The scientific case for the ESS project

Contributions to the development of the scientific case

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Prologue

The concept of the *European Spallation Source (ESS) – a next generation neutron source for European science and technology* – arose out of a panel set up by the European Commission to examine the provision of neutrons in Europe. In 1994, the CEC approved a proposal from a consortium of laboratories in several European countries to examine the technical feasibility and costs of a 5 MW sharp pulse spallation neutron source. As part of this study the Scientific Case was developed by a large number of the scientific community in Europe, from universities, industry, and large national and international research laboratories and in co-operation with the European Science Foundation.

For practical reasons, ten scientific themes were selected. The Scientific Case for each was explored by a team of leading scientists under the guidance of a Theme Co-ordinator, and a detailed report was produced for each theme. In addition, special reports were commissioned from leading experts to explore the potential exploitation of other particles at the ESS. These individual reports, which formed the basis of the Scientific Case presented in the above study report are brought together here.

It is clear from the following pages, that the purely scientific case for the ESS is exceptionally strong. However, a case for an expensive facility must be made to a significant degree on its potential to increase the exploitation of science. The Scientific Case study presented here is packed full of specific examples how the ESS would deepen our understanding of the material world and thus enhance our ability to utilise this knowledge effectively for the benefit of European society at large.

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Soft solids and neutrons

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Abstract

This document describes the application of neutron scattering to research in the areas of polymers, surfactants and colloid particles (described herein as soft solids) and the advantages that could be gained from the introduction of a high flux spallation source.

This area is often driven by commercial significance of products that are a highly complex mixture of components and structures e.g. tyres where the range of distance and time scales relevant to performance can be remarkable.

Such a range of scales defines a unique challenge for neutrons.

The report is divided into 6 sections:

(i) The challenges soft solids presents for neutrons.
(ii) The advantages of a neutron spallation source.
(iii) A comparison with other sources and methods.
(iv) A summary of past successes in this area using neutrons.
(v) The anticipated areas where a spallation source will make a significant impact for future soft solid research.
(vi) An industrial perspective.

The main finding of the document is:
The increased flux will allow smaller sample volumes in highly complex molecular mixtures to be probed with higher sensitivity and better signal to noise.

This opens up the possibility of obtaining insight into the behaviour of a range of processes of relevance to the industrial/academic world.

Examples include:

(i) The transport, penetration and mixing of polymer systems and the relationship to adhesion, lubrication and functionality.
(ii) The structure and dynamics of surfactant molecules at an interface and the relationship to surface properties including crystal habit modification, reflectivity, surface reactivity etc.
(iii) The bulk properties of materials under external flow fields.
(iv) The fluctuation in membrane surfaces and the effect in penetration.

1. Advantages of neutrons for soft solid research

“Soft Solids” such as polymers, gels, liquid crystals, amphiphile assemblies and colloids, all share the same basic properties: weak interaction between the structural units, large thermal fluctuations, large number of internal degrees of freedom and a macroscopic softness indicative of a weak modulus of elasticity.

The units forming the structures of such materials are either large macromolecules built of covalent bonds, or assemblies of molecules built by weaker intermolecular force.

Their common features make them all susceptible to the same experimental approaches. Among these synchrotron radiation, electron and light scattering and neutron scattering play important roles.

For neutrons the energy and momentum may be matched simultaneously to energy and length scales appropriate for excitations in such structures. Neutron wavelengths of 1-20Å are ideal for the study of interatomic correlations and the available neutron energies allow the measurement of excitations over many decades (neV-eV).

The neutron is a weak probe of the nucleus rather than the electron cloud and so does not significantly perturb the system. In contrast to x-ray and electron scattering the resultant data may be directly compared with theory and in many cases absolute measurements are obtained.

Neutron scattering is currently severely constrained by the weak intensities available. In comparison with present or future X-ray synchrotrons, the source "brightness" is many orders of magnitude lower. However the strong motivation for continuing with neutron scattering is the unique information that can be extracted from this technique and the technical possibilities envisaged for high power spallation sources.

In the case of soft solids the future trend is towards the study of ever more complex materials and pulsed sources are naturally suited to such studies since the complexity demands characterisation techniques which can cover simultaneously this wide dynamic length and time range in one measurement.

The specific points to note are:

- The structural units have sizes and interaction distances ranging from a few 10 to a few 10^3 Å. The structures must therefore be determined by small angle scattering methods, which are particularly easy with cold neutrons and low angle X-ray methods. In this latter case however the X-rays are easily absorbed and cannot penetrate thick samples.

- By taking advantage of the different neutron scattering length densities for hydrogen and deuterium, using selective deuteration in a contrast variation method ie. complex distributions of scattering centres can be determined. In a technological sense this advantage (over X-ray and light scattering) should not be underestimated. 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, needed in a formulation to give material functionality. Ultimately there is also need for analysing the systems under mechanical and thermal constraints close to that of actual processing conditions.

- Owing to the large size of their structural units, the dynamics of the systems are controlled by characteristic times which are larger than those of atomic systems by a factor of at least 10^3. This is a range which is now made accessible to neutron inelastic scattering by the development of back scattering and spin echo methods.

- Because of the weak interactions between the structural units, their organisation may be quite sensitive to weak forces: structural changes under constraints can easily be studied on bulk samples in complicated configurations and with applied external fields owing to the penetrating power of neutrons. Kinetics of organisational changes however may also be followed owing to the very intense flux of synchrotron radiation.

Soft condensed matter studies using neutrons therefore have grown explosively over the last decade,[1-6] and the problems being addressed are now impinging significantly on the commercial world.

2. The advantages of a pulsed neutron source for soft solid research

The potential gains that can be achieved using accelerator based systems far outweigh those envisaged for future potential reactor sources.

The present spallation source at ISIS however is approaching its optimum design specification of 200 µA at 800 MeV (100 kW beam power). The specification for the proposed European Spallation Source based on a proton accelerator will produce a pulsed beam with an average power of 5 MW in ~ 1µs pulses at a repetition rate of 50 Hz.

The new source specification will yield an increased temporal brightness of ~ 30x over ISIS and is the key factor which will open up new opportunities in the soft solids area.

The general technical advantages of the ESS that will propel the work in soft solids into the twenty first century are:

- the ability to use time-of-flight in a natural way;
- high intrinsic resolution in both momentum transfer and energy transfer, resulting in very high precision structural and dynamical studies;
- significant signal to background : the source is effectively "off" when data are being collected, with fast neutron backgrounds being easily eliminated by time-of-flight techniques;
- wide spectral range in both momentum and energy: with the trend towards ever more complex systems, access to data over as wide a dynamical range as possible is more and more essential;
- higher sensitivity and better signal-to-noise in combination with the isotopic substitution technique will allow new weak cross-section phenomena to be investigated;
- use of fixed scattering geometries which greatly facilitate the use of complex sample environments;
- the pulsed nature itself will lead naturally to the study of time-dependent perturbations, kinetic experiments such as *in situ* relaxation phenomena and the exploitation of extreme conditions which cannot be achieved in the steady state;
- determination of absolute neutron scattering cross-sections in thick multicomponent samples needing the construction of complex sample environments: this is very powerful when combined with theory or computer simulation, since the cross-section for neutron interactions may often be calculated exactly;
- The application of inelastic and quasielastic dynamic measurements under the same conditions (above);
- the ability to perform simultaneous diffraction while studying excitations. Where a complex phase has been prepared *in situ* and must be monitored simultaneously with the measurement of the excitations this will be invaluable.

The increase in source brightness will significantly change both the quantity and quality of information that can be obtained. With more intensity and pulsed systems, experiments can be performed on smaller samples with better spatial resolution in a shorter time, more dilute systems, and will enable parametric studies (eg. T, P, external force fields etc). Measured flux will also present real opportunities to study off-specular scattering, grazing incidence diffraction and surface inelastic scattering. Since the nature of the experiments more easily lend themselves to controlling sample environment the advantages mentioned above take on an even greater significance.

Time-dependent relaxation phenomena and kinetic processes will be able to be effectively investigated. The higher resolution, and an increased range in both space and time will inevitably lead to a better and more detailed understanding of complex phenomena, and begin to open up the unexplored fields of the dynamics and kinetics of surfaces and thin films. For example with an understanding of the complexities within polymer surfactant films it should be possible to design experiments that correctly probe complex industrial materials.

Coupled to this is the ability to perform full polarisation analysis which will also impact soft condensed matter studies through separation of the coherent and incoherent scattering and consequently the reduction of background noise.

Finally developments in computing over the last decade will allow full exploitation of pulsed neutron sources: with the instrumentation on the ESS complimenting this explosion.

Consequently if the ESS were available today it would make a major impact on our understanding of soft condensed matter in the areas of:

- Small angle scattering (SANS) of anisotropic and isotopic systems (structure and dynamics) of polymeric and surfactant origin. High resolution and wide Q range 10^{-5} - 5 $Å^{-1}$. Rheological properties of such technically important systems. With respect to flowing materials has made considerable advances in recent years but there are several areas where considerable work is still required. Although many properties can be measured and fitted to empirical or semi-empirical equations and constitutive relations, these are often not linked with an understanding of why materials behave in a given manner. It has been recognised that the relationship of structure, particularly micro-structure, with properties may provide important clues.

  The primary requirement for progress in the colloidal and rheological fields is ready access to high flux SANS and neutron reflectivity facilities which cover a wide range of momentum transfer, equipped with a flexible range of sample environments. In order to exploit the higher flux of an advanced source to study the subtle and small changes observed under flow or with small fractions of the species labelled, instruments must be stable (detector and monitors) to a high degree of accuracy.

- The structure of adsorbed organic molecules/polymers at air-liquid and liquid-solid interfaces; (soluble and insoluble monolayers), for these systems 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 use of isotopic labelling 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. No other experimental technique is yet able to give structural information about soluble surfactant layers at this resolution.

- Pulsed neutron techniques can and will play an important role in the dynamics of complex soft solid systems. The time scales of importance range from the rotational and translational diffusion times of constituent molecules (picoseconds - microseconds) to polymer diffusion (> nanoseconds). The short time - short length scale section of such a parameter space can be handled well with quasi elastic neutron scattering (QENS), and would benefit greatly by an increase in source intensity. While the short time - long length scale region can be studied with fast laser pulse techniques and the long time - long length scales with quasielastic light scattering (QELS), the long time - short length scale regime, which is critical in the study of soft solid is most difficult to probe with existing facilities. Future instruments that can push techniques towards times at both shorter and longer length scales will be invaluable.

- The nature of the electrochemical interface. (See later).

- Colloids - interfacial structure and particle interactions.

- Complex colloidal systems, including liquid crystalline polymers, magnetic colloids and anisotropic systems.

- Kinetic processes such as relaxation during extrusion.

- Insight into technologically important materials such as detergents, paints, inks, coatings, composite materials such as polymers and alloys, areas of food technology such as emulsion stability, foams, gels as well as lubricants and fuel additives. (See Rheology above).

  Other types of instrumentation will be of general importance for work in this area: such instruments are diffractometers (for studies of particle alignment) and spectrometers that may be used to determine anisotropic mobility and diffusivity in flow fields. Other instrumental developments and features may be important in SANS and reflection measurements. Focusing mirrors may assist the study of small sample volumes and in mapping flow patterns. The need to access a variety of time-scales (from ms upwards) of relaxational modes will impose requirements for stroboscopic as well as real-time measurements. To optimise time resolution, it may be necessary to consider instruments with short wavelengths, short sample-detector distances and high spatial resolution on multi-detectors. Such requirements would probably not arise from the usual optimisation of flux and resolution and should be borne in mind when considering a portfolio of instruments on beam lines.

- Directly measuring the dynamics of soft solids at length scales of 1-1000 nm and time scales longer than the nanoseconds typically achieved with Neutron Spin Echo may require the development of new instrumentation, most notably hybrid spin-echo/time-of-flight spectrometers, which promise to be much more efficient than current NSE apparatus. With the inherent time structure and broad neutron wavelength distribution at pulsed sources, a 1 MW spallation source will lead to critical discoveries in this area.

Table 1 shows the instrumentation requirements for SANS and NR that will facilitate the above areas.

Table1:
Instruments relevant to sold solids research

Two technique areas that are germane to soft solids applications are small angle neutron scattering (SANS) from bulk systems and reflectivity from interface adsorbed materials. Within these definitions several derivative instruments have been identified.

Type	*Flux*	*Q/Å^{-1}*	*$\Delta Q/Q$*	*Systems/samples*
SANS General	Medium	10^{-3}-1	10%	All types
V Low Q		10^{-4}-10^{-2}	10%	Anisotropic
V. low Q	Large mean flux	10^{-3}-10^{-5}		Isotropic (LS)
	High	10^{-3}-5		Kinetics
Focusing	High			Small regions/mapping
REFLECTION Vertical/ Horizontal	High	High Q 10^{-3}-0.5	Low High	(Monolayerd (thin) ($R \sim 10^{-7}$)
Evanescent wave	Off specular			In plane diffraction Lateral heterogeneity
Frequency domain	10^{-1}-10^{-4}			Dynamics 2neV-10^{-2} meV

All these machines require development in other engineering and science fields which are outside the remit of this report.

3. Comparison of neutrons with other sources

Reflectivity

X-rays can cover the same Q-range and offer higher flux than a reflection instrument. However, in specular reflection the inability to manipulate the refractive index limits the possibility of using X-rays to disentangle the quantitative elements of a complex interface. In such cases neutron reflection will be more generally applicable.

Tunnelling and atomic force microscopy probe the peripheral layer of atoms giving little depth information and are generally qualitative. Second harmonic and sum frequency generation are very new techniques, that give information about the orientation of groups in the interface but no spatial information. They will be complementary to neutron reflection in some cases.

Many of the qualitative surface analysis tools (ESCA, SIMS, FABS etc) will remain high vacuum techniques and are hence of little value for soft solid science.

Comparison of SANS with other techniques

The main techniques to rival SANS are Light and X-ray Scattering. The difficulty of absolute measurement for X-rays has already been alluded to. For light scattering although absolute measurements can be achieved, the inherent interaction strength finally limits the practical concentrations/thickness that can be achieved. Light scattering will continue to compliment SANS especially in kinetic/dynamics areas associated with large scales (0.5 - 2μm).

Fluorescence methods including evanescent wave spectoscopy are applied to similar systems but on different dimensions scales and often require additives and so are complementary to other areas including neutron scattering.

The dynamics involved with the conventional electromagnetic probes (namely photon correlation spectroscopy (PCS), fluoresence correlation (FCS) and photobleaching recovery techniques (FRAP), and Brillouin light scattering) operate on timescales that are long when compared with their neutron counterparts (QENS and NSE).

Similarly the use of multidimensional nmr in the elucidation of local incoherent dynamical motions is often too slow and does not give long range correlations.

Consequently no techniques can rival (QENS/NSE) for the study of example, fast diffusional motion in porous media, segment dynamics and reptation, membrane fluctuations (vesicles, cells, micelles, emulsions etc) or indeed the individual dynamics of molecules (polymers or surfactants) tethered to a surface. The methodologies therefore are complementary rather than rivals.

The development of neutron Brillouin scattering, which should be compared with the past development of SANS in terms of number of applications, will have a major impact on many areas of physics and chemistry of soft solids research. This development has been anticipated for many years but has not been achievable at existing sources.

Such developments will give:

a) time dependent systems too fast for real time SANS investigations and small angle spin echo spectroscopy.
b) transition from hydrodynamic to kinetic behaviour in complex fluids.
c) polymeric and large molecule liquid dynamics.
d) molecular dynamics approaching critical points, e.g. phase separation.

A brief list of the types of problem and techniques that can be applied to studying different aspects within that problem are listed under Table 2.

Table 2:
Problems and techniques for complex fluids
(Polymers and surfactants)

Problem	***Techniques***
Chemistry	
Identification/Chemical analysis	SIMS, Laser Desorption, MS-FABS, Electrospray, SCF, 2D NMR, Spectroscopy, (IR, Raman...)
Composition (Polymers and surfactants	Chromatography (CZE, SCF), MS-Ablation, MS electrospray, Chemometrics, Separation methods, Microwaves, Elemental Analysis
Processing	Computational Physics, Tomography, (NMR, X-ray, Acoustics, Dielectric...), Simple Measurement/Multivariate Analysis, On Line (MRI/NMR, Raman).
Physical behaviour	
Polyelectrolytes, Polysaccarides, Proteins	SANS, Neutron Spin Echo (NSE) Simulations, Rheology, Light Scattering, Neutron Reflection (NR), Optical Second Harmonic Generation (SHG), NMR, Electrophoresis.
H-bonding Polymers/ Surfactants	Simulations, Rheology, Light Scattering, NR, SHG, NMR, SANS, NSE.
Rheology (Surfactant/Polymer)	Light Scattering, SANS, Kerr Effect, Acoustics, Mechanical
Crystalline Polymers, Surfactant Phase Structure	Neutron Diffraction, X-ray Diffraction, Calorimetry, SANS, Electron & Optical Microscopy, Simulations.
Structure of amorphous Polymers and Surfactants	Image Analysis, SANS, Simulations, Depolarized Light Scattering, Electron & Spectro/Optical Microscopy, Calorimetry, MRI.
Segmental Interaction (c)	Simulations, NMR, Light Scattering, QELS, SANS, SAXS.
Copolymers	SANS, SAXS, NR, X-ray Reflection (XR), Mechanical Measurements, Simulations, Electron Microscopy, NSE.
Functionalisation/Molecular Architecture	Synthesis, then SANS, SAXS, NSE, Simulations, Rheology, Light Scattering, NR, XR, SHG, NMR, MRI etc.
Complexation Surfactant/Polymers	SANS, Light Scattering, IR, Neutron & X-ray Diffraction, Raman.
Configuration & Dynamics of Networks & Gels	SANS, Light Scattering, NSE, Simulations, Rheology, LD, Fluorescence, Energy Transfer.
Phase Structure, Morphology	SANS, SAXS, NR, X-ray Reflection (XR), Simulations, LM, Electron Microscopy, Theory, Spectroscopy, Raman, MRI.
Self-Assembling Systems	Ellipsometry, SFG, SHG, Light Scattering, SANS, NR, Transport, Simulations, MRI, Raman.
Surface & Interfaces, Membranes, Adhesives, Latices	Light Scattering, NR, XR, SAXS, SANS, Grazing Incidence Diffraction, Off-Specular NR, SHG, Quasielastic Neutron Scattering, Mechanical Measurements, Fluorescence, Raman, SFS.
Fracture of Rubber-Toughened Plastics	TEM, SAXS, SANS, Image Analysis, Acoustics.

