dominated by X-ray diffraction in the near future. However increased neutron fluxes could bring many slow reactions of great importance in geological processes within reach of neutron experiments.

Texture on complex systems

Natural geological material is dirty in the sense that it contains contaminations of many phases and effects of a variety of geological processes to which it has been exposed during the course of its history. Many subtle effects have to be analysed requiring high precision neutron diffraction. Large series of individual samples from many locations have to be investigated demanding high intensities in order to obtain reasonable measuring times. Texture information is needed in correlation to macro- and microstrain analysis to establish nets of three dimensional strain ellipsoids of many crustal areas. Charts of crust profiles of new quality, i.e. with the consideration of texture and its anisotropy, are visions for the future. Neutron texture analysis of geological material can provide valuable information in the course of world-wide research programs in the Earth Sciences dealing with new resources, the danger estimation of earthquakes and the prevention or mitigation of huge economic and cultural losses.

Dilute solutions

Minor and trace elements play a crucial role in a number of natural processes, for example as important indicators of mineral genetic processes and of past environmental conditions, as strategic resources, or as hazardous pollutants. The characterisation of their structural and chemical role in crystals, amorphous materials, and fluids is vital in many areas of modern geosciences. Studies based on synchrotron X-rays (especially with EXAFS, XANES, and SRIXE) are increasingly being carried out to identify and characterise the local environment and the distribution of diluted elements in concentrations down to the ppm range. Since neutrons might offer great advantages in the evaluation of correlation functions in the study of melts and fluids, the application of neutron scattering experiments to natural solutions, glasses, and melts of different compositions is of great potential for the understanding of fluid properties and of the chemical role of selected elements in solution. The minimum accessible concentration of diluted species which one can study is directly related to the available neutron flux.

Water under mantle conditions

Fluid water under mantle conditions is a molten salt, $HO\text{-}H_3O^+$, which is isoelectronic to ammonium fluoride, $NH_4^+F^-$, and surely equally active chemically, and corrosive. Almost nothing is known about this fluid. Shock waves experiments have shown it to experience a conductivity increase from 10^{-7} ohmxcm at ambient to more than 10^{-1} ohmxcm at only 20 GPa and 900K. These conditions, which are typical of the upper mantle, are entirely accessible with present-day apparatus and *a fortiori* with the high pressure-high temperature set-ups which will be available ten years from now.

The chemical activity of H_2O is of course a fundamental problem *per se*, but it also is important to understand the phase relationships between presumably hydrous minerals of the deep-upper mantle such as β-wadsleyite and, possibly majorite or γ-ringwoodite. One important parameter to measure, in connection with other studies such as optical, Raman, or resistivity studies, is the structure of this molten salt.

Planetary materials

Light molecular compounds are important for fundamental physico-chemistry and planetology. These include mostly hydrogenous compounds such as CH_4, NH_3, H_2O, HF and H_2 itself. Also, the newly discovered "hydrides" such as $Ar(H_2)_2$, $(O_2)_3(H_2)_4$, or $(CH_4)_n(H_2O)_m$. The first four can be studied with the existing sources, but H_2 and the "hydrides" certainly cannot (complicated structures, very small volumes).

This is a challenge for a new source to measure the structural variations of such solids under high P/T conditions in order to describe their chemical properties and stability domains.

5. Applications: environmental and related issues

Natural hazards

The Earth Sciences have a special relationship with environmental issues involving such areas as natural hazards and the use of natural materials (*i.e.* resources). There are several key problems.

The accurate prediction of earthquakes and volcanic eruptions is a crucial area of Earth Science investigation. The impact of both on mankind is of obvious importance (consider the recent earthquake in Kobe, Japan or the eruption of Mt. St. Helens a few years back). In spite of the research that has been done in the area of prediction, it has not been possible to give exact information as to when either types of events will occur. Prediction is partially hindered because the mechanisms causing both are not fundamentally understood. There still exists, for example, relatively little understanding on how deep earthquakes occur. Several mechanisms have been proposed.

Rheological studies have focused on the deformational properties of silicates as a function of pressure, temperature, the presence or absence of a fluid and differential stress. High pressure experiments to study the conversion of olivine to β-Mg_2SiO_4 have been undertaken to understand the physical properties of subducting lithosphere. The metastable persistence of olivine beyond its equilibrium pressure stability, in relatively cool subducted slabs, followed by a sudden transition to β-Mg_2SiO_4 has been proposed as a mechanism for deep focus earthquakes. Neutrons can be used to clarify the mechanisms behind such phase transitions.

The dehydration of hydrous phases in cool subducting slabs undergoing compression and heating in the mantle has also been proposed as a possible mechanism for producing deep level earthquakes. Since neutrons are ideally suited for studying hydrogen in materials (see above), this question is ideally suited for future investigations at neutron facilities.

The prediction of volcanic eruptions is critically dependent upon an understanding of the rheological properties of magmas. It is well known that water is very important in controlling the viscosity of silicate melts, for example, and it is the viscosity of a magma that controls to a large degree the explosive nature of most eruptions. Research is needed to understand the mechanism of how protons act to depolymerise silicic melts and neutrons are ideally suited for such studies. An understanding of volcanic eruptions can only be obtained through fundamental studies on the physical and dynamical properties of silicate melts.

Quarries

Quarries producing huge rocks and stones mainly for building and arts purposes suffer from large amounts of waste of up to 70% of the total production due to small relaxation clefts not determined beforehand. Systematic texture investigations are needed to study connections between texture and the development of clefts in materials without preferred natural fissionability.

Preservation

Historical buildings and art monuments suffer from structural relaxation processes due to thermal strain in connection with atmospheric corrosion and pollution-driven reactions of the mineral constituents. Systematic texture investigations are needed to study correlations between texture and anisotropies of adsorption and moistening properties for preservation and impregnation purposes.

6. Research highlights for the future

Some of the most significant issues in the Earth Sciences are those related to the prediction of earthquakes and volcanic eruptions. The reliability of the relevant models largely depends on the knowledge of the physicochemical properties of the materials involved (oceanic crust, upper mantle, continental crust). First and foremost among these properties is the role of water in these materials and in the behaviour of magmas.

To draw an effective parallel, one may consider the problem of weather prediction based on atmospheric models. It is quite evident that present day prediction of up to five days was not even foreseeable two decades ago. As regards the prediction of earthquakes due to plate subduction, if and when it becomes possible, it will be entirely dependent on the accuracy of the models which have been constructed.

At the present time we can expect to obtain considerable knowledge in this direction, in part by the use of neutronics under mantle conditions. The only obstacle being the comparatively low flux of existing neutron sources.

Given the availability of a next generation neutron source, two possible key projects could be taken into consideration by the Earth Science community:

1. *The structural role of the hydrous component in hydrous and nominally anhydrous minerals under high pressure and temperature conditions representative of the Earth*'s *interior*.
This project would be of great interest to many fields of research in the areas of: mantle rheology, subduction, earthquakes, tectonophysics, etc..

2. *The structure and reactivity of multi-component melts and their relationships with the solid phase under pressure and temperature conditions representative of the Earth*'s *interior*.
This project would be of great interest for: magma rheology, volcanic activity, rocks and minerals genetics, and many other related fields.

Materials science

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1. Scope of materials science

In this working group materials science is seen as the scientific area which links solid state physics with materials engineering and technology. Unlike solid state physics, which mainly deals with the origin of certain physical properties such as magnetism, superconductivity microplasticity etc. of solids with given perfect crystal lattice structure, materials science is essentially concerned with the property control via microstructure. The latter comprises lattice point defects which are not in thermodynamic equilibrium, dislocations as one-dimensional defects, interphase boundaries and internal interfaces (grain boundaries) with associated interfacial energies as well as the vast group of three dimensional defects, e.g. cavities, microcracks, pores, voids, bubbles, precipitates or dispersoids.

It is the task of the materials scientist to analyse the microstructure and to elucidate the microstructure/property relationship with the ultimate goal of

- understanding the basic mechanisms
- tailoring materials for specific technological applications
- predicting the materials performance and life time, e. g. under severe service conditions (high-temperatures, applied stresses, hostile environment etc.)

As a most powerful microanalytical probe, neutron scattering has been used extensively to analyse - apart from dislocations - the various aforementioned microstructural constituents and their influence on the materials properties. It must, however, be pointed out that due to its complexity, a comprehensive analysis of the microstructure usually requires usage of complementary techniques such as X-ray scattering, transmission electron microscopy (TEM), scanning electron (SEM) and tunnel microscopy (STM). The same holds true for assessing the vortex structure in superconductors, and for magnetic structure analyses. For the latter, e.g. the Magneto-Optic Kerr Effect ('MOKE') has increasingly been used to complement neutron scattering techniques.

In contrast to composite materials as 'artificial materials', the microstructure of 'classical' materials (e.g. alloys) is usually optimised via thermo-mechanical treatments. These lead to the required dislocation microstructures, grain sizes, textures and dispersions of second phases. In this context, a better understanding of deformation, the kinetics of nucleation and growth of both grains and of second phase precipitation which involve diffusion of individual atoms, is of paramount interest. The elucidation of microstructure/property relationships requires a quantitative description of the microstructure and its evolution during processing as well as

formulation of micromechanical relationships. Unlike the final microstructure of 'classical' materials, the microstructure of composite materials (e.g. metal matrix, ceramic matrix, and polymer matrix composites) is usually no longer confined by thermodynamic constraints but rather by the chosen volume ratio of the constituents and the fabrication technology. The properties of composite materials for structural applications are often controlled by the structure and chemistry of the interface between the matrix and the reinforcing fibres or particulates, and by the likely associated residual stresses. This also holds true for artificially structured magnetic multilayers and for mismatching interfaces such as results from joining (welding, diffusion bonding) different materials. As artificial structuring offers a large potential for tailoring material properties, the analyses of interfacial structures will become increasingly important in materials science.

Accordingly, the current trend will continue for developing novel processing technologies such as

- powder metallurgy (P/M)
- mechanical alloying (M/A) or high energy ball milling
- molecular beam epitaxy (MBE)
- sputtering and laser ablation
- rapid solidification (R/S)
- sol-gel synthesis

leading to microstructures and related properties which cannot be obtained via conventional processing routes. In particular, the emerging new class of materials with nanocrystalline structure which can be synthesized via M/A, R/S or sol-gel must be mentioned.

2. Key areas where neutron scattering is useful or essential

In this section key areas in materials science and related problems are identified in which neutron scattering will be used as an important or even unique microanalytical probe. They have been classified according to the usage and functionality of materials.

2.1. Superconductors

As the key technique neutron diffraction has furnished insight into the atomic structure of high-temperature superconductors. From a determination of the oxygen sites and their occupancy with concentrations deviating from the stoichiometric one, a better understanding of the origin of superconductivity in high-T_c superconducting materials has been obtained. These will be used in μ-sensor devices as well as in junctions and contacts where the control of the interfaces is a crucial problem. For wire applications the critical current density is still not sufficient. Currently new

technologies are being developed for the fabrication of thin films with a pronounced texture in the coarse grained material. Neutron diffraction will be most useful for an analysis of the fabrication dependent texture and a correlation with the superconducting properties such as the critical fields and critical currents.

The latter requires a knowledge of the field-dependent vortex structure, which can be assessed by neutron scattering. In particular, in high magnetic fields neutron scattering is as unique for providing this piece of information as it will continue to be for precise structural analyses.

2.2 Magnetic materials

2.2.1. Magnetic structure analysis

Traditionally, neutron scattering was unique for carrying out ab initio magnetic structure analyses. In special cases synchrotron experiments can provide more detailed information, particularly when high Q-resolution is required. However, neutrons will remain the technique of choice for powders, and the invention of the CRYOPAD at ILL further enhances the capabilities of magnetic structure analysis. Neutrons can determine the spin and orbital components of the magnetic moment from form factor measurements. Alternatively, magnetic moments can be measured by the method of X-ray magnetic circular dichroism (XMCD). It should, however, be pointed out that neutrons are sensitive to the magnetic induction, whereas in the case of X-rays the orbital and spin contributions of the magnetic moments are to be combined to an atomic magnetic moment using sum rules. For rare-earth metals, the sum rules appear to hold fairly well, but for 3d metals they are not yet completely tested and there are notable cases where they do not work. We stress that X-ray techniques and neutrons are complementary to each other since they probe different quantities. Furthermore, there is experimental evidence that for thin and ultrathin films there may be problems with the sum rules in XMCD. Polarised Neutron Reflectivity (PNR) is important in this context since it yields the total moment with high accuracy. In the future, high neutron fluxes may allow form factor measurements for ultrathin films (see also below).

For the next 10-20 years, it can be foreseen that the bulk of magnetic structure analyses will be carried out by neutrons. For instance, artificial hard magnetic materials such as NdFeB magnets or recently developed nitride based materials are technically important and Polarised Neutron Diffraction (PND) can make a significant contribution in determining the bulk magnetic structure. Neutron diffraction can also be used to probe microstructures in technically important magnetic materials. The information size is at present on the order of $(1\ \mathrm{mm})^3$ which may be reduced to $(0.5\ \mathrm{mm})^3$ when higher fluxes become available. Neutron tomography can be used to determine ferromagnetic as well as antiferromagnetic domain structures with the same increase of spatial resolution.

2.2.2. Magnetic excitations

Measurements of spin wave excitations or magnon dispersions are important for providing exchange coupling constants. This information can then be used for technical applications such as magnet designs. For instance, the domain wall thickness depends on the competition between exchange energy and crystal anisotropy. Domain walls, in turn, determine the shape of magnetic hysteresis loops. Neutrons are and will be the only source of information on magnons dispersions.

Spin wave dispersions can be determined uniquely with neutron methods in bulk materials. Brillouin light scattering gives spin wave frequencies for small Q only, whereas ferromagnetic resonance (FMR) gives Q=0 spin wave frequencies. In sufficiently thick films (for example, typically >3nm for Fe) the volume-modes (standing waves across the film) can be used to determine the exchange constant J. In the future, with higher flux, spin wave measurements with neutrons may be possible in thin and ultrathin films.

2.2.3. Giant magnetoresistance (GMR) materials (spin valves and colossal MR materials), multilayers and ultrathin structures

There is growing interest in the fabrication and application of artificially structured thin magnetic films and multilayers. This interest is partly driven by the potential application of magnetic multilayers as magnetic field sensors in information storage devices and in moving mechanical parts. Aside from applications, there are fundamental issues to be addressed concerning the magnetic structure and disorder in magnetic films and at interfaces. From magnetic hysteresis measurements the magnetic structure in multilayers may be deduced in an indirect way. However, polarised neutron reflectivity studies are the only method to provide a complete analysis of the magnetic structure, including the coherence length of colinear and non-colinear spin structures in magnetic multilayers as well as magnetic disorder at buried interfaces. This information, derived from specular and off-specular polarised neutron reflectivity measurements, is instrumental for understanding the basic interaction mechanism (e.g. interlayer exchange coupling) in the magnetic multilayers and for optimisation of devices such as spin valves. Reflectivity experiments with polarised neutrons yield information only on the depth dependence of the magnetisation from the surface. The perpendicular component may, however, be determined by geometry known as grazing incidence surface scattering. This technique, well known in X-ray scattering, has been applied only in a few cases with neutrons. It is extremely flux limited, so makes a strong case for more flux.

In the case of thin magnetic layers PNR can determine the vector magnetisation profile perpendicular to the interfaces on an atomic scale given sufficiently high flux. This can be done in a layer of constant chemical composition. An example of the information that can be accessed is the interface polarisation which occurs in Fe/Pd and Co/Pd multilayers. The presence of the ferromagnetic Fe layer induces a

significant polarisation in the Pd layers which can be probed with PNR or ND. In contrast with XMCD, PNR with polarisation analysis (PA) determines the in-plane magnetic vector magnetisation profile. Magneto-optic Kerr effect (MOKE) or SQUID magnetometry can be used to determine the magnetisation reversal process in complementary experiments. In the absence of domain formation all components of the magnetisation are thus determined by PNR. Such information is important in spin valve and GMR multilayer structures but also for understanding exchange coupling and testing model predictions directly.

A key development made possible by increased flux will be that PNR can be extended to the Q range where atomic scale information becomes accessible (typically 0.1 - 1 $Å^{-1}$). Currently, measurements are limited to around 0.3 $Å^{-1}$.

2.3. Electronic and optical materials

This vast class of materials comprises semiconductors, materials for solar cells and photovoltaic applications as well as optoelectronic materials. From an economical point of view, this class of materials is the most important one. Nevertheless, apart from small-angle neutron scattering analyses (SANS) of oxygen precipitation in silicon, neutron scattering has found only little usage in this key area of materials science. No drastic changes of the present situation are currently foreseen.