4. Achievements in soft solids using neutrons

Many "scientific breakthroughs" have been accomplished using neutrons. The advent of a new source such as the ESS will both add to this wealth of knowledge and provide an avenue into new, as yet untested, territory. Briefly the key achievements already established using neutron methods are:

4.1 Polymers

a) Structural

- The dimensions of the gaussian coil structure of a single long chain in the melt[7] and the affirmation of the screened excluded volume model[8].
- Single chain behaviour in blends - phase separation and miscibility[9-11].
- Universal scaling laws verified on polymer solutions[12] and microemulsion systems.
- Structure of diblock copolymers[13-16].
- Relationships between microscopic and macroscopic deformations for rubber elasticity [17-19].
- Structure of a polymer layer at an air/water interface and the density profile normal to the interface[20-22].

b) Dynamic

- Depending on the time scale of observation, the dynamics of polymer melts are governed either by elastic behaviour of viscous flow. This viscoelasticity relates to the topological constraints which are imposed by the mutually interpenetrating chains. Studies on polymer melts have been successful but much remains to be done.
- The microscopic basis of elasticity so described by the theoretical models of reptation[23-27]. Neutron spin echo has been used successfully to look at polymer motion (reptation) and particle fluctuations and is a strategic field in the study of the "molecular" rheology of complex systems as it presents a route to a fundamental understanding of the technologically important macroscopic rheology. The lack of good experimental information has meant that only in one or two areas have there been theoretical developments of significance. This will improve greatly with a new source.
- Single chain dynamics within a bulk system response (α and β relaxations). For example in a pioneering neutron spin echo experiment the dynamic structure factor resulting from the secondary relaxations in 1.4 polybutadiene was investigated shedding light on the conformational changes underlying the β-relaxation process[28].
- Cross links in networks for rubber and triblock copolymers.
- The deformation and relaxation of elongated polymer melts under shear. Small-angle neutron scattering (SANS) has been used to study the structure of polymer solutions micellar, microemulsion and particulate dispersions under shear for about 15 years[29-33]. The technique can therefore be considered as relatively mature. Many simple experiments are now complete but there is considerable demand for further work and many questions will be answered only if there are advances in facilities and instrumentation.
- Interdiffusion of mixed polymer films[34-36].
- Surface induced ordering of a block copolymer film37-38].
- The influence of heterogeneity of polymer glasses on the thermodynamics.

c) Liquid crystals

- Correlations in smectic B phase by studying the modes of various structures.
- Conformation of LC polymers using contrast variation.
- The structure of water in lyotropic and microemulsion phases.

d) Surfactants

Structure

- The measurement of simple micellar shape, size and effective structure[39].
- The determination of the interaction profile in a concentrated micellar system[40].
- Location of species in mixed surfactant micelles and their relationship to curvature[41-42].
- Curvature, structure and form measurements (shape, layer thickness, penetration etc) of simple microemulsion systems in equilibrium and at the inversion points between O/W and W/O emulsions as well as at extreme conditions of temperature and pressure[43].
- Structural measurements in non-liquid media eg. microemulsion structure in a) semi-solid (plastic crystalline) phases b) near- and super- critical fluids and c) in gels (soft solids).
- Structure of adsorbed surfactant layers at an air/liquid interface[44].
- Mixture composition at the air/water and air/solid interface[45].

Dynamics

- Fluctuations in the interface and its relationship to elasticity and elastic constraints for droplets and vesicles[46].
- Simple spread monolayers of insoluble surfactants such as fatty acids show a rich polymorphism as the temperature and surface pressure are varied on a Langmuir trough. The phase behaviour of these materials is now quite well understood[47-48].
- Alignment under shear of surfactants self-assembled into anisotropic species[40-50].
- Correlated undulations in lamellar phases. The coherent dynamic structure factor.

e) Particulate colloids

- Stabilisation of colloids using polymer adsorbates (polymer brush dynamics)[51].
- Effects of intensive properties on the stabilisation of surfactant coated colloids.
- The structuring of colloids at an interface using reflectrometry[52].
- Studies on the coalescence of colloids as precursors to film forming.

5. The future for neutrons using a spallation source

5.1 General comments

The natural progression of this work is to carry the investigations into more complex bulk and surface structures.

This progression falls into the categories:

(i) more realistic complex multicomponent systems of relevance to the problems experienced in material science and to their understanding and ultimate control.
(ii) the behaviour of systems under external fields (E, flow, P, T etc) relevant to the conditions faced in various processing functions (eg. electrochemistry, rheology etc).

In this latter case, for example, historically, electrochemists tended to view the electrode as a structureless source/sink of electronic charge - a view enforced by the absence of techniques providing a more realistic picture of "real" electrode surfaces. Although scanning probe microcopies and *ex situ* surface science techniques are improving this situation with regard to the outer surface topology there is presently little or no insight into sub-surface features. Focusing however on the strengths of neutron methods, it is worth noting that the hydrogen system has a central role in electrochemistry, at least in part due to the predominance of aqueous media. There are many issues relating to H-adsorption/adsorption that are surprisingly poorly understood. Possible reasons include the fact that many spectroscopic probes employed by electrochemists, notably XPS, are "blind" to H-adsorbates. Neutron methods particularly with isotope variation, will prove very powerful in this regard.

Theoretical descriptions of rheological behaviour are usually based on microscopic or mesoscopic models. The need to test such models against experiment to obtain a fundamental understanding of flow behaviour will lead to a continuing and growing demand for investigations in this area. Much on this area may be expected to develop with improved facilities for neutron research and will continue to aid industrial thinking and progress.

(iii) More systematic studies of transient states ($S(Q, \omega)$), which yield better models and insights into dynamic behaviour than available at present. Kinetic experiments have been limited by the need to obtain a reasonable neutron count on the multidetector in a reasonable period of time. The possibility of a high flux spallation source does offer the possibility of "time-slicing" over much shorter time intervals (seconds rather than minutes).

These general areas translate into the specific topics indicated below for the various soft condensed matter areas.

5.2 Bulk dynamics of soft solids (polymers surfactants and hard colloid particles etc.)

- Many industrial processes involve a minor or major element of extensional flow, these range from simple pipe flow to deliberate alignment by extrusion (eg. crystalline particles in a flow). The volumes of uniform flow for such investigations (eg. diffraction methods for alignment) are often small and high flux sources would greatly aid development. The data obtained for extrusion will provide a molecular level set of molecular dimensions as a function of extrusion conditions. These data then need to be combined with continuum data ie., stress and velocity field measurements to derive constitutive equations which span the dimension range from macroscopic to molecular. The need for the ESS as a source is due to the increased path length of neutrons through the sample which will be required for two reasons, a) to avoid wall effects such as "stick-slip" events in some polymers, b) to reduce the pressures needed for the extrusion to viable values.

- Many materials including polymer melts undergo microscopic deformation under flow. For example, measurements of emulsion structure flow and polymers under extrusion processes Quasi-elastic and inelastic scattering can be applied to polymer melts in extrusion to obtain a more complete description of the energy spectrum in polymers as they are extruded. Questions such as "are there any correlations between internal Rouse or reputation modes with the velocity imparted by the extrusion process ?" can then be addressed.

- The unravelling of dynamic modes that determine material properties (S(Q,ω) for polymeric systems, star polymers, dendrites etc. and the importance of geometrical or topological interactions.

- The use of particle structure factors coupled to the ability to have high intensity beams and polarisation analysis will enable small scattering cross section events to be followed. For example the properties of tailored peptide based polymers, that may be used as “smart” complex fluids and rheological modifiers at low concentrations will be studied. Whilst in polymer melts careful labelling of selected parts of molecules measured under flow will be key in the developing science of structure/rheology relationships for polymer processing. In particular, the roles of molecular branching and polydispersity will be investigated.

- Phase dynamics of diblock copolymers - charged or polyelectrolyte systems applied to processing.

- Transport behaviour in multicomponent systems will be extended to their behaviour under flow. Since phase behaviour is often considerably modified by a stress-field, materials such as polymers with particles, multi-component micellar dispersions and mixtures of different particles will attract attention. The signal may be small in these systems consistent with the extent of partial labelling. The changes in phase behaviour of surfactants with water and/or oil under shear are also likely to be of considerable interest.

- The thermodynamics, dynamics and transport properties of complex fluids in porous media of varying pore size are important in soil remediation and the application of the enhanced oil recovery. Contrast matching of the solid matrix allows components of the complex fluids to be studied. Typical questions to address are how does the interfacial surface area of the hydrocarbon change with time during oil recovery or remediation? How does the flow of water or surfactant change hydrocarbon distribution within the soil or rock? What is the mechanism of hydrocarbon dissolution etc.

- In the same manner the study of transport of fluids in gel systems is highly important in the food, pharmaceutical and agrochemical industries. The possibility of Neutron Spin Echo to address diffusion of molecules in porous media, the dynamics of gels and cross-linked networks, as an application to controlled release, and how to select/design polymers to give desired release profiles are highly relevant questions that the new source will be able to address directly.

Likewise multicomponent transport through membranes presents a general problem in various separations technologies. For example, how do polymer membranes used in various pharmaceutical delivery systems work. How does the polymer transport during release? What is the mechanism of release? What are the structure and dynamics of the polymer (a) at the interface with the active agent inside the capsule, (b) at the interface with the outside world, (c) in the bulk of the polymer membrane? Extension of grazing incidence neutron scattering or reflectrometry to inelastic processes will be very useful here.

- Dynamics of microemulsions at high temperature, pressure and ionic strength. Such systems are of interest in fields as varied as the above encapsulation methods through to oil recovery.

With present instrumentation it has been necessary to study self-assembly systems at a surfactant volume fraction of 0.01 or higher. The flux expected of the new instruments will open up new possibilities for the detailed study of micelles in the region of the CMC and associated dynamic phenomena eg. micelle breakdown and micelle-vesicle spontaneous transitions and structural phase changes.

For microemulsions this will allow:

a) Investigation of the size redistribution mechanism on mixing large and small droplets (the time scale of this process is approximately 1s).

b) The use of microemulsions as steric templates for the *in situ* synthesis of surfactant-stabilised nano-particle spheres, rods and discs (eg. CdS, a photocatalyst). To date the concentration of particles has been too low to enable the kinetics and hence mechanism of their formation to be followed. Similarly it will be easier to explore small structures in the presence of larger ones eg. water nano-droplets in a water-in-oil-in-water dispersion. These systems are of relevance to the food industry. Another example would be to specifically probe the structure of enzyme - water-surfactant microreactor clusters in the presence of water-in-oil microemulsions. Such systems are used for novel and selective organic synthesis.

c) The study of surfactant systems generally at lower concentrations, where the system behaviour is closer to ideal, eg. reverse vesicle systems, flexible rods. In the latter case, from the size dependence on temperature, the energy required to break the rods can be determined.

d) Using the high sensitivity which would become available the various regions of Q space can be exploited more effectively than hitherto, enabling new information to be obtained on the nature of interfaces and solvent penetration. (This applies to many areas not just microemulsions).

- The conformation of polymers in complex media (eg fibres, films, foods etc), where they often impart the material functionality.

- The process of reactive blending where complex mixing and reactions can occur. The regions where thermodynamics takes over from mechanical mixing (see interfacial section).

- The structural effects of changes in rubbers as a result of additives such as silica, carbon, graphite etc. in relationship to the wear/structure/functionality relationships.

- The effect of plastisizers on the coherent structure factor S(Q).

- Radical polymerisation of block copolymers blends and the effect of heterogeneity and shear on the bulk properties of the material.

- The aging of polymeric glasses studied through secondary relaxations and the comparison to normal supercooled liquids. Such relaxation processes are of utmost importance because they determine the mechanical properties of glassy polymers of technological interest such engineering thermoplastics. 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 dynamics (including breakup) of bicontinuous surfactant phases are not understood to a level to test theoretical predictions. Can this be rectified and can, for example, such systems be polymerised to yield new types of calibrated filter?
- The influence of heterogeneity on the thermodynamics within polymer glass.
- Detailed compositional profiles including ions/diffuse layers at the surface of particles, emulsions and microemulsion droplets.
- Diffusion of water in complex environments; complementary approaches to nmr.
- The rate of formation and breakdown of micellar units. In principle, techniques such as stopped flow, pressure jump and temperature jump might be used if measurements could be made in the seconds time domain. The ESS will allow this to occur.
- Dynamics and shapes of giant micelles under shear, how they break up and how to develop insight on new theoretical models.
- Polymer – surfactant interactions.
- Protein – surfactant interactions - adsorption crystallisation and denaturation.
- Protein – lipid organisations are only partially understood. Even less is known about the structure of proteins in membranes, particularly when considered in association with other molecular constituents.

  The lipid membrane is not a natural environment for the proteins but is a statically and dynamically heterogeneous system exhibiting a high degree of coherence. This leads to cooperative phenomena, including protein-induced phase separation, protein aggregation and crystallisation and lipid selectivity of proteins. The association of membrane proteins into quasi-crystalline aggregates will allow such two-dimensional arrays to be studied with diffraction techniques, within the floating membrane methods, and so address questions such as the global shape of membrane proteins, the arrangements of various elements of the structure, the location of individual amino acid residues and the associations of membrane proteins with other molecules within and near the membrane. The high flux capabilities of a new source can be coupled to the developments in modern molecular engineering to afford unique opportunities that were hitherto unreliable.

- Non equilibrium colloidal behaviour. The fine structure within coagulating colloid particles complementing the light scattering microanalysis. The use of a multidetector to give intensity over a wide Q range and time range would provide interesting information on the evolution of fractal structures in for example microemulsions and nanoparticle dispersions.
- Rheology for particulate dispersions has already been established as a basic subject for neutron scattering experiments using steady shear to examine changes from static conditions.

Kinetic experiments following changes after applying a shear gradient or after applying steady shear to follow changes (relaxation) after stopping the shear would provide new information about the mechanism of approach to equilibrium. There is a vast range of pertinent timescales. It is to be expected that real-time measurements of structural evolution will improve as the instrumentation and sources develop. The use of stroboscopic methods, in which separate time slices of cyclic (eg. oscillatory flow) or repeated processes are recorded and combined, is expected to develop for studies in the time scale of a millisecond.

- On a longer time scale the higher intensity of the beam will open up new areas in experiments close to contrast-match on concentrated dispersions since it would minimise the effects of multiple scattering.

5.3 Interfacial properties of surfactants and polymers

The use of neutron specular and off specular reflection to study all aspects of disordered and semiordered interfaces is a rapidly growing area.

Langmuir-Blodgett films have been studied for many years, however, future work will be directed at unravelling the surface behaviour of complex molecules such as polyelectrolytes, bio-molecules, liquid crystal polymers, molecules with specific functions such as dipoles or chromophores or even mixtures of molecules. A good understanding of the structure of the spread monolayer is an essential part of understanding the behaviour of such molecules at interfaces.

Neutron reflection is a very useful tool for the study of spread monolayers but its advantages over X-ray reflection will become more apparent as more complex systems are studied through contrast variation methods. Also the high flux planned for the ESS and the ability to focus the beam will allow measurements to be made in a few seconds. This will be a big improvement, allowing measurements to be taken as a function of surface pressure at realistic compression rates rather than attempting to hold a certain pressure for the duration of an hour-long measurement when film relaxation and dissolution can make interpretation of results unclear or erroneous.

The areas that can be tackled include:

- The degree of penetration of the surfactant into the aqueous subphase.
- The intermolecular distances and the segregation of species in a mixed monolayer into patches can be investigated by measuring off-specular scattering.
- Off-specular scattering is very much weaker than the specular reflection and has tended to be the preserve of synchrotron X-ray experiments. However it will become viable with the high flux available at the ESS and with the advantages of isotopic labelling is likely to become the method of choice for determining the long and short range in-plane structure because of the advantages associated with isotopic substitution.
- The degree of scrambling of the layers in non centro-symmetric (ABAB.) organic multilayers as a function of distance from the substrate surface will perhaps enable the improvement of electrooptic or ferroelectric properties of the systems.

- Biosensor studies and ways to improve their performance rely on an understanding of adsorption/penetration of a solute at a deposited monolayer or multilayer, possibly containing an immobilised protein. Using a neutron transparent substrate in contact with the solution, it is possible to determine the degree of penetration of the solvent and solute as well determining the distribution of any immobilised guest molecules in the film. The high flux of the ESS, allows a reduction in sample size and this will make a major impact in this area as it will remove the sometimes insurmountable problem of preparing large uniform samples. The reduction in sample size would also make complementary experiments with synchrotron radiation more informative and will also complement spectroscopic and electrochemical experiments.

- Spread monolayers can act as templates for solute adsorption at an interface. Technologically this is very important but much is still unknown. Neutron reflection and off-specular scattering are the provisions of ideal tools for investigating this area. The major benefit from the ESS will be the provision of instrumentation that can measure the in-plane structure over a wide off-specular Q range. This will only be possible because the high intensity of the ESS that will auger very tight resolution perpendicular to the plane of incidence.

Three areas of immediate interest are:

(i) In the investigation of biomineralisation, spread monolayers can induce crystallisation of certain forms of inorganic solutes which would not normally precipitate. This approach can be used to gain insight into the early stages of biomineralisation. Similar methods will also be applicable to the development of biocompatible surfaces, where the early stages of surface fouling can be studied.

(ii) The build up of self-assembling multilayers as an alternative to using Langmuir-Blodgett deposition is also an attractive area. Layers are added to the surface one at a time by either chemical or physical adsorption from suitable solutions, with possibly some treatment to activate groups after deposition. There are still many problems associated with obtaining good packing of the molecules and neutron reflection using deuterated materials will play an important part in understanding this.

(iii) Spread monolayers of lipids are often used to mimic a cell membrane and its interactions with its surrounding solution proteins, DNA etc. The adsorbed amount and the thickness of the adsorbed layer can be determined from neutron reflectivity. The in-plane periodicity of the adsorbate can be measured by off-specular scattering. For this to be successful a reflectometer with much better in-plane Q-resolution than is currently available will be necessary. Experiments such as these are possible now with synchrotron X-radiation but neutron scattering would confer the advantages of contrast variation which would permit the individual scattering from similar organic materials (eg. proteins and lipids) to be distinguished.

In this latter regard fluctuations in lipids and proteins in biomembranes are central to a large part of the biological function of these materials. These fluctuations include molecular motions transverse to the membrane plane as well as in-plane density fluctuations, sometimes referred to as "dynamic heterogeneity". Lateral inhomogeneities reflect membrane elasticity on biophysically significant length and time scales. Such in-plane structural features which are reflected in the off-specular reflected component, generally yield a much weaker signal than the specular making it difficult to determine and interpret. A more powerful source would therefore make an obvious impact.

It is clearly not possible to study evolution on time scales like 10^{-4}s with a reflectometer approach, however even static pictures of such inhomogeneity and its modification by proteins or other membrane components would be a major advance.

Solid-liquid interface

- Segment density profile perpendicular to a surface of homopolymer coils or homopolyelectrolytes as a function of their charge density.

- The behaviour of block copolymers at all three interfaces will enable the study of what factors control the interfacial structure of these materials and to what extent they may be tailored to achieve particular interfacial properties. Polymers, for example, are increasingly being used in the form of thin films, where the coatings confer desirable surface properties to commodity products, substantially adding value eg, thin film forms are crucial in the microelectronics industry, eg. as resistors, and also in device packaging.

  Studies of the effects of interfaces on phase separation in thin films are thus highly relevant to practical coating processes from solutions and latices. In addition to these immediate practical applications however the slow dynamics and large length scales of polymers make them ideal as model systems for the study of ordering processes in confined geometries, in which role they can shed light on problems of more general applicability in condensed matter physics.

- Surfactant structures at air/liquid, solid/liquid and liquid/liquid interfaces with the aim of being able to model surfactant adsorption at these interfaces quantitatively and relate this to detergency and anti-corrosion.

- The composition and structure of surfactant mixtures at the same three interfaces, with the objective of being able to predict the composition of complex surfactant mixtures at any interface.

- The adsorption of proteins at the solid/liquid and liquid/liquid interface with particular attention to the effects of surface modifications on the adsorption and to denaturation processes.

- Adsorption of mixed systems, polymer/surfactant, protein/surfactant etc in relation to stability, structure and functionality.

- Complex fluids and the structures induced by a solid/liquid interface.

- Fluctuations of an interface on a range of dimension scales. The width of the interface?

- Polymer adhesion and the role of block copolymers at the surface. In many of the applications of polymers, surface and interface properties are of the highest importance. For example, the degree of adhesion between two polymers is determined by the degree of interpenetration of the polymers at the interface between them; modifications of the structure of the interface, perhaps by the segregation of additives or chemical action can lead to substantial changes in adhesion, either advantageous or deleterious.

- Similarly the arrangement of the chains close to the interface between a polymer and non-polymer in a composite material determine many of the most important properties of such composites and are of substantial interest both academically and industrially.

- Polymer-polymer interfaces; their interpenetration and induced structure.

- The role of surfactants/polymers in the phenomena of lubrication. Work has recently begun to use neutron reflection (and off-specular scattering) for studies of flowing surfaces and boundaries of sheared systems. This is likely to be an area of considerable growth particularly if progress can be made towards an understanding of important areas of engineering practice such as hydrodynamic lubrication and the behaviour of boundary lubricants at interfaces.

- Although neutrons are not central to liquid crystal/polymer liquid crystal systems the study of structural arrangements at substrate surfaces would have a significant bearing on the understanding of display devices. This needs to be followed up. For example general areas within liquid crystals that would benefit from the specifications of the ESS are:
  a) Simple specular reflection at the solid/alignment layer/liquid interface to determine peneration of liquid into the alignment layer.
  b) Glancing angle diffraction to observe the smectic layers as they are truncated by the surface. This is a very demanding experiment because with incident angles below the critical angle, only a small fraction of the beam intensity reaches the depth that needs to be probed. Feasibility is marginal on current sources but would become perfectly feasible on a new arrangement.

Liquid-liquid interfaces

- The adsorption of amphiphilic species at the interfaces (eg. enzymes).

- The hydrodynamics of film drainage in thin foam films in air, between liquid phases etc. The advantage of using labelled compounds and time-slicing could produce new information in this important and relatively unexplored area.

- Surface roughness and diblock copolymers.

- Polymers, particularly copolymers, are used at liquid-liquid interfaces in many situations; emulsions stabilisation, homogenisation of liquids, liquid-liquid extraction. There is almost no knowledge of the organisation of polymers at liquid-liquid interfaces although in principle reflectometry is able to provide this information. The problem is that currently available instruments require the upper liquid layer to be very thin and the maintenance of this liquid layer is difficult. With a higher flux source, thicker liquid layers (which are easier to maintain) can be used and a sufficiently strong specularly reflected beam obtained for analysis. This type of experiment would be unique to neutrons.

- Intrinsic surfaces properties of polymers and surfactants such as friction and wettability, and the biocompatibility of materials used in medicine, are determined by the composition and dynamic properties of the material very close to the surface. These surface properties are often very different from the properties of the bulk, but with modern neutron capabilities they are now open to study.

- *In situ* polymer layers at an electrochemical interface and the associated structure and dynamics.

- *In situ* polymerisation at electrode surfaces and their properties.

- *In situ* electrochemical processes and the electrode surface. This breaks down into three challenges:
  i) vertical spatial distributions at electrode interfaces: these measurements are presently possible albeit on long time scales, and yield important structural information that relate to transport and reactivity parameters. Faster measurements are needed.
  ii) lateral surface inhomogeneity measurements will give considerable insight into the nature of inhomogeneous deposits and rough surfaces, as found in "real" electrochemical applications.
  iii) In both the above cases, there is a very high premium on obtaining dynamic information on structure. The underlying reason is that electrode activity commonly varies with time. One can readily envisage structural changes that *might* result in these effects, but few methods are able to provide this dynamic structure-property correlation. This is an area in which neutron methods could provide unique and vital information, complementary to that from spectroscopic probes.

5.4 Industrial needs for the future

Most industrial systems are complex mixtures of molecules yielding specific properties through formulation and processing steps. To help, aid and simplify this complexity, there is a need for the understanding of appropriate "model" systems and the concepts and insights they reveal. Many of the above areas aid this approach (model/concept) eg. studies of entanglements, polymer/surfactant adsorption, molecular interpenetration, compositional analysis, encapsulation, flow in complex environments, stability and functionality relationships etc.

In manufacturing processes, as discussed earlier, shear and stresses may affect both the macromelecular conformation, the molecular crystallinity and the compatibility of polymers and hence greatly influence the final polymer properties. This can relate to the compatibility of different polymers within the blend and/or to the crystalline and amorphous regions within a single polymer. Consequently in order to optimize the manufacturing processes and get the best performance of the final product, it is important to study and understand the molecular response when exposed to such macroscopic parameters like deformation, pressure, shear etc.

The rheology of colloidal dispersions, polymer solutions, polymer melts and composite materials attracts particular attention as they frequently display non-Newtonian behaviour. The material properties, such as viscosity and storage modulus, may vary with either (or both) deformation rate or strain amplitude giving rise to phenomena such as shear thinning, thixotropy and dilatancy.

There is a continuous spectrum of mechanical behaviour from liquids to solids. It will be desirable to perform measurements on a variety of materials such as plastic or lossy solids occurring as foods and as filled polymers as well as true fluids. Sample environments on beamlines will increasingly use extruders and tensile strain as well as conventional flow geometries to accomplish this. For example the ability to make time-resolved measurements of the development of phase separation etc. in an extruded product (eg. soap, chocolate, inorganic paste) or aggregation in processing of soft solids pastes and slurries would make the ESS invaluable.

For surfactant systems the introduction of reactive components in micellar and inverse microemulsions will lead to the production of new materials eg. polymerization or synthesis of inorganic nanocrystals in inverse microemulsions and the formation of porous inorganic materials generated by carrying sol gel reactions in bicontinuous phases.

Similarly as 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 in reactive control 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.

There are also opportunities for neutron methods to help in the area of electrochemistry. Examples of potential applications include "buried" interfaces (in polymer or electroplated metal multilayer structures, or in membranes), distribution of electrocatalyst sites in polymeric or metal oxide matrices, characterisation of composites, penetration of intercalants (Li^+ insertion into metal oxides in batteries), in studies of liquid-liquid interfaces (phase transfer catalysis or biological systems), and in corrosion of metals and alloys. The ability to make measurements *in situ*, using electrodes of practical geometry maintained under potential control and exposed to technologically relevant conditions of temperature and pressure is a unique advantage offered only by neutron methods when coupled to the appropriate sample environment. In the latter context, this would provide access to electrochemical processes in exotic media, such as supercritical fluids (carbon dioxide) or liquid sulphur dioxide or ammonia, both areas becoming extremely important in industrial applications.

Finally but equally importantly the properties of materials are often controlled to a significant extent by the presence of impurity species eg. "dopants" in polymer packaging materials. Taking the case of food packaging further high flux will enable the probing of mobility of these low level species. Such experiments would represent a genuine breakthrough in this field.

Summary

The group believes that the case from a high flux spallation source has been demonstrated for soft solids research on both scientific grounds and those of the ever increasing industrial search for product performance.

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Liquids, amorphous materials, ionic conductors

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1. Introduction

Disordered materials play a central part in our daily life. Water covers two thirds of the Earth's surface and is the major component of our bodies. Glasses are in our windows, in optical fibres for communications and even eaten as candy or used as stable coatings on medicines. Ionic conductors are in batteries in cars (electric cars in the future), mobile telephones and computers. However our scientific understanding of disorder is still inadequate; we cannot yet answer many basic questions, let alone detailed ones.

During the present century scientific studies of condensed matter have been dominated by ideas based on well ordered crystalline materials. The reason for this is obvious; the intrinsic symmetry of crystals can be used to simplify theoretical descriptions to such an extent that they can be applied to 'real' systems. However the same ideas and methods cannot be directly applied to disordered materials such as liquids and glasses, because of the lack of symmetry, and even in the case of highly disordered crystals they can be inappropriate or misleading. The study of disordered materials requires techniques that are optimised differently from those for crystalline materials. The information obtained from an experiment is continuous and different at all points covered by the experiment (there is no redundancy of information due to symmetry). Quantitatively precise measurements must therefore be made at as many 'points' as possible. ***Neutron scattering*** is one of the ***most important*** of the available methods, for a variety of reasons:

Structure and dynamics

The energy and momentum of thermal neutrons are appropriate to the ranges of interest in condensed matter. Length scales from 10^{-4} to 10^{2} Å and energy scales from 10^{-4} to 10^{4} meV can be studied with current techniques. Large areas of (Q,ω) space can be covered (other techniques may have a wider range, but only for one of the variables).

Isotope substitution

The method of isotopic substitution (or contrast variation) can be used to distinguish the positions and dynamics of different atomic species. H/D substitution is the most commonly used example of this technique.

Light atoms

Scattering cross-sections vary almost randomly across the periodic table, so neutrons can easily distinguish light atoms within a framework of heavier atoms, for example neutrons can 'see' water very easily in a Hg compound, while X-rays 'see' predominantly Hg.

Magnetic moment

The neutron has a magnetic moment, allowing studies of magnetic behaviour on a microscopic scale. This also makes the technique of polarisation analysis possible, allowing the separation of nuclear and magnetic scattering or coherent and incoherent scattering.

Theoretical interpretation

The quantity measured in a neutron scattering experiment can be related *directly* to the atomic positions and velocities in the material, as described by appropriate correlation functions. In contrast, for example, in X-ray diffraction the cross-section depends on momentum transfer and in light scattering (e.g. Raman or infra-red) it depends on energy transfer.

Penetrating power

The penetrating power of neutrons allows the study of materials in unfavourable conditions, for example bulk samples of corrosive liquid metal alloys can be studied at high temperature and pressure in thick walled TiZr alloy containers.

Weak interaction

The weak interaction of the neutron, while unfavourable with regard to the time taken to achieve statistical accuracy, allows necessary quantitative corrections to experimental data to be made with suitable systematic accuracy (e.g. sample and container absorption, multiple scattering). In addition data can easily be absolutely normalised by comparison with a vanadium standard. For studies of disordered materials the importance of these aspects should not be underestimated.

These advantages have been known and exploited for many years. Because of them ***neutron scattering has made many seminal contributions to our understanding of disordered materials***, in spite of the problems caused by lack of intensity. However, experimental methods develop rapidly and new techniques using X-rays from third generation synchrotrons, or in NMR for example, are becoming competitive for certain applications. This does not mean, though, that neutron scattering will become redundant - rather ***neutron scattering should become more important***. Its intrinsic advantages mean that neutron information is often required as the basis from which analysis/interpretation of other data is made. The central role that will be played by advanced computational methods, such as simulation or modelling, cannot be stressed too much. In this respect computing is the one area where the price/performance ratio can be predicted to continue decreasing for the foreseeable future, whereas all experimental methods get inexorably more expensive. The fact that neutron scattering results can be compared *directly* with those of simulation, should make neutron scattering *the* complementary experimental technique. The combination of improvements in experimental range, sensitivity and accuracy that will result from the construction of ESS, and developments in computational methods and other experimental techniques, will have a radical effect on the type and complexity of problems we can investigate in this field, and on the ways that we investigate them. This will produce a significant increase in the demand for neutron beam time, and for improved facilities, and broaden the range of applications.

Most research on disordered systems, up to the beginning of the 1990's, concentrated on 'model' systems from which we gained a general understanding of some of the basic physical processes determining their behaviour and properties. During the 1990's developments in neutron sources and instrumentation, and in methods of computer simulation and modelling, have led to a strong trend towards more complex 'real' systems, especially those with technological applications. Since most modern materials are not well ordered crystals, this work is increasingly important. The scientific aim is to extend our knowledge of the basic *structure* and *dynamics* of disordered materials, and their relationship with the *interatomic interactions*, to the point where we understand how this controls *function*, i.e. the properties of interest in an application. Usually this requires investigations over a wider range of 'parameter space' than is common at present, including 'extreme conditions'. The critical information will be obtained from the derivatives of $S(Q)$ and $S(Q,\omega)$ with respect to these parameters (e.g. composition for multicomponent systems, isotope variation, T, P, E, B...) measured over the widest possible Q and ω ranges and with more element specific information. The demand for information, produced by this trend towards complexity, will not be met by any single experimental technique. It will require all of the developments of new neutron sources, third generation synchrotrons, computers and so on. When they are put together, these will offer tremendous new possibilities for technologically relevant research.

Many exciting possibilities for new research can be foreseen on a ten year scale. In some cases demonstration experiments have already been done, and have shown that neutron scattering is the most appropriate technique, or an indispensable part of a series of complementary techniques, but the relevant problem will not be solved without access to more neutrons. Sometimes this requirement can be satisfied by more, or improved, instrumentation on existing sources. In other cases it is ***absolutely necessary*** to have ***new, more intense neutron sources*** with ***specially optimised instrumentation***.

2. Past achievements of neutron scattering

Neutron scattering has made some of the most significant contributions to our understanding of the fundamental physics governing the microscopic structure and dynamics of liquids (and glasses). Some particular aspects are highlighted below.

Experiment and theory

The interplay between neutron scattering and theoretical developments has been considerable. Early measurements could be directly interpreted in terms of van Hove correlation functions. Precise neutron scattering data required more detailed treatment which led to, for example, the development of memory function formalism and then later to mode coupling theory. This itself spawned a whole new area of research into the glass transition, and so on.

Experiment and simulation

There has been a similar interplay with the development of computer simulation. The early developments of hard sphere Monte Carlo simulation by Alder and molecular dynamics with (soft) interatomic potentials by Rahman, were prompted by the need to explain neutron scattering data on simple liquids. The potentials used in simulations are almost always validated, where possible, by comparison with neutron scattering data, even including the most advanced simulation methods such as ab-initio Car-Parinello simulation.

Dynamics of simple liquids

The first experimental measurements of $S(Q,\omega)$ for simple liquids provided much of our basic understanding of single particle motions (e.g. diffusion) and collective modes [1], which could not be described by theory developed for crystals (e.g. phonons). Polarisation analysis was used to separate single particle and collective motions (this was only really a demonstration experiment, but must be regarded as an experimental tour-de-force [2]). Dispersion curves were measured for collective modes in liquid alkali metals [3].

Isotopic substitution

Isotopic substitution was used to determine partial structure factors and partial radial distribution functions for binary liquid metals and molten salts [4]. This led to, for example, an understanding of 'charge ordering' in ionic liquids and its relation to the Coulomb interaction between ions. Such information could not be obtained from single diffraction measurements due to the mutual cancellation of relevant features, itself produced by charge ordering.

Ionic solvation

The same technique was extended to study solvation in ionic solutions, using both substitution of H/D in water and ions in the solution (e.g. Cl) [5]. This work showed that tables of solvation numbers in standard textbooks, obtained by indirect methods, were often totally wrong.

Metallic glasses

Almost all our knowledge of the structures of metallic glasses comes from the very detailed neutron scattering work carried out using isotopic substitution, principally of Ni in Ni based glasses [6]. This led to important ideas concerning the role of chemical (concentration) fluctuations in structural ordering.

Network glasses

Very accurate structural measurements for network glasses, over a wide Q range [7], have confirmed the importance of specific chemical bonding and flexible bond (e.g. torsion) angles, and indirectly confirm Zachariasen's random network model.

Technique development

Techniques developed in neutron scattering studies of simple liquids and glasses are now routinely used in, for example, studies of polymers or in biophysics.

The glass transition

Neutron scattering has been the most important technique in studies of the glass transition, particularly in testing the predictions of mode coupling theory [8].

3. Generic advantages of ESS

This section describes the general technical advantages of ESS which are of relevance to studies of disordered materials.

3.1 Structure

3.1.1 Range and resolution

Structural studies of crystalline materials can be improved by increased resolution. In contrast, medium resolution usually suffices for disordered materials, but without the advantages of symmetry it is necessary to have as wide as possible a range of information (e.g. momentum transfer). The structure factor must be measured with high precision at all points within this range. The current (routine) capabilities can be summarised as:

Q range ($Å^{-1}$)	***r range/ resolution (Å)***	***Applications***
0.5 - 15 (reactor)	12/0.4	General studies of microscopic structure with high statistical precision for e.g. isotopic substitution.
0.5 - 30	12/0.2	Studies of microscopic structure with reduced inelasticity corrections for light atoms and increased real space resolution for covalent bonds.
0.001-0.1 (SANS)	6000/60	General studies of macroscopic structure. (SANS normally uses long wavelength neutrons and is not exactly compatible with other diffraction measurements using short wavelengths. The intermediate region 0.05 - 0.5 $Å^{-1}$ is not well covered.)