2.4. Layers and coatings

Neutron reflectometry is a powerful tool for studying functional layers in electronic packaging. The gas adsorption process, e.g. of hydrogen, can be directly followed on a molecular scale and correlated with the characteristics of gas sensors. Neutron reflectivity studies will also provide access to analyses of submerged interfaces which are frequently associated with lubrication and adhesion phenomena. Here advantage is taken from the fact that unlike synchrotron radiation, neutrons are sensitive to light elements such as carbon, hydrogen and oxygen. The two latter elements also play an important role in corrosion, stress corrosion, and oxidation. The potential of neutron reflectometry for studying the kinetics of the oxide scale formation on a magnetic material was recently demonstrated. Nevertheless, neutron reflectometry and scattering have not yet been applied to their full potential in this area. This, however, is foreseen to be changed in the near future as annual losses of several billion dollars caused by oxidation, corrosion, wear and friction have prompted the intensive search for specific protective layers.

2.5. Structural materials

This broad class of materials which cannot be comprehensively dealt with in this report, is in millions of tons essentially used for engineering applications, e.g. building constructions, automotive bodies and engines, aeroplane fuselages and gas turbines, industrial gas turbines and power plants. It comprises alloys (steels, aluminium-,

nickel- or titanium-based) and polymers as the most heavily used structural materials but also engineering ceramics and artificially structured composites (see sect. 1.). Neutron scattering is essential or useful for characterisation of many microstructural aspects in these materials. A few examples will be given below.

The demand for light-weight high-temperature materials with improved fuel economy of engines and gas turbines has prompted intensive efforts to develop ceramics and intermetallic compounds, e.g. the titanium aluminides (γ-TiAl, α_2-Ti_3Al), which both offer high specific strength and stiffness at elevated temperatures but suffer from poor ductility and fracture toughness. For this reason, the processing of brittle materials requires a stringent quality control as their performance and life time is limited by the presence of flaws the size of which might be critical for instable crack growth to occur under an applied load. Typical critical flaw sizes in engineering ceramics and in intermetallics range from 2 to ~20€µm. Flaws in this size range with densities as low as 10^7 cm^{-3} can be assessed by means of high-resolution SANS experiments covering a Q-range from ~10^{-4} ² Q/nm^{-1} ² 10^{-1} as was recently demonstrated for liquid phase sintered alumina. Through variation of the neutron wavelengths, the multiple scattering effects blurring the SANS signals could be accounted for. It may be anticipated that neutron scattering will increasingly be used for following the densification process (sintering, hot isostatic pressing) and kinetics of brittle material processed via powder metallurgy, and for quality control. Another area where neutron scattering is being used extensively, is for measurements of internal strains/stresses and crystallographic textures. The main advantage of using neutron compared to standard X-rays relates to the high penetration power of neutrons in most structural materials. Therefore with neutrons, the average texture of bulk samples, and the complete strain tensor within selected volume elements in the bulk of a larger component can be determined non-destructively. The minimum size of these selected volumes for strain measurements is about 1 mm^3. A dream would be the possibility of reducing this size significantly to about 50x50x50µm^3 volume in the bulk of a larger sample, and still be able to measure the crystallographie orientation(s), the strain, and the phase composition. This would allow measurements of e.g. the movement of single selected nuclei/grain boundaries during annealing, local strains at inclusions such as particles or reinforcements, 3D grain boundary arrangements, and linebroading for determination of dislocation densities in the selected volume.

In principle, the information necessary for an understanding and modelling of plastic deformation, strain hardening, recrystallization and grain growth can also be gained from X-ray scattering using high-energy photons (> 100keV) from synchrotron sources, which penetrate deep in most materials. With the available high photon flux, very small volumes can be probed with the cross beam technique. However, due to the small diffraction angles of high-energy photons, the diffraction volume becomes highly elongated in the forward direction of the beam (e.g. 20 µm x 20 µm x 500 µm).

To what extent the elongated "needle" shape hampers solving the problems addressed above, at synchroton sources, depends on the specific problem under investigation. For most studies, however, a more cubic shape of the selected volume is essential. This renders neutron diffraction as being superior for such studies if the neutron flux at the sample position can be increased by a factor of ~50 compared with current facilities. Such an increased neutron flux would also allow time-dependent measurements of phase separation leading to precipitate microstructures.

2.6. Nuclear materials

Magnetic SANS complemented by high resolution TEM have provided insight into the fundamental mechanisms which lead to radiation-induced embrittlement of ferritic pressure vessel steels in light-water fission reactors.

Current efforts in developing fusion reactor technologies have prompted intensive studies on the response of various materials to the bombardment with 14 MeV neutrons and high-energy α-particles. Neutron scattering has already been used for analysing the precipitate microstructure in some steels which are considered as structural materials for the first wall of a fusion reactor.

2.7. Smart materials

Smart materials (e.g. shape memory alloys, piezo- and pyro-electric ceramics, non-linear optical and optically sensitive materials, field responsive polymers, liquid crystals) are not really smart but rather show responsive behaviour if an external variable such as temperature, stress, electric or magnetic field or light exposure is changed. This effect renders these materials the potential for being used in sensors, actuators, switching devices and displays. Apart from analysing the fundamental physics of martensitic transformations, which are relevant for shape memory alloys, neutron scattering has not yet been widely applied to this class of materials.

2.8. Ionic Materials

These materials will be used for energy storage devices such as batteries, fuel cells and electrolytic cells, and for gas sensors. Fast ion conductors are candidate electrolytes for high efficiency electrolytic cells. With incoherent inelastic neutron scattering it has become feasible to identify the most mobile ionic species, and to assess the characteristic length and time scales of the diffusion process involved. For such studies and for the determination of the hydrogen exchange in nickel batteries as well as of hydrogen adsorption on gas sensors neutron scattering is seen as a unique probe also in the future.

2.9. Nano- and microsized particles ('fine particles')

Materials made from compacted nanocrystalline powders (cf. sect. 1.) sometimes exhibit mechanical and magnetic properties which are quite different from those of their coarse-grained crystalline counterparts. They show e.g. much higher yield

strengths at low temperatures and already display superplastic behaviour at moderate temperatures. This feature can be used for near-net shape forming, even for nano-crystalline ceramics. As nano-crystalline materials and composites are fabricated via powder metallurgy, control of the powder compaction process and of retained sinter porosity and flaws is seen as an area where neutron scattering will be quite important (cf. sect. 2.5).Neutron scattering has already been successfully employed to investigate the diffusion of hydrogen in nano-crystalline metals and to elucidate the influence of the propensity of grain boundaries on the hydrogen mobility.

2.10. Inorganic biocompatible implant materials

Cobalt-based and titanium-based alloys are considered to be biocompatible and are heavily used as implant materials in hip and knee joint replacements. Hitherto, wear of the implants has been of major concern and has prompted the search for biocompatible wear-resistant coatings or protective layers. Even though neutron reflectometry is a powerful technique for layer and coating analyses (cf. sect. 2.4), it has not yet been applied to biomedical materials.

3. Experiments which need a higher neutron flux

With respect to the previous section, in this section some experiments are summarised which require a higher flux at the sample position than is currently available:

- Experiments aiming at studies of the dynamics.

These have often suffered from too low counting rates. This holds true if available samples are small (biomaterials, in single crystals of any new material), but in particular if the aim of the study is the time development of the dynamics, e.g. in the neighbourhood of phase transitions, a region where the soft-mode issue is most interesting.

- In-situ reflectometry to follow the growth of thin films and interface roughening (- sect. 2.2 and 2.4)
- Analyses of flaws and microcracks with μm-size ranges in brittle material by means of high-resolution SANS (- sect. 2.5 and 2.9)
- Selected volume diffraction for the determination of internal strains, grain orientation, and phases in a volume as small as that of a single grain (i.e. ~50 x 50 x 50 μm^3) (- sect. 2.5)
- Time resolved experiments to follow powder-densification processes with about a one minute time resolution (-sect. 2.5 and 2.9)
- Time resolved experiments to follow phase separation with a millisecond time resolution (-sect. 2.5)
- Industry-related studies.

With the present fluxes available, scattering experiments for solving industrial problems (e.g. process and quality control, 3-D strain mapping in engineering structures) often take too long to be employed as a routine technique by the industry.