ESS offers specific advantages for significant improvements in our capabilities:

Q range (Å^{-1})	***r range/ resolution (Å)***	***Applications***
0.5-70	12/0.09	Improved real space resolution due to the higher Q range, allowing the distinction of different chemical environments for specific atom types, or the separation of different chemical bonds in complex systems.. Improved treatment of inelasticity corrections due to the use of higher incident energies and lower scattering angles.
0.05-0.5	120/12	In this region cross-sections are often small and featureless, so high flux is needed for accurate measurements. It is important for the derivation of terms in interatomic potential via theoretical expansions or the determination of three body interaction via derivatives of the structure factor, for example.
0.001-30	6000/0.2	The ability to measure a continuous, self-consistent, structure factor over such a wide Q range will allow self consistent modelling of complex systems, e.g. polymers, over the entire range of relevant length scales. This connects microscopic ↔ mesoscopic ↔ macroscopic structure and hence chemistry ↔ physical properties ↔ function.

3.1.2 Count rate

The design specification should give 30 times the flux of ISIS. If this is coupled with expected improvements produced by new research and development in guides, detectors etc. before ESS is built then we should be considering (conservatively) an increase in effective count rate of between 100 and 1000 for different applications. This will have a radical effect on the way that many studies are carried out. Projects that cannot now even be contemplated, since in practice they would take many years, will become routine. This is particularly important in relation to technologically relevant research. While 'pure' research can be pursued over a number of years, the time scale for technologically relevant research (meaning a whole 'project' rather than a single 'measurement') must be much shorter. An increase in count rate is then not simply equivalent to an increase in 'beam time', so a new high intensity source is not equivalent to a number of low intensity sources. In fact both are required; lower intensity sources can be used to prepare experiments or develop techniques in order to ensure the optimum use of the higher intensity source.

Typical applications of the increased count rate of ESS will be:

'Phase diagram' studies

- composition dependence (more than one variable)
- thermodynamics (T,P)
- applied fields (B,E)

Small samples

- hard to prepare or newly synthesised
- under extreme conditions
- special isotopic samples
- thin films

Kinetic studies

- phase changes
- chemical reactions
- processing
- environment changes (T,P,B,E)
- *in-situ* studies

High precision studies

- three body correlations from S(Q) derivatives (T,P)
- small isotope differences
- low concentrations, densities

3.1.3 Polarisation analysis

The application of polarisation analysis to the study of disordered materials has so far been limited by the available intensities at reactor sources, and the lack of efficient white beam polarisers at pulsed sources. It seems likely that polarised ^{3}He filters will solve the latter problem within a few years, so then the high flux at ESS would open up a wide range of new experiments. In structural studies polarisation analysis will allow the separation of atomic and magnetic scattering in amorphous magnetic materials and the 'removal' of incoherent H scattering (and associated inelastic scattering) for hydrogenous materials that are not amenable to deuteration.

3.1.4 Geometry and anisotropy

Pulsed neutron sources offer distinct advantages for structural studies of anisotropic systems (e.g. liquid crystals, aligned polymers, materials under applied fields).

- A large part of the structure factor can be obtained with a fixed geometry relative to the sample, e.g. $Q_{\perp}$ or $Q_{\rfloor}$ at ± 90°.
- More generally a large area of **Q** space can be covered in a single measurement, whereas with a reactor source only a single line is covered.
- The fixed geometry arrangement makes the design of some types of sample environment much easier e.g. stress rigs, magnets, pressure systems.

3.1.5 Complementarity

It is useful to describe here the possible uses of other techniques, and how they complement neutron scattering.

X-ray diffraction (synchrotron)

Laboratory based X-ray systems do not offer sufficient precision over a wide enough Q range to be generally applicable in structural studies of disordered materials. Problems of corrections, particularly Compton scattering and normalisation, can be severe. Using synchrotrons there are a number of approaches for improving the capabilities:

- *Warren-Mavell technique.* This is a method of significantly reducing the Compton scattering, but at a considerable cost in count rate so a tuneable, high intensity source is needed if it is to be generally used.
- *Hard X-rays.* Recent structural measurements using very hard X-rays appear promising. Many of the correction problems are minimised and the Q range can extend up to 25 Å^{-1}, subject to the intrinsic effective limits imposed by the form factor. High penetration

(relative to conventionally used wavelengths ~1 Å) means that samples in more complex environments can be studied. However less stable chemical systems may suffer from radiation damage.

- *Anomalous scattering.* It has not yet proved possible to determine partial structure factors with sufficient accuracy using anomalous scattering. However the method will undoubtedly improve significantly in the next ten years. Except in a few cases it cannot be used in combination with the techniques mentioned above, though, so there will still be problems related to data corrections.

Light scattering

Light scattering is the obvious technique for studies of 'mesoscopic' liquids such as colloidal suspensions. Neutron scattering might become complementary if the range of useful wavelengths in small angle scattering could be extended to higher values.

EXAFS, XANES

These methods have often been considered poor in relation to neutron diffraction since the (equivalent) Q range is small and the absolute precision is poor. However they do provide information that is highly element specific and can be used for small samples or very low concentrations, with a fixed geometry and with complex sample environment. The quantitative accuracy of measurements, and the theoretical calculation of EXAFS or XANES spectra from structural models, are improving all the time. Because of intrinsic complexities, EXAFS and XANES will always be complementary to diffraction, but not competitive with it.

NMR methods

New NMR methods, and improvements in the sensitivity or specificity of existing methods, continue to be developed. NMR is very powerful for studying some specific light atoms, e.g. H, so there is a strong overlap with neutron scattering. The technique mostly provides information on local bonding, though information on second coordination shells can now be obtained, so it may be considered equivalent to EXAFS or to the very high Q part of the diffraction pattern. It is element specific; only a restricted range of elements are suitable but they happen to be important ones in a technological context. Solid state NMR, particularly within the context of modern high field magic angle spinning methods, including those relying on sophisticated techniques such as multiple quantum excitations, will play an important role in materials studies. With the ability to extract information from wide-line spectra, the list of elements available for quantitative study is growing to the point at which a large proportion of the technologically important nuclei can be used; it has thus become a truly useful complement to neutron scattering studies. However more work is needed on the theoretical calculations of quadrupolar couplings and asymmetry tensors, for example, if apparent inconsistencies between NMR and diffraction are to be avoided.

Simulation and modelling

The greatest opportunities for complementarity will come from the combination of different data sets using computer simulation or modelling, for example RMC. This allows the optimal use of each individual technique, where it provides most information and has least problems. X-ray and neutron diffraction often have significantly different weightings for the contributions of different atoms. Anomalous scattering or isotopic substitution can be used to highlight specific elements as appropriate. In particular cases, where concentrations are low for example, EXAFS will be a suitable method. Multiple quantum NMR can be used to provide very specific information on local bonding geometry and coordination; this needs to be consistent with the averaged information provided by high Q neutron diffraction.

3.2 Dynamics

3.2.1 Range and resolution

In neutron scattering studies of the dynamics of crystalline materials it is generally possible to take advantage of the symmetry so that all of the most important information can be measured within a restricted region of (Q,ω) space (e.g. phonon dispersion in a single Brillouin zone in a crystal). The lack of symmetry in a liquid or glass means that it is necessary to measure at all Q and ω. Currently neutron scattering allows very wide parts of (Q,ω) space to be covered (see table 1), but the same relationships which allow this wide range also make particular regions difficult to cover. The increased flux at ESS will allow more optimised instrument designs which will produce a major technical advance in our capability to access (Q,ω) space and hence a significant improvement in our understanding of the microscopic dynamics of disordered materials.

To describe the developments in the study of the dynamics of liquids and glasses that will be made possible by ESS it is useful to draw an analogy with developments in structural studies in the past 20-30 years. ESS should enable studies of the dynamical structure factor, $S(Q,\omega)$, to the same 'level' that we can now study the static structure factor, $S(Q)$. Currently we can only measure $S(Q,\omega)$ in the 'intermediate' (Q,ω) range with high accuracy.

Table 1:

$Q(\text{Å}^{-1})$ **$h\omega$ (meV)**	**10^{-3}**	**10^{-2}**	**10^{-1}**	**1**	**10**	**10^{2}**
10^{-4}	Light		can be	–	–	–
10^{-3}	scattering	ESS	done	can be	–	–
10^{-2}	Light	ESS	now	done	–	–
10^{-1}	scattering	ESS	ESS	now	–	–
1	Light		ESS/ESRF	now	can be	–
10	scattering		ESS/ESRF	now	done	–
10^{2}	Light		ESRF	ESS/ESRF	now	now
10^{3}	scattering					now

(Q,ω) ranges covered by current and future techniques and sources.

Neutron Brillouin Scattering (NBS)

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, for example the velocity of sound, 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, e.g. 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 (large size and long time simulations are needed). NBS will provide an important 'bridge' between the information available from light scattering and neutron scattering, due to the extension of the available Q range to lower values than those presently achievable.

NBS is intrinsically a time-of-flight technique, so it is well suited to a high intensity pulsed source such as ESS. It requires the use of short wavelength (high velocity) neutrons at small scattering angles, with a high resolution measurement of the energy transfer. Scattering cross-sections are generally low so with the increased useful flux from ESS such experiments, which have only just become feasible, should become routine. Optimised instruments for higher and lower energy transfers could be built on the 50 and 10 Hz target stations. These instruments would also find applications in other fields, for example magnetism or critical behaviour.

Good energy resolution

- Coherent scattering studies of the (phonon) density of states of glasses and molecular liquids, using high incident energies (500 meV) with high enough energy resolution, have only recently become feasible using MARI at ISIS. However the count rate is low, so even single measurements of sufficient accuracy take many days. Progress in this area will therefore be limited until ESS is built. In particular it will not be possible to use the combination of high resolution and isotopic substitution which allows both the separation of modes and their identification (i.e. which atoms contribute).

- Development of TFXA at ISIS has also broken new ground in high resolution, high energy, incoherent scattering studies. As a general technique in chemical spectroscopy this is very powerful since the neutron cross-section does not involve the unknown matrix elements that complicate interpretation of Raman or infra-red spectra. However the time scale for measurements involving hydrogen modes must be reduced from hours to minutes before it becomes as routinely used; many non-hydrogenous systems cannot be studied at all with present intensities. This would certainly be possible with ESS.

- The unique feature of the IRIS spectrometer at ISIS has been the combination of a high energy resolution with a wide range of energy transfer, on a single instrument. The enhancement of these features at ESS, due to the increase in count rate, together with the option of polarisation analysis, will make such instruments very powerful for studying both quasi-elastic and inelastic scattering in materials where a wide range of time scales are relevant.

Inelastic scattering of very high energy (eV) neutrons is dealt with separately (section 4.4.2).

3.2.2 Count rate

There are some types of study which, although unique to neutron scattering and technically feasible (to some extent) have rarely been carried out. One of the main reasons has been the considerable amount of beam time required, even at the worlds highest flux source (ILL). The increasing demand for beam time has made it harder and harder to develop and use such methods. With the building of ESS and related developments in instruments, detectors and particularly polarisers, they should become relatively routine.

Isotopic substitution

Almost certainly the most important technique in neutron diffraction studies of liquids and glasses has been isotopic substitution, allowing accurate element specific information to be obtained. Apart from the special case of H/D substitution providing information on H motions, the method has not generally been applied in dynamical studies. Some studies of molten salts have been done in the past, but the results should only be considered as qualitative and could not (then) be easily interpreted.

'Small samples'

As for structural measurements, an increased count rate is vital to allow studies as a function of many variables, of small samples under extreme conditions, or those with small concentrations of the atomic species of interest.

Optimised corrections

A high flux allows more optimised design of experiments to reduce the size of data corrections; sometimes this improvement in systematic accuracy will be more important than an improvement in statistical accuracy. This is particularly true for some studies of disordered materials.

3.2.3 Polarisation analysis

Applications in dynamical studies include the separation of coherent and incoherent scattering (individual and collective motions) in simple liquids and the separation of hydrogen modes in complex systems that are not amenable to deuteration. The more specific application in the use of neutron spin echo is dealt with in section 4.4.3.

3.2.4 Complementarity

Inelastic X-ray scattering

New developments in inelastic scattering of synchrotron X-rays, using triple axis methods, are starting to achieve an energy resolution of the order of a few meV. This technique is very demanding; there will be further developments but 1 meV seems a likely resolution limit. Current experience is too limited to yet know how quantitative a technique (in the sense of an absolute measurement of $S(Q,\omega)$) inelastic X-ray scattering is likely to be. It should be viewed as a complementary development; the fact that it is being done at all illustrates the importance of this particular (Q,ω) region. In the future X-rays will be the choice for some studies and neutrons for others. This will depend on the relative weighting of the mode(s) of interest and the resolution required; in some cases it may be necessary to combine the two methods. One fundamental disadvantage of inelastic X-ray scattering is the absence of incoherent scattering, so the motions of individual atoms, e.g. $S_s(Q,\omega)$, cannot be studied.

Light scattering

Developments in laser and detection technology mean that light scattering will always be the fastest method for studying atomic dynamics, and techniques now cover a tremendous range of time scales, from 10^{-15} to 10^{2} s. However all information is confined to $Q \approx 0$ and there is the problem, noted above, of unknown matrix elements (sometimes these are favourable, and sometimes not). Light scattering can also be very sensitive to impurities or surface effects. In general there are *clear* advantages in studying dynamics with *both* neutron and light scattering techniques.

NMR

Field gradient NMR can be used for studying diffusion of e.g. H, and should probably be the technique first used (in cases where it is applicable) if purely macroscopic information is required. However NMR works in the time range 10^{-4} - 10 s, whereas neutron scattering works in the range 10^{-12} - 10^{-8} s, so the information can be different. Incoherent or coherent neutron scattering must be used when the Q dependence is required; NMR spatial resolution is limited to $Q < 10^{-2}$ Å^{-1} but neutrons cover the range 10^{-3} - 10 Å^{-1}. There is also a subtle difference between the macroscopic diffusion coefficient measured by NMR and the chemical diffusion coefficient measured by neutrons.

Simulation and modelling

Despite many claims, the number of MD simulations of the structure of disordered materials that agree (within the errors) with the experimental $S(Q)$ is tiny; even fewer agree with $S(Q,\omega)$. If MD is to realise its full capability as a predictive tool then it is vital that accurate interatomic potentials are used, i.e. ones which actually reproduce the available data. In this respect the complementarity between MD simulation and inelastic neutron scattering is obvious. The simulation can calculate exactly the same correlation functions as are measured by neutrons, but in addition can calculate many functions which cannot be measured experimentally (e.g. density-density, force-force). Measurement of $S(Q,\omega)$ is very important since it is well known that dynamics are far more sensitive to the precise details of the interatomic potential than structure. With the increase in computing power in future it will become possible to 'tune' potentials by comparison with neutron scattering results. In cases such as quasi-elastic scattering studies of molecular liquids, for example, where often many different contributions overlap, neutron data could be used to determine the potentials and then the simulation used to 'analyse' the data by separating the contributions.

4. Specific applications of neutron scattering in (disordered) materials science

4.1 Liquids

4.1.1 Elemental liquids

Hydrodynamics ↔ atomic dynamics

Neutron scattering has provided us with a detailed understanding of the microscopic structure and dynamics of simple liquids (condensed inert gases, liquid metals). On a macroscopic scale the dynamics are well described by hydrodynamics. What is now missing is a description of the intermediate range, which is accessible using NBS. A few successful pilot experiments have been performed on optimised systems [9,10], but these are at the limit of what is at the moment technically and practically feasible, even at the highest intensity sources. Experiments can be divided into two categories.

- 'Low energy'. The transition from hydrodynamics to viscoelastic response in fluids where the velocity of sound is lower than the typical velocity of thermal neutrons (e.g. Ar, Kr, Cs).
- 'High energy'. The dispersion of collective modes in liquids with a high sound velocity (e.g. Li).

It is possible that even things such as the modelling of combustion processes could benefit from NBS studies in the linearised hydrodynamics-microscopic dynamics transition region.

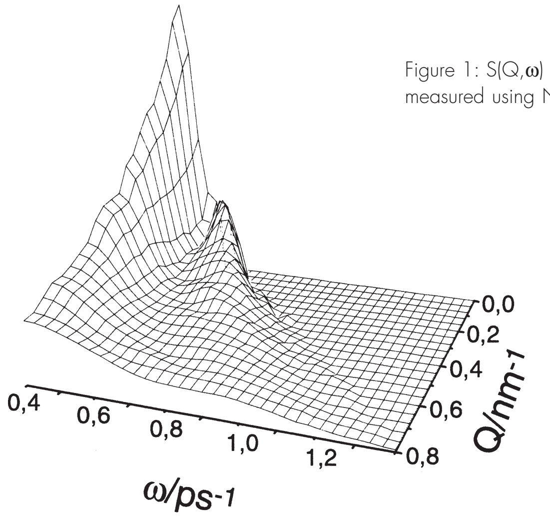

Figure 1: S(Q,ω) for ^{36}Ar at T=300K and P=200 bar, measured using NBS [9].

Phase diagrams

Despite studies over 30 years no simple liquid structure has really been studied in detail all through the phase diagram. Even less has been done for the dynamics. For instance there is a lack of understanding of phenomena close to the critical point which cannot easily be described using current simulation methods, e.g. in liquid metals there is a metal-insulator transition, which may or may not be coincident with T_c, where there may be significant changes in the interatomic potential. Only a small amount of work has been done so far, along single lines in (T,P) space, e.g. close to the co-existence curve [11]. Further studies require the high count rate offered by ESS because of the lower scattering cross-section at lower density, the need for more (T,P) points etc., in addition to the practical geometric advantages for sample containment offered by the possibility of measuring S(Q) using only a restricted range of scattering angles.

High systematic accuracy

Very precise structure factor measurements are required in a number of specific areas:

- Long range terms in the (two body) interatomic potential can be derived directly from accurate measurement of S(Q) in the low Q region (0.05-0.5 Å-1), for example van der Waals coefficients. This has been discussed for many years but still no suitable instrument exists for making sufficiently accurate measurements with high incident energies, and hence small scattering angles.

- The effects of three body interactions are not well understood. This applies both to the low density (gas) and high density (liquid) limits. Theoretically there are possibilities to derive three body terms by measurement of $(\partial S(Q)/(\partial P)_T$. Again this has been discussed for many years, but only some small demonstration experiments have been done [12]. The main requirement is for very high systematic accuracy (3-body contributions are typically less than 1%).

- High accuracy measurements as a function of T and P are needed to unravel some of the complex bonding behaviour in liquids such as S, P, Se and Te, e.g. the viscous transition in liquid S [13], the molecule-network distinction between liquid and amorphous P.

- Bonding electron distributions in disordered systems containing light atoms, e.g. Li, Be, could be studied using the combination of extremely precise neutron and X-ray diffraction measurements [14].

4.1.2 Multicomponent liquids

Molten salts

Structural work on molten salts needs to be extended to three and four component systems [15], in particular those of interest in chemical processing such as electrolytic production of aluminium or treatment of radioactive waste. Some proposals for future accelerator driven sub-critical power reactors are based on molten salt (or liquid metal alloy) technology and detailed information will be required. Neutron scattering is well suited because (a) containment of corrosive or even active samples is not a problem, (b) isotopic substitution can often be used (e.g. Cl). EXAFS studies may well be complementary; X-ray diffraction is usually difficult, if not impossible. The requirement is for high precision (for isotopic studies) and investigations across the phase diagram. Such projects are only feasible with a new high intensity source. Other goals should be the study of e.g. oxides and sulphides, requiring higher temperatures, and in-situ studies of molten salt electrochemistry.

Liquid metal alloys

The largest field of current interest is in the generic area between metals (electronic conductors) and salts (ionic conductors). The interest is in relating the microscopic structure and dynamics and the interatomic potentials producing them, with the macroscopic electronic/ionic conductivity. Many systems exhibit some form of clustering or quasi-molecular behaviour so both structure and dynamics are complex [17]. Often the real need is to study a ternary phase diagram and the effect of T and P, i.e. 5 variables.

Dilute systems

Of particular fundamental interest in terms of single particle dynamics are dilute concentrations of light atoms in heavy ones (e.g. He in Ar) or vice-versa (e.g. Hg in Ar). This requires accurate measurements, possibly with isotopic labelling and polarisation analysis.

Isotope substitution in dynamics

There is as yet no general understanding of, or even formalism for describing, the collective dynamics of multicomponent liquids. Ideas such as 'fast sound' have aroused much interest, and controversy, in recent years [18]. The best way to obtain the required information experimentally is to measure partial dynamical structure factors by using isotopic substitution in inelastic scattering experiments. Dynamics are also a much more sensitive test of interatomic potentials than structure, so such measurements could be used in conjunction with molecular dynamics simulation to derive suitable potentials.

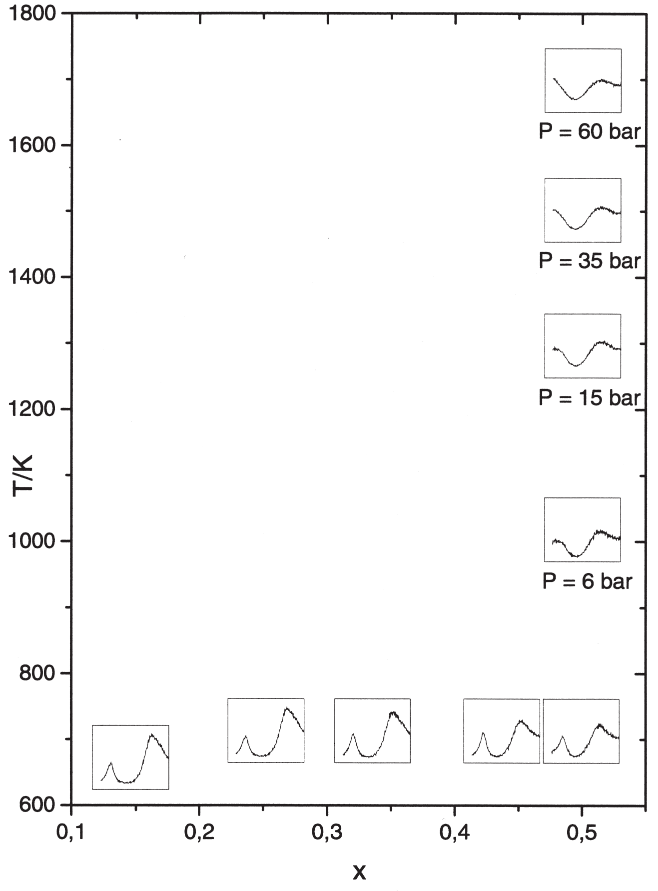

Figure 2: Low Q structure factors for molten Cs_xTl_{1-x} alloys as a function of x, T and P. Only very sparse coverage of this three dimensional parameter space is feasible at present [16].

Phase separation

There have been many studies of critical phenomena involving macroscopic length scales, such as phase separation, from a structural point of view. NBS offers new possibilities for the direct study of the (slow) dynamics of such transitions, giving information on both time and length scale fluctuations [19]. Cross-sections tend to be high so the intensity requirements are not so severe, but lower angles and better energy resolution can be needed. Also of interest are studies of structure and dynamics of supercritical mixtures close to the demixing (gas-gas) phase transition. Such studies could take advantage of isotopic substitution and of complementary simulations, aimed at deriving the potential parameters for unlike atoms (failure of the Lorentz-Berthelot type rules).

4.1.3 Molecular liquids

During the past few years there has been a dramatic improvement in capabilities for studying light atom molecular liquids (e.g. hydrogen containing) due to the development of the SANDALS type diffractometer [20]. This allows both a reduction in the effects of inelastic scattering, by the use of small scattering angles and high incident energies, and measurement out to high Q, giving accurate determination of covalent bond lengths and coordination, which becomes more important as the complexity of the molecule increases. The higher intensity available at ESS will allow a reduction in beam size and the consequent availability of detectors at even lower angles than those currently used, giving further improvement in these respects. The most challenging example is still water; studies have been made over a wide range of state conditions varying from glassy to super-cooled liquid to super-heated vapour [21]. However it is clear that further improvements in inelasticity corrections in particular, which will be possible because of the higher flux at high incident energies available at ESS, are absolutely necessary if subtleties of the hydrogen bond network are ever to be understood.

As far as dynamics are concerned, the extra rotational degrees of freedom in molecular liquids make theoretical treatments more difficult. Higher resolution over a wider energy range and routine polarisation analysis will give a considerable improvement over current possibilities for studying systems with a wide range of relaxation times. This will allow a more sensible comparison between neutron scattering results and computer simulations/modelling, particularly for inelastic/quasi-elastic studies where multiple contributions overlap and give large uncertainties in parameters derived from fitting procedures [22].

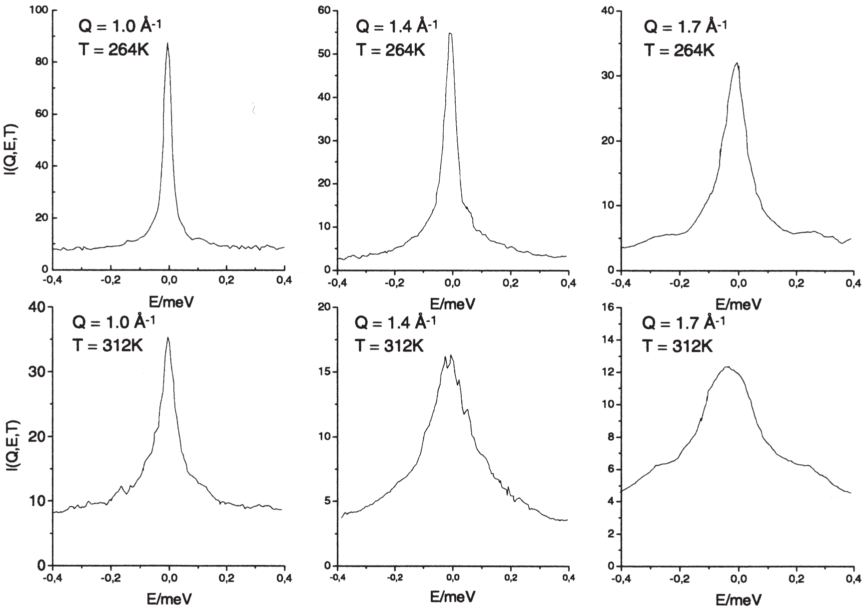

Figure 3: Quasi-elastic scattering data for quinoline, showing the need for high resolution and a wide energy range within the same measurement [23].

4.1.4 Solutions

Neutron scattering studies of ionic solvation in fluids (principally water) have been well developed, but mostly they have been confined to high concentrations and there has been no real work on phase diagrams [24]. More recently work has been done on non-ionic systems, for example hydrophobic interaction of Ar in water [25]. Methane in water is supposed, under certain conditions, to form a system of clathrate cages which may actually induce pipe blockage in deep-sea oil drilling. This phenomenon is poorly understood and neutron scattering using

H/D substitution provides a unique tool with which the solute/solute, solute/solvent and solvent/solvent interactions can be probed. However, even with a single, relatively simple, system the beam time requirements for a proper study are prohibitive. If we consider only two parameters, such as temperature and concentration, take into account the need to perform multiple H/D substitutions on both a solute (e.g. urea) and a solvent (e.g. water), then we are currently considering (in practice) a project of 5-10 years [26]. There is no alternative technique for such studies, so ESS is vital if significant progress is to be made. We can also see that work is tending towards still more complex systems, with links to biophysics (water function in biological macromolecules is an increasingly 'hot' topic), food processing etc. [27]. Studies of simple systems are a prerequisite for understanding colloidal systems and biopolymers etc.

The high count rate at ESS will allow studies of electrolyte solutions at low concentration, possibly with isotopic substitution. Such studies are of paramount technological importance, mainly in the supercritical regime, for waste oxidation, turbine corrosion, supercritical fluid extraction etc.

4.1.5 Liquids in porous media

The study of fluids in porous media is still in its infancy, despite a high and growing level of interest. Most work has so far been relatively qualitative. Experiments have shown clearly that liquid structure and dynamics are altered within pores [28], e.g. freezing temperatures are normally depressed and even a change in the universality class of the superfluid transition of ^{4}He has been observed in porous glasses of different confinement structure [29]. However more detailed work requires the development of porous glasses with much better controlled pore sizes and size distributions, and of porous crystalline materials (e.g. zeolites) with reproducible crystallinity and larger pore sizes. The indications are that this will happen within the next few years due to methods of liquid crystal templating, such as used for mesoporous non-crystalline silicates of type MCM-41. (The study of this process in itself may be an important area of future work.) More accurate experimental methods will then be needed to allow better subtraction of scattering due to the medium from that due to the enclosed liquid. It will also be necessary to develop techniques for measuring at length scales intermediate between atomic sizes (e.g. 2-20 Å) and pore sizes (e.g. 100-500 Å), since this is where the most important information will be obtained. Improved precision from ESS will allow the study of smaller liquid loadings. The geometry of pulsed source instruments will also be advantageous for anisotropic systems, e.g. clays [30].

4.1.6 Liquid-glass transition

Despite the interest in the liquid-glass transition in the last few years, mostly concerned with verification of the predictions of mode coupling theory (itself developed to explain the dynamics of simple liquids) [31] , there are still a lot of unexplored areas. Most work has been done on 'fragile' glass formers, where the (slower) α and (faster) β relaxations tend to have similar time scales within the length scales accessible to neutron scattering. For 'strong' glass formers, which actually comprise most of those with simple atomic structures, the time scales are more separated and the technical requirement is for high energy resolution across a very wide energy window. This is now possible using instruments such as IRIS, but the count rate is too low for detailed studies as a function of temperature (the systems tend to be predominantly coherent scatterers). There is also considerable controversy concerning the significance of 'boson' peaks in the density of states [32]. Detailed studies using isotopic substitution in appropriate simple systems should help to clarify their origin. Through investigation of the changes in microscopic dynamics under hydrostatic pressure it will be possible to discriminate between different models for the relaxation processes, by decoupling temperature and density effects.

4.1.7 Polymers

Polymers are the subject of a separate theme. The one particular area which should be mentioned here is the study of the *microscopic* structure of amorphous, liquid and partially crystalline polymers [33]. ESS will enable the extension of this work into the mesoscopic region, in order to understand the effect of microscopic structure within chains, and the inter-chain interactions, on the physical properties of the polymer.

4.1.8 Liquid crystals

NMR methods are very powerful probes of liquid crystals but there are two aspects which are poorly understood and which will benefit from neutron scattering results. One is molecular flexibility and its role in the formation of thermotropic liquid crystals and liquid crystal polymers. The other is the distribution of molecular orientations and the correlation of orientations of neighbouring molecules. Neutron scattering using H/D substitution (e.g. on a SANDALS type instrument) offers the opportunity to measure these. For instance by suitable isotopic labelling of a certain fragment it is possible to determine the effective intramolecular potential (e.g. to rotation of that fragment) and intermolecular orientational. This type of study is still in its infancy but it is clear that the level of information depends very much on the quality of the data. For instance it is often desirable to compare runs where the labelling on a very small fragment is changed, so the statistical accuracy of the data is important. High intensity will also become important for studies of aligned liquid crystal samples where it is no longer possible to improve statistics by adding detectors at the same magnitude of Q. It is also worth noting that this is an area where simulation and experiment are beginning to approach each other.

4.1.9 Quantum fluids

Quantum systems are the subject of a separate theme. However there is a clear overlap between the requirements described here for studies of simple liquids and those of quantum fluids, e.g. ^{4}He, ^{3}He, H_2 and D_2. The current trend is the study of such systems in confined geometries, e.g. porous glasses.

4.2 Glasses

4.2.1 Network glasses

Structural studies of network glasses have in the past concentrated on model two-component systems, such as SiO_2, B_2O_3, $GeSe_2$ etc. More recently work has extended to more complex systems, particularly to the effect of so-called 'modifiers', e.g. alkali oxides in SiO_2 [34]. This has involved either the use of isotopic substitution of (usually) the metallic species, or the use of EXAFS in combination with (X-ray or neutron) diffraction. Such studies have been aided by the high real space resolution obtained from the high Q range of pulsed neutron sources. The future need will be for higher intensity to allow the use of smaller isotopic differences and smaller modifier concentrations.

Now that relatively complex glass structures can be investigated there is also a trend towards studies of (four and five component) glasses with technological applications. This is only possible using neutron scattering as one of a set of complementary techniques, such as X-ray diffraction, MAS NMR, EXAFS etc., but neutron data will always be crucial since it provides the most quantitative data over the widest range. Among the applications are likely to be studies of doped glasses for optical fibres, pressure or magnetic sensors etc. Often there will only be small amounts of material (fibres or thin films) or low atomic concentrations, so high precision is required.

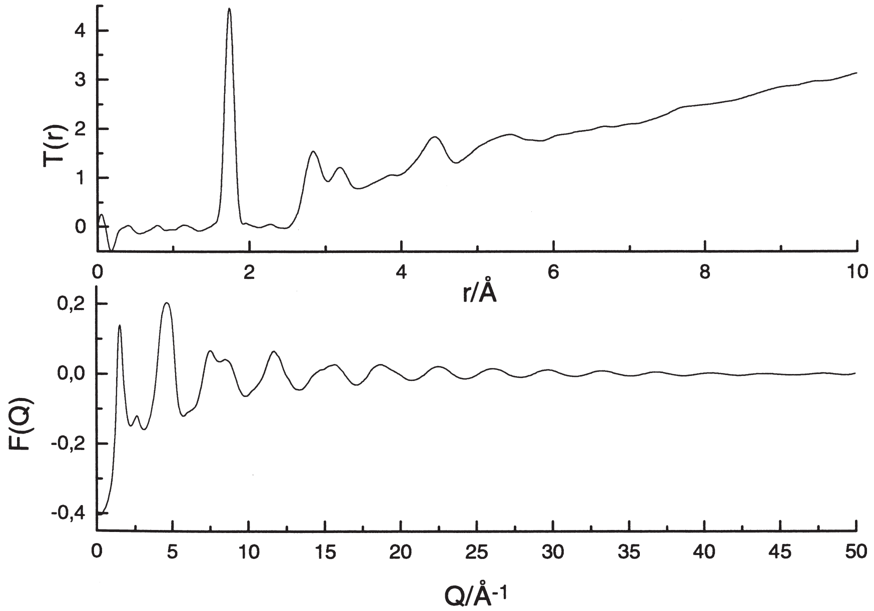

Figure 4: S(Q) and T(r) for vitreous GeO_2, showing the excellent real space resolution that can be achieved from wide Q range data [35].

Another approach will be to study the formation of glasses 'in-situ' using sol-gel techniques. This offers possibilities for preparing glasses with 'tailor made' properties (e.g. optical coatings) by control of the fabrication process. Thin films will be common, so high intensity is required.

The study of aluminosilicate glasses, particularly under extreme conditions, is also an area of interest in earth sciences. Other systems of interest are chalcogenides, e.g. As_2S_3, whose electrical properties can be significantly changed by doping with e.g. Ag [36]. Such materials have applications in electronics, as photosensors etc. An understanding of their behaviour will depend strongly on a knowledge of their structure; neutron diffraction using isotopic substitution is a very appropriate technique in this case.

New types of amorphous thin films have been developed in the past few years using CVD or similar techniques, for example amorphous hydrogenated carbon and related systems [37]. Such materials show very favourable physical properties, for example hardness, chemical inertness and photoconductivity, if deposited in the right conditions. However there is little understanding of this on a microscopic level. Neutron scattering has been able to provide some important information, for example demonstrating the existence of molecular hydrogen in the material [38]. Currently the limitation is the need to prepare large volume samples, possibly with isotopic substitution (H/D), for neutron scattering. ESS will allow the study of smaller samples (or considerably improved accuracy for larger samples), with improved treatment of inelastic scattering due to hydrogen in diffraction measurements.

Only recently has it proved possible to measure the vibrational density of states of network glasses with sufficient statistical accuracy, over a wide enough energy range and with high enough resolution (using MARI) to begin to distinguish many of the different modes [39]. However such experiments are still extremely time consuming and little real progress will be made without a much higher intensity pulsed source. A principal goal would be the use of isotopic substitution in such studies, allowing the selective identification of modes. Complementary inelastic X-ray scattering, light scattering and computer simulation will also be important.