4. Neutron scattering competing with X-Ray synchrotron scattering

In materials science various microscopic probes are used, as they often yield complementary information for the solution of scientific and technological problems (cf. sect. 1.). Amongst these neutron scattering has been and will be an important one. However, concurrently with technological progress and its associated needs for advanced materials and devices, novel microanalytical probes are developed and instantaneously used by the materials science community. Scanning tunnel and atomic force microscopy as well as synchrotron X-ray scattering fall into this category.

In the past, complementarity between neutrons and X-rays was based on the fact that they accessed different areas in Q-ω space with different resolution : X-rays provided good Q-resolution and extensive Q-coverage but essentially no information about time dependence. Neutrons could see magnetic induction, whereas X-rays could not. Neutrons measured in the bulk, whereas X-rays did not penetrate. This simple-minded definition of complementarity is clearly gone forever with the 3rd generation synchrotons. Now neutrons and X-rays can both provide time-dependence and both see magnetism (cf. sect. 2.2.). With the ability of high-energy photons (E ~ 100 keV) from synchroton sources, bulk analyses of thick-walled samples have become feasible. This in principle, allows structural materials and parts to be investigated with X-rays at, in fact, a much shorter time than with neutrons. As, however, pointed out in sect. 2.5 the volume from which the scattering information is gained is, due to their small scattering angle, needle shaped. This must be seen as a drawback for some studies.

Nevertheless, the interactions of neutrons and X-rays with matter will remain different: electromagnetic versus nuclear, relativistic versus non-relativistic. This, in general, will provide complementary information which will tell more then just a single technique.

Currently the following areas to which essentially neutron scattering has been applied hitherto, are seen to be challenged by X-ray scattering:

- Magnetic structure analyses
- MOKE magnetometry can complement the information yielded by PNR in thin magnetic film structures, providing magnetometric and domain imaging capability. However the spatial resolution is at best a fraction of a micron. In the bulk, magnetometry techniques and electron microscopy (e.g. Lorentz EM) are important.
- Residual stress and texture analyses

(high energy photons to be used)

- Phase separation kinetics

(Using anomalous X-ray scattering, unlike neutron scattering the chemistry of the precipitating phases can be analysed rendering this technique a potential one for studies of ternary and quaternary systems)

- Interfacial structures

(Using X-ray topography information can also be obtained of the dislocation structure in epitaxial and semi-coherent interfaces; cross-sectional high-resolution electron microscopy is also increasingly being applied in this area)

On the other hand, in low-energy inelastic scattering the neutron technique remains unique:

- Quasielastic scattering

Diffusion and local motions of atoms have been successfully studied using incoherent neutron scattering. Most of the systems were hydrogen containing compounds (organic as well as inorganic) or metals. The phenomena studied included all types of the motion as e.g. hydrogen diffusion and even tunnelling in metals, and rotations of molecules. More recently diffusion in metals and glasses has increasingly been studied. In future collective motions in biomolecules or glasses appear to emerge as an attractive subject. A better understanding of quasielastic coherent neutron scattering is needed, however, to achieve this goal.

- Inelastic studies

Dispersion relations of, for example, high-temperature superconductors or the soft-modes in refractory metals illustrating the phase stability of these materials.

5. Industrial use of neutron scattering

Industry is mostly interested in solving its actual problems, and to invest only in those projects for which a short-term pay-off might be expected. However, most of the problems in materials science which have been tackled in the past, and will be tackled in the future by neutron scattering, are in the pre-competitive phase of industrial development. This may explain why much money has not been spent by industry for neutron research.

In industry processing today, properties and functionality of materials and devices are increasingly developed and 'tailored' on the basis of modelling the microstructural evolution and its influence on properties and functionality of manufactured parts and devices. Many of these models which are nowadays (sometimes routinely) employed by industry have received input from or have been verified by neutron scattering. This fact is well recognised by industry. Therefore, the impact of neutron scattering on industrial applications must be seen as quite important though rather often indirect.

6. Resumé

The materials science group considers neutron scattering to remain an important microanalytical tool - in some areas still being unique - for solving materials science problems.

From the neutron scattering point of view, in the short term a higher flux at the sample position of instruments at existing sources is required allowing for

- accessing new phenomena (examples above)
- sampling of smaller volumes
- time-resolved kinetic experiments
- analyses of smaller samples
- better statistics and shorter measuring times
- more allocated beam time.

This could be achieved by

- improved instrumentation
- development and installation of novel neutron-optics devices.

This approach requires a joint co-operative effort of the various European neutron facilities. In the long term, a new neutron source with a higher flux is highly desirable.

Engineering

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1. Introduction

The discipline of engineering brings perspectives to bear on carrying out experiments and interpreting the results which are different to other scientific fields. These have an effect on how we view the present and the future and are worth summarising at the outset. The cost of production of engineered products and the cost penalty of shortened lifetime basically drive the need for engineering measurements rather than curiosity. The measurements need to be made rapidly, reliably and cost effectively and, if necessary, in a proprietary manner, in today's competitive business environment. There is a need for formal standardisation of measurement methods and of interpretation. A sensible distinction between engineering and materials science is that the former focuses on the engineering component per se rather than the detailed properties of the constituent materials. Of course, one uses all the tools of materials science to understand the behaviour. For engineering the equivalent of theory, such as the Heisenberg model in magnetism, is finite element modelling (FEM) utilising Newton's Laws, and constitutive equations which determine material response.

The geometry of the engineering component, designed to do a specific job, is usually what makes neutrons indispensable. For example a pipeline engineer would be interested in a girth weld in his 900 mm pipeline not in a 100 mm mock-up. Finally, neutron research does need to make an impact on society in order to survive and engineering provides a mechanism for this in the areas of cost, safety and reliability.

This report summarises the impact which neutron scattering has had and will have, in our view, on engineering. We cover the effect of small angle scattering on colloid and microstructural engineering. We cover the impact of diffraction on stress determination, plastic deformation, and fatigue and lifetime in components. We have included the intensity requirements for the near future and what will be required for the new fields which we think could develop, as well as the suitability of carrying out synchrotron X-ray studies in each area.

2. Engineering and colloids

The study of simple colloidal systems, which are characterised by a range of spatial inhomogeneities between 0.5 nm and 10 μm, by small angle scattering methods and reflectometry, is well advanced. The corresponding understanding is also advanced. However, measurements on real-world colloids with a view to process control and on the stabilisation of complex colloids, are in their infancy. The requirements of industry are to know the aggregation and dispersity as a function of temperature,

pressure, electric and magnetic fields, added surfactants, stabilising polymers and salts as well as different flow conditions. The neutron requirements to achieve this need are a wide Q range, particularly down to 5 x 10^{-4} $Å^{-1}$ to access μm length scales, and high fluxes. The SANS technique has to be used, rather than only SAXS, because contrast-matching with H and D is the way to pull out the density variations in the colloids. The incoherent background from hydrogen limits the precision of the measurements and this could be alleviated by the elimination of the nuclear spin-flip scattering with polarised neutrons. The present collection time over a wide Q-range is of order several hours, double with use of polarized neutrons. For kinetic studies to be useful, intensity gains of 1000 are required.

Two areas which will be expanded by industry in the near future are the characterisation of asphaltenes, the heaviest fractions of recovered production, and enhanced oil-recovery. Both areas are high cost areas, for which there is high pay-off if the right process conditions can be established. The interest is in oil, water and surfactant mixtures on quartz surfaces, or quartz and clay surfaces, at temperatures and pressures as high as 400°C and 1 kbar to model sandy oil reservoirs. The techniques of choice will be SANS and reflectometry.

3. Metallurgical microstructures

The earliest application of SANS was to clustering in metallic alloys. Neutrons are indispensable for examining the clustering behaviour of neighbouring elements in the periodic table such as FeCr alloys whose mechanical properties depend critically on concentration, and on magnetism. One important recent application was to the ageing of duplex steels used for elbows in the primary loop of light water nuclear reactors. The ferritic phase decomposes under irradiation and this causes mechanical embrittlement. The SANS experiment established the character of the embrittlement.

Several new fields of research are readily envisioned. It will be necessary to characterise damage caused by 14 MeV neutrons in materials and components for fusion reactors. Examples include the effect of irradiation on the brazed joints between molybdenum cooling pipes and their graphitic coatings for first-wall applications. Time-resolved measurements, such as the in-situ study of precipitation in the early stages of radiation damage by α-particles or electrons would greatly enhance our understanding of radiation effects. This field would require x10 increases in flux, but with the right elements could be done with synchrotron X-rays. As yet, scanning the inhomogeneities on a scale, for example of 0.5 mm, in a sample has not been carried out and would be of great importance for welded structures.