4.2.2 Porous glasses

Glasses can be prepared with a very wide range of porosities (often by the sol-gel methods mentioned above). These can have specific commercial applications. Some porous glasses consist basically of small glass particles stuck together in a random ('fractal') arrangement. Other have more continuous structures. Detailed study of their structure, on microscopic, mesoscopic and macroscopic length scales, awaits the availability of instrumentation that can make suitable studies in the low Q region. It also requires more powerful computers to make atomistic models on the appropriate scale. The interest would then be in controlling the glass porosity (possibly studying the preparation in-situ) and tailoring it for specific applications.

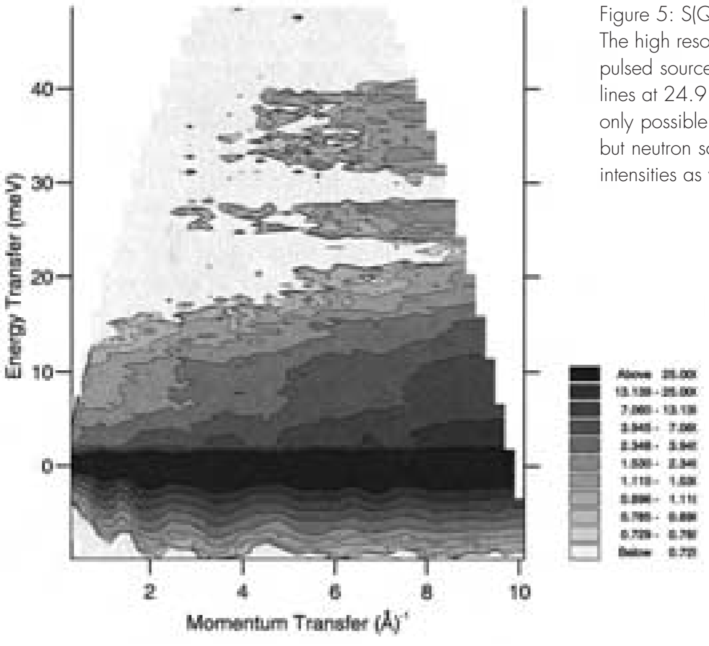

Figure 5: S(Q,ω) for $GeSe_2$ glass [40]. The high resolution now available from pulsed sources allows separation of the lines at 24.9 and 27.0 meV, previously only possible with Raman scattering, but neutron scattering gives absolute intensities as well.

4.2.3 Molecular glasses, orientational glasses and plastic crystals

Interest in molecular glasses (i.e. systems with no long range order containing molecules), orientational glasses (molecular crystals with no long range orientational order) and plastic crystals (molecular crystals with short range orientational disorder) has increased in recent years, partly due to the discovery of the fullerenes [41]. Some of these materials also show ion (or proton) conducting properties with strong links between the orientational disorder and ionic mobility. Often the phase diagrams are complex and detailed study is time consuming, particularly for dynamics which can show long period hysteresis effects.

4.2.4 Metallic glasses

Neutron scattering made a major contribution to structural studies of metallic glasses in the 1970-1990's, using isotopic substitution [42]. Most systems studied were produced by melt spinning since this was the only technique capable of making bulk samples. However this severely restricts the range of compositions. A higher intensity source would allow the study of materials prepared by sputtering or other PVD/CVD methods, though anomalous X-ray scattering may become the most appropriate method where higher atomic number elements are involved. Interest in melt spun metallic glasses is now concentrated on detailed questions involving variation in properties with preparation or subsequent treatment (this can have major effects on magnetic properties for example) [43]. The question of anisotropy is also being investigated [44]. Such studies require considerable accuracy which is at the limit of what can be currently achieved. Pulsed source diffraction is very favourable for studying anisotropy, as discussed earlier.

New methods for producing a wider ranges of glasses by bulk methods, such as ball milling or solid state (pressure) amorphisation have been developed. Such highly non-equilibrium methods, in particular ball milling, are influenced by many different factors which can have significant effects on the materials produced [45]. In many cases laboratory-based methods such as X-ray diffraction fail even to determine correctly if samples are amorphous or crystalline. Any definitive microscopic study of systems produced by such methods requires access to very high count rate neutron diffractometers for rapid sample characterisation, prior to more detailed study of the systems of most interest.

Studies of the dynamics of metallic glasses are currently challenging because of the high incident energies and high resolution required. This is one clear area where neutron Brillouin scattering will be applicable [46]. Metallic glasses may be viewed as model systems for studying the dynamics of disordered multi-component materials, since they are solid, and Ni based systems in particular are favourable for isotopic substitution.

4.2.5 Magnetic glasses

Very little detailed study has been made of magnetism in glasses. One major problem is that there is no simple way of separating the magnetic diffuse scattering from the structural diffuse scattering, as samples tend to crystallise before the magnetic scattering becomes entirely paramagnetic. In one or two unique cases this can be done by 'double null' isotopic substitution [47]. The more obvious method is polarisation analysis; however current count rates are too low to make this generally feasible. More recently the combination of neutron and X-ray methods via computer modelling has offered new possibilities [48]. These technique developments, coupled with high count rate polarised diffractometers and also the possibility to look in the low Q region (the cross-over between 'short range' and 'domain' ordering, which may be crucial for macroscopic properties) will open this field up. The technological emphasis will inevitably be on thin films (magneto-optical recording media etc.) so high count rates will be needed for small samples, whose anisotropy may also be important. However new bulk materials, such as the rare earth metaphosphate glasses, will also grow in importance. In addition magnetic metallic glasses are a possible route to production of nano-crystalline materials with favourable magnetic properties.

4.2.6 Ion conducting glasses

Such materials have become increasingly of interest in recent years since they offer the prospect of high ionic conductivity with improved mechanical properties (compared to crystalline materials), for use in batteries or fuel cells for example. Neutron scattering has been used to study structure-conductivity relationships in the first study of its kind combining neutron diffraction, X-ray diffraction and (multiple edge) EXAFS data [49]. However this type of work, over the phase diagram of a complex system such as $(AgI)(Ag_2O)(B_2O_3)$, takes years with present facilities. Interestingly, despite the high ionic conductivity, the diffusion rates tend to be low, meaning that quasi-elastic scattering studies of dynamics are at the limit of what is currently possible [50]. The trend in materials may be away from inorganic systems to 'rubbery electrolytes' (polymeric materials with a high salt content) where H/D substitution will be of great interest.

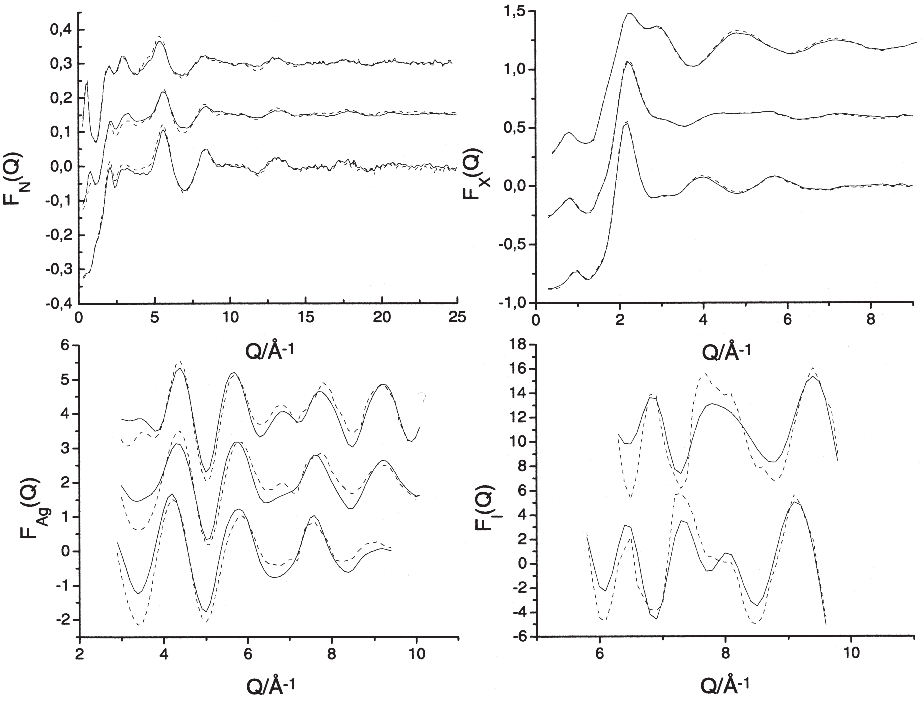

Figure 6: Combined neutron diffraction, X-ray diffraction and EXAFS data for $(AgI)_x(AgPO3)_{1-x}$ glasses [49].

4.2.7 Ion conducting polymers

Ion conducting polymers are of considerable future importance in lightweight battery design, e.g. for electric cars, 'smart windows' and other applications. They are also one of the best examples of why neutron scattering is a necessary and important technique, and why ESS is needed. Structurally they involve length scales from 1 to 1000 Å; dynamically there are relevant motions with time scales from 10^{-12} to 1 s [51]. It is clear that the ionic conduction is closely related to the dynamical relaxation of the polymer, which is itself determined by the structural order both on the short range (i.e. cross-linking of chains) and the long range (i.e. partial crystallinity). The salt contents tend to be low, so most of the scattering comes from the polymer matrix. Optimised materials (from the point of view of conductivity) tend to be complex polymers with additives. Neutron scattering offers the possibility of using selective isotopic substitution (e.g. H/D, Li cations, Cl anions) in studies of both structure and dynamics, and polarisation analysis to separate H motions. Studies can be made over a wide range of both length and time scales (a large (Q,ω) window). Suitable accuracy cannot at present be obtained on a reasonable time scale. H/D substitution is too chemically complicated and expensive to be used for many different samples with different compositions, so routine polarisation analysis is vital for dynamical studies.

4.3 Disorder in crystals

4.3.1 Defects and disorder in crystals

Disorder in crystals has conventionally been studied by single crystal diffuse scattering. Most analysis has been qualitative, at best analysing widths of diffuse scattering peaks or directions of streaks. In the past few years the application of RMC methods, originally developed for structural studies of liquids and amorphous materials, has pointed the way for more generally applicable quantitative analysis [52]. A simpler approach is the determination of radial distribution functions (RDF) for crystalline powders, which is gradually becoming accepted as a powerful source of information on defects and disorder. It is now realised that disorder can be crucial in determining the properties of technologically important materials, for example high T_c superconductors [53]. The requirements for such studies are severe since the diffuse scattering contribution may be very small, so high absolute accuracy is needed.

Neutrons are preferable for powder studies for a number of reasons:

- Diffuse scattering tends to increase with Q, while the X-ray form factor decreases, so X-rays scatter least in the most important region.
- The problem of absolute normalisation for X-rays has not been solved. Accurate normalisation is very important for such studies.
- There can be sample problems with X-rays, for example those with preferred normalisation (even a small amount of this can produce big errors in the RDF's derived) or which may be intrinsically multiphase (e.g. ceramics) and may not be adequately averaged over the scale of the X-ray beam.
- The high Q range accessible on a pulsed source is be a big advantage for high real space resolution (needed in, for example, studies on rotational disorder in fullerenes or the structure of quasi-crystals).
- There are considerable opportunities for the combined use of these neutron scattering methods with EXAFS. Neutron data can help to de-correlate thermal factors and coordination numbers in EXAFS data.
- Although work is only just starting there are also considerable gains to be made in the study of disordered magnetic materials, for example spin glasses or the new giant magnetoresistance materials.

4.3.2 Fast ion conductors

One particular application is crystalline fast ion conductors. In many cases of interest the conducting atoms tend to be light (e.g. Li, Na, O), which have lower relative cross-sections for X-ray scattering, while the framework is 'heavy'. This use is now well established for 'pure' model systems. The growth area will be in studies of materials for applications such as battery or fuel cell electrodes and sensors; for example La(Sr)MnO_3 is an oxide conductor at high T [55], of interest in fuel cells, and a giant magnetoresistance material at low T [56], of interest for magnetic recording devices. These materials are usually complex and need to be studied as a function of composition, different dopants etc., and under specific conditions (e.g. high T, applied voltage). Crystallographic information needs to be correlated with local structure and diffuse scattering information for multi-phase samples. There is also much scope for in-situ studies, such as operating batteries or fuel cells, because of the high penetration of neutrons.

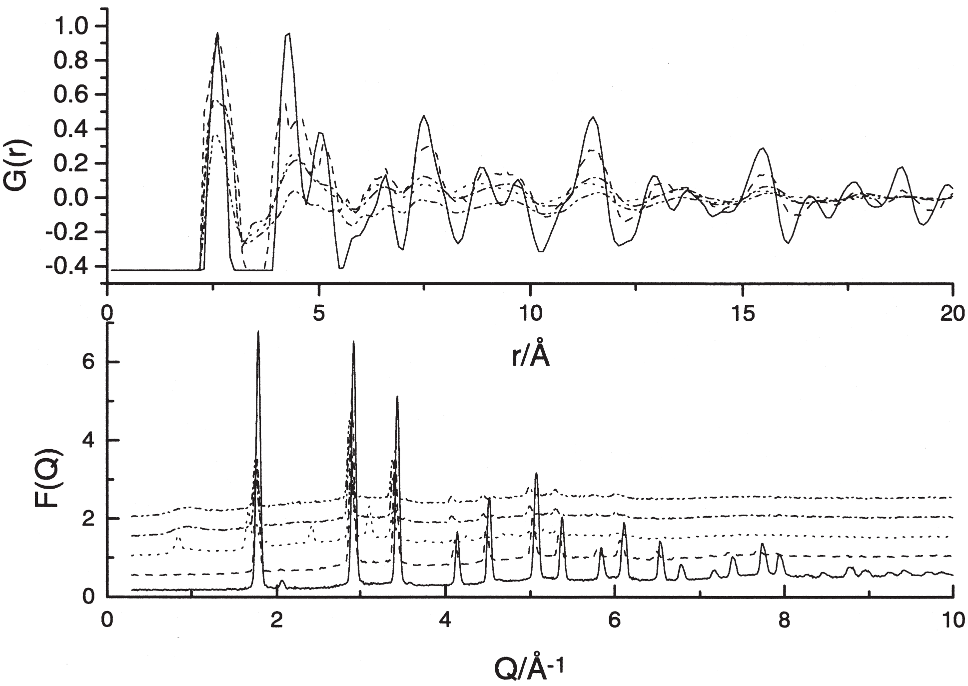

Figure 7: Structure factors and radial distribution functions for three crystallographic phases of the fast ion conductor CuI [54].

4.3.3 Proton conductors/hydrogen storage materials

This is a growing area of importance for batteries, fuel cells, hydrogen storage etc. High conductivities can be achieved with very low concentrations (< 1 %) so high accuracy is needed (the protons are difficult enough to see with neutrons, let alone X-rays). H/D substitution is obviously an important technique, particularly for incoherent quasi-elastic scattering studies to determine conduction mechanisms [57]. Materials with optimised properties are often complex, which increases the need for a quantitative step in source intensity.

4.3.4 Quasicrystals

Quasicrystals can be mentioned here in the context that the techniques discussed above are applicable to these systems, though RDF analysis has only been tried once [58]. The technical requirements are very severe.

4.3.5 Ceramics

Most ceramics contain both crystalline and 'amorphous' phases, and sometimes more than one crystalline phase. RDF methods are very suitable for studying such systems in a comparative sense since they simply average over all short range information. Neutrons are advantageous for looking at bulk samples which may be inhomogeneous on the geometric scale of an X-ray beam. There are new opportunities for studying structure/property relationships, particularly in-situ studies. e.g. Si_3N_4 ceramics for coatings in future car engines [59]. The strength of the material can depend on reducing the amount of the amorphous component, but only via preparation of a material with an initially high amorphous content and then recrystallising.

4.3.6 Melting and freezing

Neutron scattering studies in this area have so far been limited by the difficulty of accurate temperature control over necessarily small samples [60]. The possibility to study much smaller samples at ESS will produce new possibilities, again particularly in the area of diffuse scattering studies of short range order/disorder. Combined diffraction/EXAFS studies will offer possibilities to study 'local melting' around impurities, in bulk materials, but X-ray diffraction (synchrotron) or ion channelling will be best for studies of surface melting.

4.3.7 Nanocrystalline materials

Ball milling and new chemical techniques can now produce small particles of many materials with dimensions of a few nm or less. Because of the high surface area/volume ratio these can have enhanced properties, e.g. magnetic or catalytic, which can be controlled to a certain extent by the exact preparation method [61]. Many neutron studies are limited by the small sample volumes available, or the fact that the particles are prepared in a 'matrix' of other material which produces a high 'background'. ESS will offer new opportunities for small sample studies, isotopic substitution to reduce backgrounds, combination of EXAFS, NMR and diffraction, studies of magnetism in nanocrystalline materials etc. Often such materials are not 'well defined' crystallites, but have a substantial 'amorphous' component. The advantages of neutrons in such cases have been described above. However, even with ESS, it seems likely that neutron studies of clusters produced in atomic beams will be at the limit of feasibility.

4.3.8 Solid state amorphisation

There has been a growth over the last decade in new methods of preparing bulk amorphous materials, for example ball milling or high pressure techniques. This can offer a route for production of materials with tailored properties, e.g. new magnetic materials, possibly as a pre-production stage for preparation of nano-crystalline materials [62]. It also raises the fundamental question of what is meant by an 'amorphous' material. Neutrons again have all the advantages of sample averaging, diffuse scattering etc.

4.4 Techniques

Here we consider separately three techniques which may still be considered to be in their infancy, either technically or as regards studies of the materials covered by this theme. ESS offers significant prospects for all of them.

4.4.1 Reflectivity

Here there are significant prospects in particular studies of simple liquids and amorphous materials if the accessible Q range can be increased with higher intensity, as will be practicable at ESS. Possible applications include:

- Ordering at liquid metal surfaces [63]. There has been considerable recent progress in X-ray reflectometry studies in this area. Neutron scattering has advantages for studying surface segregation in liquid metal alloys, for example, using isotopic substitution. Complementary (or even simultaneous) studies with X-rays may then be considered.
- Molecular orientation and the local density profile at the liquid/vapour interface for molecular systems could also be studied.
- Another area of recent experimental and theoretical interest is the study of fluids near a solid substrate, of surface critical phenomena (among which are wetting and pre-wetting

transitions) and of surface layering. An example is the study of wetting in binary fluid mixtures, such as fluid alkali metal/alkali halide systems. In the study of solid/liquid interfaces the penetrating power of neutrons is particularly advantageous. In particular cases contrast variation using polarisation may be possible.