4. Engineering stresses

The residual stresses encountered in a component which is not subject to an external

stress are divided into three categories labelled I, II and III. Type I stresses can be identified with a macroscopic stress field such as that extending several cm from a weld. Type II, or intergranular stresses, are those stresses which vary over the length of the grain size in the polycrystalline aggregate. They occur because of the different thermal properties, such as coefficient of expansion, and the different elastic and plastic properties of the grains. Type III stresses are associated with individual dislocations within each grain. Both Type I and Type II stresses have engineering consequences of their own with respect to the lifetime or failure of components. However, the effects which generate stress fields also generate the intergranular differential effects among the grains and these are therefore superposed. Diffraction techniques are the method of choice for non-destructive measurements and neutron diffraction has had a clear advantage up to the present for depth profiling. There will, however, now be a number of measurements which can be made by synchrotron X-rays, equally good or better. The interpretation of residual stress measurements, made on particular (hkl) reflections, is imperfect principally because of the superposition of intergranular and macroscopic effects, but our understanding is moving quickly in this area.

4.1 Type I stresses

It is interesting to note that a portable 160 keV X-ray source is now available for high energy X-ray measurements out in the field with a penetration of 10 mm in steel. While measurements at this depth take several hours, the equipment is not yet optimised and will at the very least, provide a screening test for which components have to be examined with neutrons.

Many examples of tests on components now exist, utilising measurement volume sizes ranging from 0.1 mm^3 in rivets and steam generator tubing to several tens of mm^3 in large section girth welds and critical aircraft parts. The three following tests are typical of this developing field. Measurements have been made in the as-welded and heat-treated condition of a Ti90Al6V4 cylindrical rotor of diameter 35 cm and thickness 8.2 mm. The area of high stress is close to the weld and the hoop component possesses the largest magnitude. Because of the intention to measure the stresses after simulated use, destructive techniques were ruled out. Two of the strain components might have been obtained by synchrotron X-rays, but the radial component cannot. Secondly, very few examples exist at present of attempted full macroscopic stress tensor measurements. One recent case, where austenitic and ferritic parts are joined by friction welding, required the full tensor. The material, interestingly, cannot be heat treated because the different coefficients of expansion always build in thermal stresses. The object of the experiment was to benchmark FEM calculations on the same piece. The experiment was driven by the realisation that if the residual stress is unknown, the engineer has to assume that it is at yield and this leads to conservative and costly designing.

One spectacular recent advance illustrates how systematic studies of components can open up a completely new industrial field, in this case the non-destructive determination of remaining lifetime in turbine blades. The high temperature stability of single crystal γ–γ' turbine blades depends on the near coherency of lattice planes in the γ phase, an f.c.c, NiCr matrix, and cuboidal inclusions of the γ' phase, simple cubic Ni3Al,Ti. With high temperature use there is a chemical redistribution of minority elements as well as a strain effect which change the lattice spacing and destroy the coherency. The gradual splitting of an initially barely-resolved double peak, see Fig. 1., is a non-destructive measure of the blade's lifetime with entrained safety and economic consequences. X-rays were not used because the peaks are masked by oxide contamination on the surface after high temperature exposure.

A number of exciting new applications can be envisioned in the near future. It will be relatively straightforward to carry out in-situ heat treating experiments to optimise thermal treatment. In particular, measurements of case-hardened components in nitriding or carburising atmospheres could be carried out. This requires good time resolution to follow the process, good spatial resolution to look near the surface and good angle/time resolution to resolve developing minor phases. All these call for higher fluxes, at least a factor of ten greater than presently available. Difficult problems arise in stress measurements when the grains are large, say of order 0.2 mm or larger. We envision using neutron light pipes to compress the neutron beam. Since the aim is to examine the grains one by one, the worsened angular divergence would not be too serious a disadvantage. There is a need for mapping the stress, as well as the grain orientation, in large forgings with a measuring volume of a few mm on a side. When forgings containing stresses are machined, the re-equilibration of the stresses makes the machined parts distort. Likewise, the grain orientation, the texture, affects all the mechanical properties. As yet, texture has not been incorporated into finite element models of forgings, but we are confident that this will happen in due course. The driving force for this kind of field is elimination of waste. One world-class enterprise discards 25 M $ of materials per year because it is not up to specifications as regards mechanical properties. Currently, it would take about 36 hours at a high flux source to scan a complete 15 x 15 x 50 cm^3 aluminium forging, and to be useful flux increases of ten or more need to be made. A forging of this size would not be readily scanned with synchrotron X-rays.

To make full tensor measurements of stress at a particular location requires many more than the minimum of six measurements because of the experimental uncertainty of each value. To make this approach practical we require increases in flux of at least 3. A number of applications, all of which require small measuring volumes, will have a strong engineering impact. These include rivet stress fields, surface and interface stresses, thermal barrier coatings and mapping of crack fields where a gauge section of 0.1 x 0.1 mm would be ideal. For these cases increases of a factor 10 in flux would make the measurements routine.

4.2. Type II stresses

The field of intergranular stress measurement is about 10 years old. Originally experiments were carried out on metal-matrix composites, such Al:SiC, ceramic composites such as Al_2O_3:SiC and zirconium alloys, in order to obtain the average stresses in the respective phases or crystallographic directions. The drive to measure intergranular stresses in zirconium alloys, for example, comes from the fact that creep and growth in a radiation environment strongly depend on the texture and the stress. Recently, emphasis has been placed on the effects of thermomechanical treatment such as extrusion, rolling or creep loading. It is fair to say that our present understanding is imperfect and that the science aspects will represent a growing field. However, it is likely that most of these experiments can be done equally well with neutrons and synchrotron x-rays.

An interesting field is developing in ceramic multilayers such as Al_2O_3:ZrO_2 which can be used for burner casings in the exit chambers of jet-engines. These multilayers have a resistance of crack growth because of the stress distribution through them. Coatings on more conventional structural materials, designed for wear or to resist high temperatures, are also examples of composite systems.

There have only been three or four examples of incorporating composite materials into engineering components, but one new and exciting development was the study of Type I and Type II stresses in a prototype turbine disc. Here the emphasis was on replacing a cylindrical Ti turbine disc by a ring of Ti with a buried Ti:SiC ring element and thereby reducing the weight of the structure by nearly 50%. The macrostress field associated with the different effective coefficient of expansion of the Ti:SiC and the Ti was observed. The geometry would have prohibited investigation with synchrotron X-rays.

5. Plasticity

The plastic deformation of the grains in a polycrystalline aggregate is anisotropic, depending on dislocation movement along particular directions in the slip plane, such as the [110] direction in the (111) plane for f.c.c. materials. Different crystallographic orientations of grains distort differently under load. The inhomogeneous deformation on the scale of grain size is at the origin of type II stresses. Slip also causes realignment of the grains and hence changes the texture. The measurement of texture and type II strains are the principal tools for investigating the correctness of polycrystalline models of plasticity at the level of the grain behaviour which are central to the understanding of stress measurements. Eventually the polycrystalline models, refined by comparison with experiment, will be incorporated into the constitutive equations describing material response as a function of time and position, which are used to model component behaviour in FEM models. The collection of complete stress maps as a function of sample orientation will be important for comparison with the polycrystalline models.

One direct engineering significance of plastic deformation is that it can be a measure of the remaining lifetime of a component so importance is placed on non-destructive measures of plasticity. There is a strong logarithmic correlation between plastic deformation and diffraction peak linewidth, and a linear correlation between diffracted peak intensity of selected peaks and plastic deformation in high strength steels for example.

6. Fatigue

Fatigue is the repeated loading of a structure and there are two regimes, one with a high number of cycles at a low load compared with the yield point, and one with a low number of cycles at a load approaching or exceeding the yield point. On an aircraft, old rivet holes are treated to produce compressive hoop stresses which resist radial crack growth. High cycle fatigue gradually lowers this beneficial residual stress. The residual stress is in this case the probe of fatigue and the technique of choice is neutron diffraction for measurements at depth. Since the stress field is limited to the vicinity of the rivet hole, detailed mapping requires smaller measuring volumes and consequently flux increases of up to a factor of 10. When residual strains are absent, it is very difficult to assess the effects of fatigue experimentally. The mechanisms of the effect of fatigue on residual strain are not yet quantitatively understood. It was recently shown that the mosaic spread of single crystal turbine blades is a linear function of the plastic deformation to which it has been subjected in low cycle fatigue. This observation again provides a non-destructive tool to measure accumulated damage and hence lifetime in turbine blades. Very few neutron experiments have been reported in the area of fatigue and the field is ripe for development because of its engineering significance.

7. Future applications

A number of future developments were identified and these are given in Table 1.

They include experimental improvements, new field developments, and organisational ideas to benefit the field of engineering. Each suggestion is given a rating in terms of importance and achievability on a scale of 1 to 5 and the flux increase necessary for routine use is estimated where appropriate.

Table 1

Topic	Importance	Achievability	Flux Increase Requirement
Digitised sample boundary measurement	5	5	
Multiple simultaneous strain direction measurement	5	5	
Hazardous sample "blockhouse"	4	4	
Standards and accreditation	5	4	
Neutron workshop for engineers	5	4	
One pulse measurements with Bragg edges	3	5	5
One pulse measurements with scattered beam	5	1	1000
100 x 100 x 100 μm^3 sampling volume with light pipes	3	2	100
In-situ engine studies, stress temperature	5	3	1000
In-situ welding	5	2	100
In-situ cutting	4	2	100
In-situ stress-relieving	3	5	10
In-situ powder processing (sintering part)	2	3	
In-situ processing & drawing	5	1	
Fatigue studies (strobing)	5	4	10
Rotating machinery	4	5	10
Texture mapping	4	4	10
Explosives (deterioration & crevice detection)	4	2	10
Biomaterials	3	1	10
Neutron Tomography	3	5	10

8. Attenuation lengths for neutrons and synchrotron X-rays

The attenuation lengths for 1.5 Å neutrons and 0.07 Å (177 keV) synchrotron X-rays, which represent typical wavelengths used for stress measurements, are given in Table 2. The neutron attenuation was calculated from the sum of scattering and absorption cross-sections with no account taken of Bragg edges. The X-ray attenuation takes account of the photoelectric effect, incoherent scattering and pair production.

Table 2

Element	neutron attenuation length (cm)	X-ray attenuation length (cm)
Al	9.8	2.9
Ti	1.9	1.6
Fe	0.9	0.8
Ni	0.5	0.6
Zr	3.5	0.6

From Table 2 it is readily seen that, with the exception of Al and Zr, the geometry of the component rather than the elemental composition is what determines the suitability of neutrons or X-rays for strain measurements.

9. Conclusions

The use of neutrons in engineering is still a young field and many factors, particularly the speed and ease of measurement and the standardisation of the technique must be addressed before there is widespread acceptance in the engineering community. We have described cases where neutrons have made a real impact and can see areas which will open up in the future. Some experiments, such as those on small samples, can be done on general purpose instruments. Often these may also be done with synchrotron X-rays.

However, where bulky tensile test equipment, or large furnaces or ancillary machinery is needed, or where irregularly shaped or large or heavy products are tested, it is clear that a specialised engineering spectrometer is needed. It will be a

challenge to increase the cost efficiency, to minimise the set-up time and meet the needs and budget of the engineering community.

Fig. 1: Diffraction peak profile before and after creep deformation in turbine blade material

Further applications of neutrons

This report has focused almost entirely on uses of neutrons in scattering experiments. However, as is well known, the early reactors were not developed for these reasons, and the usefulness of neutron beams was not really recognised in so far as the construction of dedicated sources until the 1960's. Neutron sources have had an enormous impact on our lives quite apart from neutron scattering. The production of isotopes, the field of nuclear medicine, neutron radiography, and neutron activation analysis are all examples of important uses of neutrons that do not involve scattering. (We omit the generation of power from this list as it is strictly connected with the fission process, not the production of neutrons. Unlike a reactor, a spallation source cannot be a source of energy, even though it produces neutrons.)

This workshop did not attempt to address these many uses of neutrons in a comprehensive way, but we have collected here a number of points so that this aspect of the use of neutrons is not forgotten.

Applied physics and engineering

We have identified four different areas of technical applications of neutrons, which are listed in Table 1, together with their subtopics. Some additional comments will be made on some of these topics.

The use of neutrons in radiography has some advantages over X-rays. Neutrons, and especially fast neutrons, are more penetrating than X-rays. They are also sensitive to the light elements, in particular to hydrogen, and unlike X-rays, they can easily distinguish between elements which are neighbours in the periodic table. Neutron radiography has been used for the destructionless testing of weldings and bonds, the investigation of concrete solidification, of micro-fractures in materials, as well as for real time investigation of the distribution of lubricants in running machines, or of the boiling of liquids in tubes or vessels.

Neutron radiography has recently been further developed to what is called neutron tomography. With neutron tomography one can obtain 3-dimensional images with ~100 μm resolution, for instance of the inner parts of small mechanical or electrical devices.

The competing method of radiography with synchrotron radiation has seen huge progress recently. With synchroton angiography methods one can even obtain images which distinguish between different elements. Also, with fast neutrons one could very easily do element sensitive tomography; unfortunately, though, this has not yet been done.

Table 1

Topics in Applied Physics and Engineering

1. **Structure Analysis**
   Radiography
   3-D tomography
* [Diffractometry]

2. **Element Analysis**
   Neutron activation analysis (in-pile)
   Prompt activation analysis
   Neutron autoradiography
   Depth profiles

3. **Structure Modification**
   Medical radiation therapy
   Material tests under (low temperature) irradiation
   Defect creation and amorphisation
   Sterilisation

4. **Element Transmutation**
   Transmutation doping
   Isotope production
   Cross-section measurements
   Radiochemistry
   Waste incineration and clean energy production

* this promising field of industrial application will be described in a separate survey.

Trace analysis after in-pile neutron activation is the most widespread technical application of neutrons. At some small research reactors, some 10^4 probes per year are analysed alone for the environmental public services. Other applications are in medicine, geology, criminology, history of arts, archaeology, in the analysis of sophisticated materials, and, increasingly, for quality assurance purposes.

Depending on the isotope, the method is sensitive to concentrations better than 10^{-10}, in special cases it might be possible to detect traces down to 10^{-15}. The advantages of the method are that no impurities are added to the sample during analysis, that it tests the whole volume of the sample, that it is destruction free, that it detects elements whose presence in the sample may not have been suspected, and that it gives an absolute measure of concentration. Results are independent of the chemical state of

the element tested, and are available within hours. The method, however, is used mainly for the analysis of the heavier elements.

The method of in-beam prompt activation analysis also has a large potential, but has not yet been used widely. With this method, the activation of the sample is carried out in a neutron beam outside a reactor. Powerful coincidence techniques using prompt γ and/or electron-rays are possible. With large solid angle γ-detectors, customary now in nuclear spectroscopy, high sensitivities could be reached. The method is especially useful for the detection of the light elements, in particular of hydrogen, for which many competing methods are not available. Using a scanning microfocussed neutron beam, space resolved element analysis can also be envisaged.

It should also be possible to combine prompt neutron activation analysis with the foregoing neutron-radiography methods, by using position sensitive detectors and vertex reconstruction methods, in use in many fields of physics and medicine.

In neutron autoradiography, two dimensional images are obtained by irradiation of photoplates after neutron activation. The method has very successfully been applied to problems of art history. The method would profit from the use of position-sensitive electron detectors for image formation, in coincidence with large (not position sensitive) γ-detectors for fingerprinting the elements, in order to obtain truly element resolved images.

Since the early eighties, silicon transmutation doping has found increasing use in the production of high-power electronic chips. Today, 150 tons of doped silicon are produced annually with this method.

An important case of isotope production, besides the widespread use of isotopes in science and in medical diagnostics and therapy, is the production of ^{3}He, which is used widely in low temperature physics. The production of ^{3}He can only be carried out at powerful neutron irradiation facilities.

In the institutes for radiochemistry, among other things, training in the handling of highly radioactive material is carried out, usually on a research reactor. The training of future specialists in this field is important for the handling of existing nuclear waste.

Finally, there exist proposals to transform long-lived nuclear waste into short-lived waste by irradiation in a very intense neutron field, possibly with a large net gain in energy in a completely closed cycle. The feasibility of this proposition is still under discussion. There exist further projects to transform existing long-lived isotopes into short-lived ones via low lying nuclear levels which can be specifically excited in the strong radiation field, suitably tailored, of a nuclear reactor. For this purpose more detailed spectroscopic studies of the isotopes in question are needed.