- Diffusion or ion conduction at interfaces, e.g. between an electrode and electrolyte in a battery or fuel cell.

4.4.2 DINS (Neutron Compton scattering)

Pulsed neutron sources allow the use of very high energy neutrons, e.g. ~ eV. This application is still in its infancy, but in principle it can provide unique information on the momentum distribution of (predominantly light) atoms in condensed matter, and hence on anisotropies in bonding etc. At present the limitation is the poor energy resolution that can be achieved. An improvement in resolution implies a lower count rate, so an increase in the flux of high energy neutrons is of fundamental importance for the development of this technique. The high flux of ESS, together with the introduction of highly stable detector systems and improved theoretical resolution functions that are already under development, offers the exciting possibility of using the recoil atom as a probe of the local environment. This is entirely analogous to EXAFS, but is most sensitive to the environment around atoms of low mass (e.g. H) where EXAFS fails. Possible applications include:

- The level of quantum effects in simple monatomic fluids such as Li, He and Ne [64].
- Quantum effects in simple molecular liquids, e.g. ortho- and para- hydrogen [65].
- Work on the condensate fraction in superfluid ^{4}He, and on ^{3}He-^{4}He mixtures (such work is already very successful [66]).
- Identification of H sites and content in metals (important for hydrogen storage), or of H bonding (including the presence of molecular H_2) in semiconductors (e.g. silicon for solar cells, carbon for ultra-hard coatings) [67]. Here there are many possibilities for complementary studies with neutron diffraction and other techniques.

4.4.3 Spin echo

Neutron spin-echo has not yet been widely applied within the area of science covered by this theme - the best case is early work on the glass transition in $(KNO_3)(Ca(NO_3)_2)$ [8]. The advent of broad band neutron polarisers, and the higher flux of ESS, will enable many experiments which are at the limit of, or outside, current capabilities, for example:

- Measurement of (slow) diffusion in e.g. oxide glasses or ion conducting glasses [68] - are theories involving fractals, percolation transitions etc. applicable?
- Investigation of magnetic ordering, clusters and domains in amorphous metals by depolarisation analysis over a wide wavelength band (complementary to muon depolarisation studies).
- Studies of slow dynamics at intermediate range in mesoscopic structures (combined spin-echo/SANS).

5. Requirements for the ESS

- Specially designed and optimised instruments for such work. In the case of structural measurements in particular the requirements are not the same as those for crystallographic studies. Special attention must be paid to low intrinsic backgrounds, low backgrounds from sample environment equipment etc., and also high stability for detectors, monitors etc. The requirements for diffuse scattering studies are particularly severe.

- Investment in computer hardware and software to make necessary data corrections routine and rapid (effectively automatic). Advantage can only be taken of the possibilities offered by ESS if the data treatment time is less than the data collection time. Further developments of inversion methods, e.g. $(Q,\omega) \leftrightarrow (r,t)$, are needed in many areas.

- Investment in specialised sample environment. This must not only be able to reach the specified conditions but must also operate with high reliability.

- Almost all instruments of interest are required to have small angle scattering detectors (not just low angles).

- If neutron scattering (and other non-laboratory based methods such as those at synchrotron sources) are to contribute to many of the problems of technological importance in the area of liquids and amorphous materials, on a time scale that is relevant for technological research and development, then the 'sample turn round time' must be dramatically decreased, and the instruments must be able to deal with prototype materials as they are produced, i.e. often in small quantities and without deuteration in the case of hydrogenous materials.

6. Conclusion

It is clear that the acceleration in the synthesis and development of modern materials, a large fraction of which fall into the category of 'liquids and amorphous materials and ionic conductors', is such that an ever sharper focus must be on the question '*why* do these materials have the properties they do?'. Such a question inevitably leads to a quest for understanding at the atomic level and this surely represents one of the most challenging problems in modern physics and chemistry, with an importance that goes far beyond those traditional home disciplines into materials science, the life sciences, engineering, geology, archaeology, space science …

Neutron scattering has played, and continues to play, a central role in the study of liquids and amorphous materials and ionic conductors. It has provided seminal input to many aspects of our current understanding of these systems, but its full potential is far from having been realised. Neutron scattering methods could have an even greater impact in the future as the keystone in a necessarily multi-disciplinary approach aimed at understanding the microscopic basis for the properties of increasingly complex new materials. Construction of ESS is an essential pre-requisite for this to occur.

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Solid state chemistry

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Introduction

Clearly present neutron sources in Europe (ILL, ISIS, LLB, HMI, Risø, ...) can still work for the next 15 years. Improvement of instrumentation and upgrade of some experimental facilities can lead to significant gains in intensity and resolution for performing additional interesting experiments. However, many important areas need a substantial increase of neutron flux. Small samples, and/or low-signal effects prevent, today, the use of neutrons for solving many fundamental and technological problems related to new materials. The proposed Spallation Neutron Source (SNS) in Europe (European Spallation Source, ESS) is the long-term solution for tackling these problems and for providing one of the most powerful tools in the analysis of condensed matter at a level never attained before.

Solid State Chemistry (SSC) lies between Physical and Inorganic Chemistry and extensively overlaps with Solid State Physics. The term Materials Science in its non-engineering aspect could be a better term for naming this broad and interdisciplinary field. Structural Physics has been also used as a term to describe this field that uses "diffraction" as the main experimental tool. Among the structural problems in condensed matter research we have included the "magnetic structure" of magnetic compounds, a field strongly associated with neutron scattering.

The past twenty years have witnessed important achievements in the understanding of condensed matter. The key role that the availability of neutron sources and the performance of neutron scattering experiments has played in understanding such processes is unquestionable. This has been particularly true in the area of SSC. Problems where neutron diffraction experiments have been of basic importance are:

- Location of light elements and distinction between adjacent elements in the periodic table.
- Examples are the oxygen positions in High T_c superconductors, the structural determination of the all-carbon fullerene solids an their derivatives, hydrogen in metals and hydrides, and the determination of atomic site distributions in solid solutions.
- Systematic studies of hydrogen bonding
- Host-guest interactions in framework silicates.
- Role of water in crystals.
- Magnetic structures, magnetic phase diagrams and magnetisation densities.
- Relation between static structure and dynamics (e.g. clathrates, plastic crystals).
- Aperiodic structures: incommensurate structures and quasicrystals.

In this report we shall be concerned with problems related to the "ground state" (or free energy minimum average state) of long range ordered matter. This does not mean we shall treat only materials in "normal conditions", for instance the study of materials under very high pressure, or under a strong laser illumination, is perfectly relevant to our subject. Neutron diffraction is usually the technique of choice for investigating such states of matter. We will not be concerned with the "excitation" (energy exchange between neutron and sample) aspects . The most important neutron scattering techniques, scientific problems, materials and aspects relevant to SSC will be briefly discussed and the present limitations emphasized.

1. The complementary use of X-ray synchrotron radiation and neutrons

Clearly X-ray diffraction with Synchrotron Radiation (SR) is a technique with increasing impact in structural science and it is a field in which new developments are coming thick and fast. For many problems, SR is the technique of choice: topography, small angle scattering (except contrast problems), surface crystallography, protein crystallography, interfaces, phase identification in transient solid state chemical reactions, transformations under pressure, very high resolution powder diffraction, etc. However, as far as high precision of structural parameters is concerned, SR has drawbacks in comparison to neutrons, resulting from its fundamental interaction with matter. Certain points are stressed below:

- The advantages of thermal neutrons with respect to X-rays as far as diffraction is concerned are based on the following properties of thermal neutrons: constant scattering power (b is Q-independent) having a non-monotonous dependence on the atomic number, weak interaction (the first Born approximation holds) that implies simple theory can be used to interpret the experimental data, the magnetic interaction is of the same order of magnitude as the nuclear interaction, and, finally, low absorption, making it possible to use complicated sample environments.

- Powder diffraction with SR can be used for *ab initio* structure determination and microstructural analysis due to the current extremely high Q-resolution. Structure refinement is better done with neutrons (or using simultaneously both techniques) because systematic errors in intensities (texture effects) are less important and because scattering lengths are Q-independent in the neutron case.

- Anomalous dispersion is becoming a technique providing new information and contrast from diffraction experiments, so facilitating structure refinements and making possible site/chemical selective diffraction enhancement.

- The possibility to study single μ-crystals with SR for crystal structure determination and refinement could render powder diffraction useless. In practice however there are many unsolved problems preventing the routine use of this technique.

- Sample environment is still a problem with SR (much more complicated than for neutrons) even for high energy X-rays. The reason is that, for highly penetrating X-rays, sample scattering is mainly concentrated around the primary beam and spurious scattering (coming from the sample's surroundings) is virtually unavoidable.

- Magnetic X-ray scattering allows in principle the separation of orbital and spin components. However, SR cannot compete with neutrons in the field of magnetic structure determination from powders. The contribution of SR to that field is on details of magnetic structures (already known from neutrons) for selective elements using resonant magnetic scattering (rare earths, U, ...). At present the low quality of many available single crystals prevents the use of magnetic diffraction as a routine tool.

The extremely fast development of SR instruments and methods is opening new opportunities with this technique. The complementary aspect of SR and neutrons should be stressed.

2. Advantages of a new spallation source over a reactor

Neutron diffraction in Spallation Neutron Sources (SNS) has some advantages over steady state sources that must be pointed out.

- The use of the time-of-flight technique with short pulses, combined with long flight paths and/or fast choppers produces data of inherently high resolution. The fixed scattering geometry facilitates the use of complex sample environments and simultaneous diffraction and spectroscopy experiments.
- The momentum and energy transfer ranges are larger than those in a reactor. The epithermal component of the neutron spectrum makes possible the very high momentum transfer giving rise to a better spatial resolution in real space.
- The neutrons are used more efficiently because the full spectrum of neutrons impinges on the sample. The moderate period between pulses allows a low-background data collection and the absence of high order contamination as monochromators are not used.
- *In situ* experiments, with time-dependent perturbations of the sample, can be naturally coupled to the pulsed structure allowing the study of the sample response as a function of time.

The experience gained with the spallation sources working today indicates that this technique is very appropriate for studies requiring very high intensity and high resolution neutron diffraction data.

There are some areas where steady state reactor techniques have still the primacy (e.g. SANS) but that may change with the next generation of SNS. This is also true for data handling, where the use of monochromatic beams greatly simplifies the analysis. The unprecedented advances in computer science and technology is however changing the situation rapidly (this is very clear in powder diffraction). Nevertheless much progress remains to be made in software development for data reduction and analysis of pulsed neutron data, specially for bulky sample environments where wavelength-dependent absorption could prevent the extraction of reliable structural parameters.

In the proposed 5 MW SNS (European Spallation Source, ESS), new experiments and new science are expected to be possible. The cold neutrons side of the spectrum will be enhanced in the Target B allowing the increase of the Q-range towards low-Q (high d-spacing), so large unit cell and magnetic incommensurate structures can be tackled with much more success than with present sources.

3. Scientific opportunities with neutrons in SSC

3.1 High precision crystallography with powders and single crystals

One of the most important applications of neutrons is in the field of structure refinement. Compared to X-ray diffraction, neutrons provide more precise displacement (thermal) parameters due to their Q-independent scattering power. The erratic variation of the Fermi length with atomic number (and isotope) within a limited range makes atoms more "equal" from the diffraction point of view. Structural parameters may also be obtained with great precision when both light and heavy atoms are present; moreover very precise distances between hydrogens and other atoms may be measured avoiding any effect due to the redistribution of charges in forming the chemical bond. In many areas of research neutron diffraction has been a most important structural probe, as in the determination of the structures of new materials in which light elements are combined with heavy elements, or in the investigation of catalytically active compounds such as transition metal hydrides.

In the last 25 years neutron powder diffraction has made enormous progress due to Rietveld's proposal for using the full profile as data for structure refinement. Refinement of crystal structures with more than 130 structural parameters can be performed routinely with present equipment and computing programs. The increase of resolution and the extension to higher and lower d-spacings with the future powder diffractometers will allow to increase the limit in complexity of a structure to be refined from powder diffraction to around 500 structural parameters.

Even though single crystal X-ray diffraction is the primary tool for solving structures and determining accurate geometries, in many cases neutron diffraction provides structural informations that cannot be obtained by the former technique. This stems from the fact that only neutron diffraction may locate hydrogen atoms in the presence of heavy metals and that the availability of high-Q data allows the precise determination of thermal parameters, anharmonic effects and site occupancies.

The easy use of furnaces and cryostats with neutrons makes the study of crystal structures as a function of temperature a routine task.

3.2 Real crystals: defects, diffuse scattering, total scattering analysis

The high sensitivity of neutrons to defects comes from the fact that the scattering lengths vary within a limited range of values. The determination of site occupancies in non-stoichiometric and/or disordered compounds is one of the most important applications of neutron powder diffraction. The most recent examples can be found in the field of high T_c superconducting oxides.

Total scattering analysis is a technique normally used in the field of liquids and amorphous solids that can be extended to the study of "defects" in crystalline powdered materials. For that it is necessary to get data of very high precision in the intensities. The application of the usual techniques in amorphous systems can provide invaluable information about defects in crystalline solids, conduction mechanisms in ionic conductors, etc.

Single crystal diffuse scattering is perfectly suited to the TOF Laue technique used in a SNS. The availability of large area detectors and the TOF technique make possible a very precise analysis of the diffuse scattering around the Bragg reflections. The intrinsically higher resolution of TOF machines permits a better separation between Bragg and diffuse scattering near the zone centre.

3.3 Structural studies of phase transition and transformations

Structural phase transitions in solids is one of the most exciting areas of condensed matter research. Neutron scattering has provided very important contributions to the field, not only because the structural details can be better determined by neutron diffraction, but because the direct measurement of the behaviour of the order parameter(s) as a function of temperature, applied field or pressure is relatively straightforward with neutrons.

Apart from inelastic measurements, providing information about fluctuations and soft mode behaviour in second order phase transitions, diffraction experiments are able to probe secondary order parameters (e.g. microstrains) accompanying the transition. A very high resolution neutron instrument can provide information about these effects from the line shape. Critical scattering should be also accessible with higher flux and resolution.

3.4 Magnetic structures and magnetic phase diagrams

Nearly everything that we know about magnetic structures is based on neutron diffraction data. Two major contributions in the early times of neutron scattering were the demonstration of the Néel model for antiferromagnetism (Shull & Smart) and the first proof that magnetic electrons in metals are localised spatially. Neutron diffraction has provided direct evidence for the enormous variety of spin arrangements taking place in solids, particularly the fact that most of them are incommensurate with the chemical lattice (spirals, amplitude modulation, fans, cycloids, etc.).

- Magnetic 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. In the last twenty-five years the Rietveld Method, combined with the increased performance of powder diffractometers, has allowed great progress in the analysis of powder diffraction data. The multiphase refinement of incommensurate magnetic structures, with the possibility of varying peak shape parameters depending on a particular class of reflections, constitutes a new analytical tool that can give information not only on the magnetic structure, but also on the correlation lengths along particular directions in reciprocal space.
- The main contributions to magnetic structure determination by neutron powder diffraction have been made using the so called "medium resolution" powder diffractometers. The accessible Q-range in normal conditions is between 0.15 and 4.5 $Å^{-1}$ (≈ 40 - 1.4 Å in d-spacing) and the best resolution is $\Delta d/d \approx 6x10^{-3}$ around $d \approx 2.4$ Å. The crystal structures of new magnetic materials involve moderately large unit cells and hence a good resolution in Q-space as well as the ability to probe large Q-ranges are required if successful Rietveld refinement are to be carried out. Magnetic structures could be rather complex and low-Q reflections contain the most important information, so high d-spacings should be accessible. These two requirements are difficult to be realised in a single constant wavelength (CW) diffractometer. The TOF technique has much more potential capabilities than CW for satisfying the above prescriptions. The better global use of neutrons and the increasing flux of spallation sources makes TOF powder diffraction with cold neutrons an absolute priority for future developments. TOF diffractometers can access long d-spacings (10-100 Å) with a resolution that is impossible to obtain on conventional diffractometers. The high resolution of future powder diffractometer will also help to detect, in case of high symmetry chemical structures, small distortions to lower symmetry, e.g. due to magneto-elastic interactions.
- Magnetic powder diffraction suffers from the lack of uniqueness of the magnetic structural model for high symmetry structures. However, many new materials have low symmetry

(orthorhombic and below) allowing powder diffraction to give a full description of the magnetic structure. The use of single crystals is absolutely necessary for high symmetries and to determine fine details of the magnetic structures. Polarised neutron and polarisation analysis are the best techniques to obtain the full picture of magnetic moment arrangements in solids.

- Problems of current interest in magnetic neutron diffraction are the study of magnetic interactions between different sublattices (complex magnetic structures, intermetallics), magnetism and superconductivity, heavy fermions, etc. A very important field, for which neutron diffraction is the technique of choice, is the stability of magnetic structures to external perturbations: temperature, pressure, magnetic fields, electric fields. A promising new field with neutron diffraction is the study of the "kinetics" of magnetic phase transitions. One should be able to follow magnetic transitions as a function of temperature and magnetic field in a short time and even with a small sample. Examples are spin reorientation transitions for which the availability of higher flux is necessary.
- With present neutron sources the limit on detectability of magnetic moments depends on the state of the sample (powder or single crystal) and on the use of polarisation techniques. This is crucial because many important magnetic systems have small magnetic moments e.g. heavy fermion materials and superconductors. For magnetic structures with nuclear and magnetic scattering occurring in the same reflections, polarisation dependent cross-section allows to detect a magnetic moment as low as $10^{-3}\mu_B$ and even $10^{-4}\mu_B$ in some cases. For other cases the limits are currently $10^{-1}\ \mu_B$ for powders and 2´$10^{-2}\ \mu_B$ for single crystals, depending essentially on the background. The ESS will improve the detectability of small moment magnetism due to its higher flux and lower background.