For completeness, we mention some other neutron capture methods used in applied solid state physics. With in-beam nuclear magnetic resonance with ß-radiation detection (β-NMR), only very few probe nuclei need to be present at a time in the sample (classical NMR needs about 10^{18} nuclei to detect a signal). This method has powerful capabilities, and was used for instance for the determination of the structure and annealing properties of various defects in silicon lattices. In-beam perturbed angular correlations and in-beam Mössbauer effect can also be used with neutron activated probes. The Mössbauer effect, for instance, is being used routinely for the study of archaeological samples after neutron activation. Finally, with recently developed methods of high resolution gamma ray spectroscopy, one can study the interaction between atoms in condensed matter on a time-scale of nanoseconds.

Potentially, in the fields of engineering and technological development, neutrons have a wider range of application than X-rays have for instance. The principle disadvantage of neutrons is that they are not easily available. Therefore, for many powerful neutron methods there exist only proofs of feasibility, sometimes followed by sporadic applications. Also, the scientists involved in this work often turn back to their own science and will not develop these methods further for routine applications. So, many of the possible fields of technical and industrial neutron application have been dormant during the past decades. While many of the powerful new nuclear imaging methods have found wide use for instance in medicine, only a few have made their way into neutron physics. There seems to lie a large underexplored field for industrial uses of the neutron.

Appendix A

Invitation letter for workshop

ESF Workshop in co-operation with the European Neutron Scattering Association (ENSA) on "Scientific Prospects for Neutron Scattering with Present and Future Sources"
Autrans, France, 11-14 January 1996

Strasbourg/Grenoble, 2 November 1995

Dear Colleague,

Thank you for agreeing to participate in this Workshop of the European Science Foundation. Together with the Organising Committee, we appreciate that you are prepared to devote your valuable time to this ambitious scientific-strategic endeavour. You have already been contacted by the respective Group Leaders of the Workshop. This letter is to provide you with more information.

Background to the Workshop

The European Science Foundation is increasingly being approached from the multi-disciplinary R&D community in Europe with requests that it should investigate, evaluate, or promote the scientific-strategic case for proposals or projects for possible future large-scale facilities for the use of basic and applied R&TD in Europe (for example, *a "Next-generation European neutron source", a "European laboratory for electrons", a"European social data base", a "European laboratory for 100 Tesla science")*. Due to the economic difficulties faced by all European communities and the decreasing resources available for large facilities (as for basic R&TD in Europe), there is a need for expert advice from an independent multi-disciplinary institution such as the European Science Foundation which supports all scientific disciplines.

A particular undertaking by the Foundation is the *'European Neutron Source Studies - Task (A)'* which is devoted to the evaluation of the scientific-strategic prospects of neutron methods and of neutron sources for basic and applied R&TD in Europe, in the fields of physical, technical, and life sciences. (This activity is also the envelope for the more specific 'Task B', under which the Foundation supports the investigation of the scientific case of a next-generation spallation neutron source.) The most important event will be the *ESF Workshop on "Scientific Prospects for Neutron Scattering with Present and Future* Sources", for R&TD in Europe on physical, chemical, technical, or

biological matter and materials, in the atomistic, molecular, or crystallographic dimension. The Workshop will be held in Autrans near Grenoble, site of the ILL and the ESRF. It is being organised in cooperation with the European Neutron Scattering Association (ENSA), financed by the ESF, with additional support from the ILL and from the EC/DG-XIIS.

Scope of the Workshop

This Workshop should provide an independent assessment of the following points:

Ten year forward look at the mid-term perspectives and opportunities feasible for matter research using neutron scattering methods and the existing neutron facilities in Europe, taking into account the impact of X-ray synchrotrons and other advanced techniques.

Forward look beyond 2005. What will be the role of the present sources at that time, and can a need be envisaged for "new" sources"?

Evaluation of "new frontiers in neutron scattering" with appropriate participation from technological and industrial laboratories.

Workshop Format

The Workshop will consist of 10 working groups, each with ~8 people. A complete list of all the groups (as presently composed) is enclosed with this letter. The Workshop will last for 3 full days. The first 2 ½ days will be for articulating statements on the general points listed above. On the final ½ day there will be an open panel discussion of the resultant issues. This will be chaired by Professor H. Curien, former French Minister of Research and Space and past-President of the ESF.

There will be an opportunity for different working groups to meet together. There are no rules as to how to operate - but we want to maximise effectiveness, and minimise gaps in subject matter.

Workshop Report

The findings of the Workshop will result in an ESF report. It should not be longer than ~100 pages, or ~10 pages per working group. The manuscript must be ready by march 1996. This deadline relates to the scheduled planning discussions for the next EU Framework Programme.

Relationship with activities focused on the ESS

Many of you will be aware that there is considerable activity connected with initial studies for the European Spallation Source project (ESS) mentioned in the introduc-

tion. Our Workshop is complementary to these activities. It is vital that we should remember that our task is connected to "Science with neutrons". We are not concerned with moderator/instrument/detector design. We are not concerned with a lengthy discussion on steady-state versus pulsed sources. We are concerned with how neutrons will answer some of the important scientific and technological questions of today and the future, and we must be aware of the advancing capabilities of other techniques. Furthermore, we should comment on whether or not we believe that in the long term neutrons can further increase their impact on various scientific fields, and whether this leads us to consider the need for a next-generation source.

Advance preparation

Because the Workshop is short - only 3 days - it is vital that you do some preparation in advance. The Group Leaders need to assemble by 1 December a list of subjects that will be discussed in Autrans in their Group. To meet this deadline, and the overall ambitious goals of the Workshop, we ask you to reply to your Group Leader and focus on the following points:

- Past achievements with neutrons
- Important experiments in the future, new problems and areas that can be addressed
- What could be done with more flux? Or with new methods?
- What could better be done with other methods, e.g. X-rays?
- Industrial applications?

It is important that you discuss these points with other colleagues to get a broad input into the Workshop.

Administrative matters

We will be sending a registration form to you with details. Meanwhile, here are a few important points.

The Workshop starts on Thursday morning at 8h30, 11 January 1996. Because of the relatively remote location of Autrans (see below) it will be necessary that everyone arrives on the evening of Wednesday 10 January. The Workshop will end on Saturday night with the final session and dinner. Buses to Grenoble and the airports will leave on Sunday morning 14 January, after breakfast. Please understand that this is a concentrated Workshop with limited accommodation. We regret that accompanying persons cannot be accepted at the centre.

Autrans is a small village about 30 km from Grenoble at an altitude of 900 m. The region is famous for its cross-country skiing. There should be snow. Our choice of hotels was very limited because of the need for ten conference rooms, allowing one for each group throughout the duration of the Workshop. The hotel is really a "vacation centre". Most rooms contain 2 beds, and it will be necessary to ask many people to

share rooms. We are hoping for good weather so that there will be a short time "off" each afternoon for walking and/or skiing.

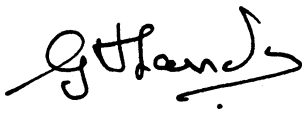
The ESF has provided sufficient funds to cover all your living and accommodation costs in Autrans. We have also received financial support from the European Commission so that we have some additional funds for travel. More information on this will be sent to you with the registration form. Note that the Workshop includes a Saturday night, thus allowing APEX fares. The nearest international airport is Lyon and bus transportation will be available.

Once again, we want to thank you for being willing to participate and to contribute to this challenging task. There is every possibility that our report will set the tone for the future of neutron scattering in Europe.

We look forward to seeing you in Autrans.

Yours sincerely,

Hans U. Karow
ESF Scientific Secretary



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Enclosure

Appendix B

List of participants

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Atomic & Molecular Aspects of New Materials - Autrans Wsh Jan.96

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Appendix C

The ENSA Survey Of The European Neutron Scattering Community

As part of the ongoing and extensive evaluation of the scientific impact of, and prospects for, neutron scattering methods and facilities in Europe the ESF recently commissioned a survey of the European neutron scattering community. The European Neutron Scattering Association (ENSA) undertook this task on behalf of the ESF, during 1995.

The principal aims of the ENSA survey were to evaluate

- The scientific and technological base of the European community
- The scale of neutron beam usage by members of the community
- The nature of neutron beam usage by members of the community
- The perceived impact and development of neutron scattering science

ENSA delegates circulated a questionnaire to their respective national communities. A total of 1026 questionnaires was distributed in the UK, Germany, France, Switzerland, the Netherlands, Spain, Italy, Hungary, Sweden, Denmark, Austria and Norway. The mode of circulation of the questionnaire and the mode of response varied with country. Whereas some returns were made by individual scientists, others were made on behalf of whole research groups or institutes. Across Europe a total of 506 completed questionnaires were returned, representing the activities of some 2029 neutron scattering scientists and research staff. Almost 65% of the 3548 known European neutron beam users were thus represented in the survey

The returns of the questionnaires provide an overview of the European neutron scattering community. A synopsis of the principal results of the ENSA survey, particularly with respective to aims 1 and 2, are presented in this Appendix. It should be noted that only minor regional variations in the nature and extent of the use of neutron beams are evident in the responses to the survey. The statistical data presented here can thus be taken as representative not only of the European neutron scattering community, but also of the individual national communities.

The European neutron scattering community by discipline

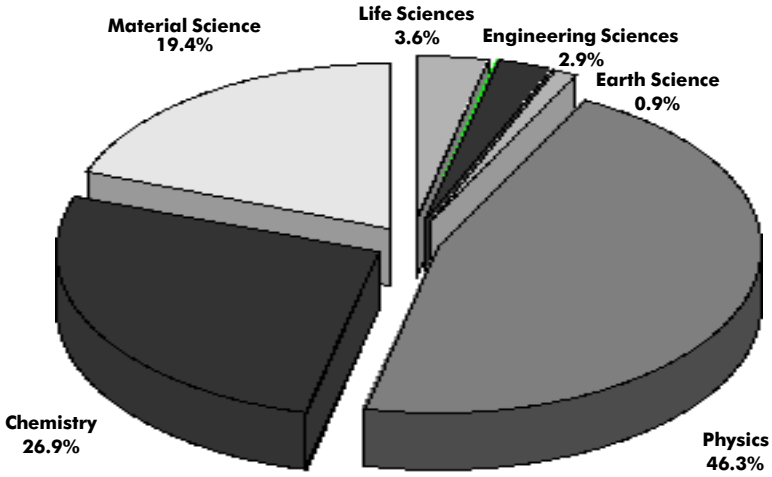

Figure1: European neutron scatterers by discipline

As shown in Figure 1, Physicists constitute less than one half (46.3%) of the European neutron scattering community. Chemists and materials scientists are extremely well represented, and together constitute a further 46.3%. Life, engineering and earth scientists represent less than 8% of the total neutron scattering community.

The European neutron scattering community by beam usage

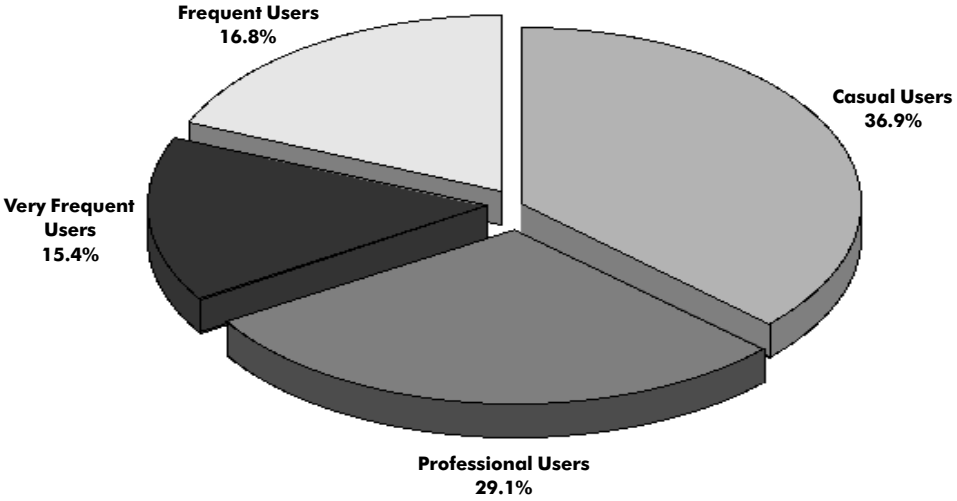

Figure 2: European neutron scatterers by beam usage

Members of the European neutron scattering community have been classified according to the degree to which they use neutron scattering as part of their overall research programme. *Professional Users* are those for whom neutron scattering constitutes between 75% and 100% of their research programme. *Very Frequent Users* devote between 50% and 75% of their research effort to neutron scattering, *Frequent Users* devote between 25% and 50% and *Casual Users* devote less than 25%. It is evident, from Figure 2, that almost 37% of the European neutron scattering community classify themselves as Casual Users. Indeed only 44.5% of the community devote more than half of their research effort to neutron scattering.

European neutron beam usage by source type

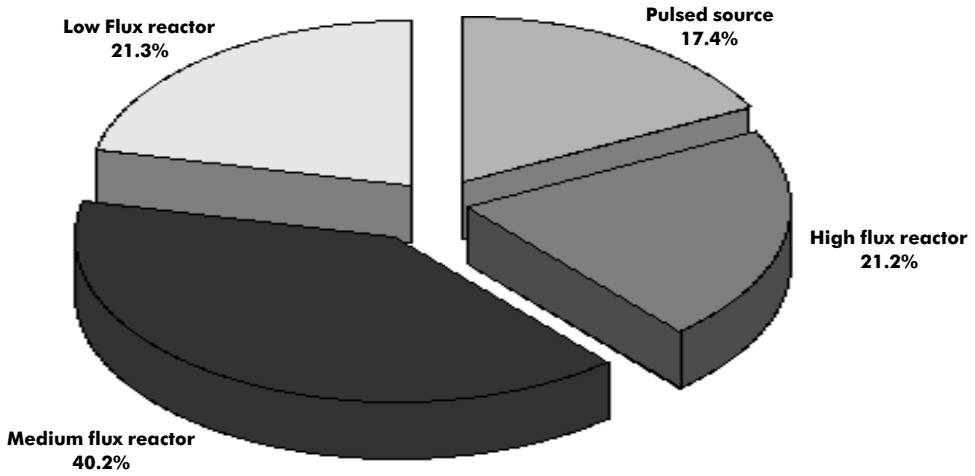

Figure 3: European neutron beam usage by type of neutron source

Low Flux Reactors are those which have a thermal neutron flux, n_{th}, of less than 10^{14}n.cm^{-2}.s^{-1}, *Medium Flux Reactors* have 10^{14} n.cm^{-2}.s^{-1} < n_{th} <10^{15} n.cm^{-2}.s^{-1}, *High Flux Reactors* (principally the Institut Laue Langevin) have n_{th} >10^{15} n.cm^{-2}.s^{-1}. Most respondents using a *Pulsed Source* specified ISIS as that source. The two major European neutron sources, ILL and ISIS, thus together account for a total of almost 40% of all neutron beam usage.

Summary

The ENSA survey has provided a remarkable insight into the nature of neutron scattering in Europe. Although neutron scattering is often perceived as a specialist tool employed principally by physicists, it emerges from the survey as a widely applicable technique which underpins a broad condensed matter science base incorporating not only physics but also chemistry, materials science, life sciences, earth sciences and engineering. Moreover the majority of European neutron scatterers use the technique as only one component of a wider research programme. This further emphasises the vital role that neutron scattering assumes in underpinning European condensed matter research.

The survey has also provided a clear indication of the vital role of high flux neutron sources within Europe. The two major facilities, ISIS and ILL, account for approximately 17% and 21% respectively of all neutron beam usage. Furthermore, in response to the ENSA questionnaire, members of the European neutron scattering community identified the need for a 78% increase in the currently available neutron beam time at high flux reactor and pulsed neutron sources.

Conclusions

We can draw three principal conclusions from the data presented in this Appendix:

- ***In Europe, neutron scattering is not just a tool for physicists***.
Chemists, materials scientists and, to a lesser extent, biologists, earth scientists and engineers constitute more than half of the European neutron scattering community.

- ***In Europe, neutron scattering is not just a tool for the professional neutron scatterer***.
Indeed, more than half of the users of European neutron scattering facilities employ neutron beam techniques as only one component of a wider research programme. Fewer than 30% of beam users cite neutron scattering as their only experimental tool.

- ***In Europe, the two major neutron facilities, ILL and ISIS, together account for 40% of all beam usage***
Additional responses to the ENSA questionnaire indicate that although the European neutron scattering community expresses a need for only 18% more beam time at Low and Medium Flux Reactors, a further 78% of beam time is required at High Flux Reactors and Pulsed Neutron Sources for the efficient execution of current research programmes.

R Cywinski, *Secretary to ENSA*
University of St Andrews
12 March 1996

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Gerard H. Lander, Workshop Chairman

Karlsruhe, May 1996