3.5 Spin density studies and form factors

This is a field where neutrons are essential for obtaining the information. No other technique gives such direct and precise information about the distribution of unpaired electrons in solids.

- The use of polarised neutrons to obtain magnetisation distribution in solids is the best we can do to study ferromagnets, paramagnets and diamagnets. The technique is based in the measurement of the "flipping ratios" obtained from polarisation dependent cross sections. Most experiments are currently flux limited, so the ESS will be essential to develop the field. In order to apply this technique we need the use of white beam polarisers, whose availability will boost the data collection rate. This should allow us to tackle more complex systems, with larger unit cells, and also very weakly magnetic systems (more diamagnetic materials).
- In the case of antiferromagnets (no interference between nuclear and magnetic reflections), the flipping ratio is not defined and magnetisation densities has to be obtained by Fourier inversion of the magnetic structure factors. Very few experiments have as yet been attempted because of flux limitations. Higher flux is needed to obtain more precise intensities, mainly at high Q values, so that the details of the spin density can be better defined.
- Schwinger scattering is, at present, an exotic field of neutron scattering but the availability of higher flux and white beam polarisers can help its development. It consists of the measurement of total charge density using polarised neutrons. More flux is essential to extend this area of application. Schwinger scattering may be the only technique to give reasonable accuracy for charge densities in materials containing heavy elements such as actinides.

3.6 Time-dependent phenomena: *in situ* neutron diffraction

Time resolved experiments are very important to follow chemical kinetics, solid state reactions, phase transitions, and in general, chemical reactions. An important example is the study of charge/discharge reactions in batteries, as they have very important industrial and practical applications. In the instruments planed for the ESS, powder diffraction patterns can be collected in ~ 4-5 seconds for phase identifications and 3-4 minutes for Rietveld refinements to extract structural information. For example, experiments on high intensity instruments at current neutron sources need ~ 3-10 minutes for phase identification (D1B, POLARIS). Hence, the limits of current instruments will be pushed by more than an order of magnitude and this will open new research fields where the time scale is of the order of seconds instead of the order of minutes. This time scale is slightly larger than that obtained at ESRF (1995) but the strong absorption of the X-rays by the reaction cells, and/or the X-ray scattering from the environment, make this technique more complex and less suitable. The low absorption of neutrons by the reaction environment and their consequent ability to probe bulk properties provide a vital advantage of neutrons over synchrotron X-rays.

In connection with TOF, kinetics should be a major point especially in connection with the pulse rate. Experiments which use the peak flux, like the study of reversible transformations by stroboscopic measurements, could be performed, gaining several orders of magnitude with respect to reactor sources.

3.7 High pressure studies

In the ESS very high pressure studies reaching 50GPa and more (pressures of ~20 GPa are currently available) with highest resolution for accurate studies of pressure effects on complex systems (or in magnetic compounds) should be possible. At the moment such possibilities are to a large extent lacking due to flux problems in neutron diffraction. SR is best adapted to this kind of experiment due to its intrinsic brilliance. However, good accuracy on structural parameters for compounds containing both heavy and light elements can be obtained only with neutron diffraction. The same is true for magnetic structures. For these reasons a very intense and brilliant neutron source is absolutely necessary to perform high pressure studies.

4. Systems of current interest to solid state chemistry

Below a summary of SSC sub-fields is given. New materials, fundamental problems and technologically interesting systems are briefly described. We have to keep in mind that it is not possible to predict what will happen in the near future concerning new materials (nobody predicted neither the existence of High-Tc superconductivity and its consequences in condensed matter research nor the synthesis of fullerenes and their derivatives!), so the subjects described below represent only the current interests in the SSC community.

4.1 Ionic solids: superconductors, oxides, GMR materials,...

4.1.1 Transition metal and rare Earth mixed oxides

In the last ten years, the interest of solid state physicists and chemists in transition metal (TM) oxides has increased greatly. The reason for the increased activity in this field is related to the discovery of High Tc superconductivity. However the plethora of physical properties and unexplained phenomena (quite apart from superconductivity) displayed by these materials makes them interesting in their own right.

The strong electron correlation in TM oxides is at the origin of the breakdown of the one-electron picture developed by Bloch and Wilson. The Mott-Hubbard picture, explained for the first time why NiO is an insulator instead of a metal and many properties of the early TM (Ti, V, Cr) oxides. The ideas of Zaanen-Sawatsky-Allen extended the Mott-Hubbard scheme to all TM oxides introducing the idea of charge-transfer insulators.

The oxides, together with halides, are also at the origin of Anderson's superexchange theory in insulators as well as the theory of double exchange in certain class of metallic oxides. The magnetic properties of many oxides can be explained within the superexchange framework and the Goodenough-Kanamori rules. One interesting (and not very much studied) aspect of superexchange is that existing between a TM ion and a rare earth (RE) ion through the bridging oxygen. The complex magnetic behaviour observed in many TM-RE mixed oxides needs still to be properly understood.

Below we describe some systems for which neutrons have played a very important role in understanding some of the structural and magnetic properties. The interest of using neutrons comes from i) their ability to provide very precise structural parameters for oxygen atoms in the presence of the heavier TM and/or RE (the example of High-Tc superconductors is well known), ii) a fundamental aspect of the electronic structure (magnetic order is a kind of electronic ordering) of oxides is accessible only *via* magnetic neutron diffraction.

4.1.2 High T_c superconductors and related materials

Solid state chemists continue to synthesize new superconducting materials of increased T_c. Besides the superconducting materials, new compounds appear as secondary phases that can show other interesting properties. The understanding of the solid state reactions leading to new materials, needs diffraction techniques to identify intermediate compounds and to establish the reaction mechanisms. SR and neutron powder diffraction are complementary techniques in this respect. Higher neutron flux than that provided by present sources is necessary to study smaller samples in which inhomogeneities (temperature and compositional gradients) are minimised.

Neutron powder diffraction is the most important experimental tool to characterize new compounds, to obtain accurate structural parameters and to correlate them with physical properties.

4.1.3 Metal-insulator transitions

Metal to insulator (M-I) transitions as a function of temperature and/or pressure are relatively rare in oxides. However chemical substitutions and non-stoichiometry can also lead to M-I transitions. The first kind of transition permits to get more insight into the mechanisms responsible for the phase transition because structural inhomogeneities are absent. In the last few years a M-I transition was shown in perovskites $RNiO_3$ (R = Pr, Nd, Sm, Eu). The structural features accompanying the M-I transition were studied and a new kind of magnetic structure was revealed in the insulating state by neutron diffraction.

The origin of the M-I transition could be the change in the bandwidth with temperature which opens a charge transfer gap between the top of a mainly O-2p band and the upper Hubbard band of Ni-3d parentage. This is related to the temperature dependent structural changes. For

R = Pr, Nd, Sm a volume increase of about 0.2% is observed on going from the metallic (high temperature side) to the insulator regime. This can be considered as a steric reaction of the structure to an increase of the average Ni-O distance of the order of 0.004Å at the electronic localisation. This produces a small decrease of the O-Ni-O angle.

The observed magnetic structure in the insulating regime implies the co-existence (alternation) of F and AF interactions. This is related to an orbital ordering resulting from the breakdown of the $Ni^{III}(t_{2g}{}^{6}e_{g}{}^{1})$ configuration due to the electronic correlations.

With present neutron sources neutron powder diffraction (even with polarised neutrons and polarisation analysis) is unable to provide, with enough precision, intensities of superstructure reflections of the order of 10^{-4}-10^{-3} of the intensity of the main reflections. The nuclear displacements due to orbital ordering are too small to be well determined. With much higher flux and improved signal-to-noise ratio this kind of problem would be tackled using powder diffraction.

High pressure is a very important variable in M-I transitions. Another perovskite, the insulating and antiferromagnetic orthoferrite $LaFeO_3$ (T_N=740K) is located well inside the charge transfer region. However a recent Mössbauer spectroscopy study under high pressure tend to suggest a behaviour similar to that observed in nickelates. Above 30GPa, a transition to a non magnetic state has been detected, characteristic of low-spin iron 3+. At even higher pressure (above 55GPA) a second transition is detected toward a low-spin iron 2+ state. These transitions might be the sign of the progressive closing of a charge transfer gap. Such a point, of great theoretical interest, needs to be confirmed by structural, electrical and magnetic measurements under high pressure. The advent of a bright spallation neutron source gives a unique opportunity for such a study, since first, neutrons are the most valuable tools to probe both oxygen location and magnetic state, second, spallation sources are ideally suited for various environments such as pressure cells, and third, a bright source, by reducing the optimal sample size, permits higher pressures.

4.1.4 Giant magneto-resistance materials

Manganese oxides with the perovskite structure have recently attracted a strong interest due to the discovery of giant negative magnetoresistance. The doping of the family $RMnO_3$ (R: lanthanide) with divalent ions M^{2+} (M= Ca, Sr, Ba, Pb, Cd...), introduces holes in the d-band that give rise to many interesting physical properties. The parent compound $LaMnO_3$, is an antiferromagnetic insulator in which an orbital ordering is established due to the co-operative Jahn-Teller effect in the electronic configuration of Mn^{3+} $(t_{2g}{}^{3}e_{g}{}^{1})$. This particular orbital ordering is responsible for the A-type magnetic structure. The hole doping increases the conductivity and permits the ferromagnetic double-exchange interactions to produce ferromagnetic metals when the doping is about x=0.15 to 0.35. It has been suggested that a charge ordering in the lattice would take place for compositions near x=0.5, so an alternating Mn^{3+}-Mn^{4+} NaCl-like lattice is established. Very recently, a transition has been identified from a ferromagnetic metal (F) to an antiferromagnetic (AF) insulator in $Pr_{0.5}Sr_{0.5}MnO_3$. The transition is due to a charge localisation due to the Coulomb interaction that overcomes the kinetic energy of carriers (Wigner crystallisation). This transition can be suppressed by the application of a magnetic field.

The appearance of this new centre of interest is mainly due to the "giant magnetoresistance effect" which may be of considerable importance in magnetic recording devices. However the full physics, related to the behaviour of strongly correlated electrons (holes) in oxides, of these systems is extremely interesting from a fundamental point of view. The structural parameters are strongly associated to the electronic and magnetic properties, for instance the M-O-M angle determines both the bandwidth and the strength of the exchange interaction. These perovskite oxides constitute very promising systems to study experimentally with neutrons, and obtain all the structural and magnetic microscopic details associated with the electronic transitions under variable temperature, pressure and applied fields.

One important application of neutrons in the study of these systems is the determination of the structural details accompanying the charge ordering processes. As in the case of orbital ordering, charge ordering gives rise to very small (but more intense) superstructure peaks (already seen by neutron powder diffraction) related to nuclear displacements. The accompanying distortions are quite small, so peak splittings can only be seen with very high resolution (synchrotron radiation and/or TOF high resolution powder diffraction). Subtle magnetic changes accompany the structural distortions and provide further insight into the electronic structure. The study of these distortions requires high flux and possibly also high resolution in the event of incommensurate correlations, as has been predicted theoretically.

4.1.5 One-dimensional systems

This is another field where neutrons are providing very interesting results for understanding the physics of 1D systems. In recent years two important 1D oxide systems have been discovered. The first is the compound Y_2BaNiO_5 which is a prototype of the S=1 linear chain possessing a non-magnetic ground state due to the Haldane gap, and the second is the Spin-Peierls system $CuGeO_3$. Most of neutron scattering works on these systems are connected to the magnetic excitation spectrum obtained with inelastic neutron scattering.

It is important to determine the true crystal structure of the Spin-Peierls dimerized ground state in $CuGeO_3$. This has recently studied by X-rays and neutron diffraction. Neutron powder diffraction has failed to discover the superstructure peaks related to the Spin-Peierls state. The first experiment giving the superstructure peaks was performed on a laboratory X-ray source with the "monochromatic Laue" technique, but the first structural model came from single crystal neutron diffraction. More detailed work is being performed at present, but one of the difficulties is the extreme weakness of the superstructure reflections. High flux is a pre-requisite for studying new systems where structural changes are subtle.

4.2 Hydrogen in metals

Hydrogen in metals and metal hydrides is a subject of continuous interest from the point of view of both fundamental properties and applications. Hydrogen will become a fuel choice for the future as oil reserves are being squandered, and it is essential from the economic and safety points of view to know the structures and behaviour of these materials.

In this field all investigations concerned with crystal and magnetic structures are performed using neutrons. The number of compounds is increasing every day; here we shall describe two sub-fields where neutron powder diffraction is playing a fundamental role:

4.2.1 Hydrogen in rare earth metals

Hydrogen in RE metals leads to solid solutions with poorly defined compositions and hydrides RH_{2+x}, RH_3 with under and over H-stoichiometry. Very interesting ordering phenomena occur as a function of composition and temperature. The systems can pass from a partially liquid H-sublattice to a well ordered system. Transport and magnetic properties are affected by H-ordering. In particular the H-ordering modifies the exchange parameters. Deciphering what kind of order is taking place is quite complicated when superstructures of magnetic character appear simultaneously with nuclear superstructure peaks.

The heavier RE show metal to semiconductor (M-S) transitions, in their b-phase RH_{2+x}, with change in temperature. The T_{M-S} is different from T_{S-M} and occurs between 230 and 290K. Such transitions (the metallic regime is in the low temperature side) seem to be related to order-disorder processes. X-ray diffraction is only able to determine the lattice deformation due to the presence of H, but not the hydrogen positions. Recent experiments have demonstrated that kinetic aspects are very important, so time-dependent neutron scattering could provide new interesting parameters characterising the ordering process.

4.2.2 Hydrides and hydrogen in intermetallics AB, AB_2, AB_5 (A rare earth, Y,Zr,Ti, B=metal)

In the last two decades, metallic hydrides (AB, AB_2, AB_5, A=Rare Earth, Y, Zr, Ti and B= metal) have been widely studied. These compounds exhibit reversible absorption of hydrogen and therefore they have been of increasing interest from a fundamental point of view but also in terms of potential applications for energy storage.

Neutron powder diffraction is a very powerful tool for studying these compounds. Whereas hydrogen is almost invisible by classical X-ray diffraction techniques, neutron diffraction is able to locate the hydrogen nuclei inside the intermetallic lattice. In practice, deuterium (D) is used to limit the large background due to the incoherent scattering of H. From refinement of neutron diffraction patterns, using the Rietveld Method the site occupancy of deuterium can be easily determined. It has also been shown that thermodynamic properties of hydrides can be adjusted by substitution on the metallic sublattice. In most cases, the metallic atoms are substituted by neighbours on the periodic table. Whereas these atoms cannot be distinguished by X-ray diffraction, if their Fermi lengths are different enough, neutron diffraction can be used to determine the sites where the substitution takes place and the influence on the capacity storage of the corresponding hydrides.

Beside their ability to store hydrogen, many intermetallic compounds are magnetically ordered at low temperature. By introducing hydrogen into the lattice, the cell volume increases, involving an increase of the interatomic distances and modifications of the electronic structure. These properties can even be tuned by controlling the amount of absorbed hydrogen. Magnetic properties are very sensitive to distances between metallic atoms bearing the moment. Such a phenomenon can be studied by collecting neutron powder diffraction patterns as a function of temperature. The simultaneous determination of the magnetic structure and deuterium ordering is a challenging problem which can be solved only with neutrons.

Neutron diffraction can give even more information if we consider *in situ* reactions. From such experiments, it is possible to follow the charge/discharge reaction of an hydride either in solid-gas or in electrochemical processes. Such in-beam experiments have been performed to follow amorphisation processes in solid gas experiments or electrode performances in rechargeable batteries.

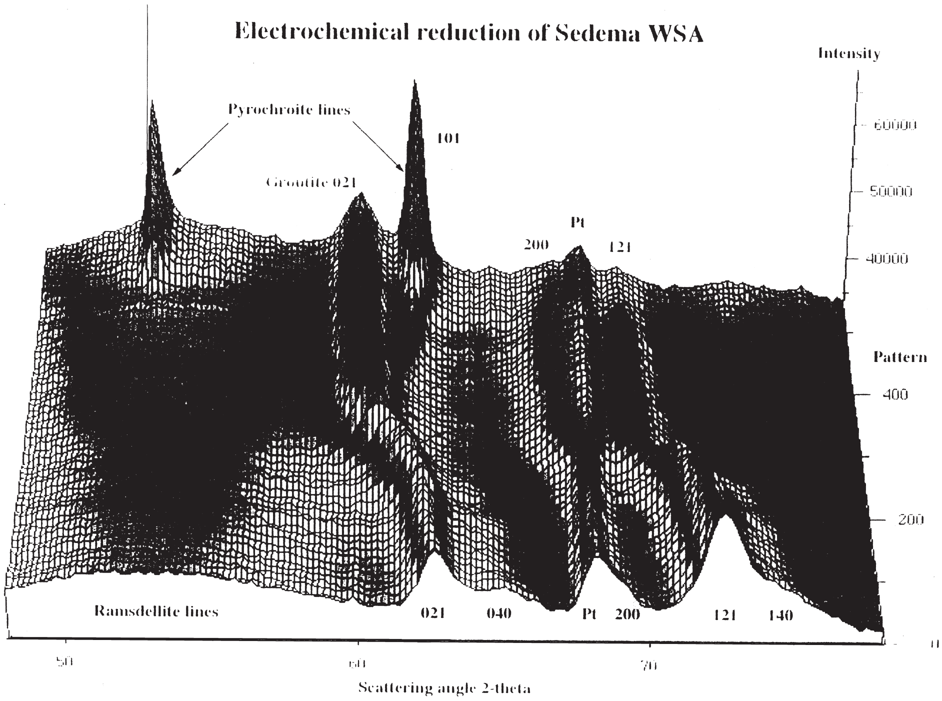

Figure 1: Neutron diffraction pattern as a function of time of the electrochemical reduction process of γ-Mn)2 used in solid state batteries [after Y Chabre and J Pannetier, Progr. Solid State Chem. 23, 1-130, (1995)].

The availability of higher neutron flux would permit the study of smaller samples and the use of H instead of D using powder diffraction. A powder instrument in a pulsed source may make it possible to perform simultaneously TOF spectroscopy to characterize the dynamics of the hydrogen diffusion in the metallic lattice.

4.3 Magnetic intermetallics

A field under continuous study is the magnetism of rare-earth intermetallic and transition metal compounds. Fundamental and applied research in this field is strongly interlinked. The search for new materials having interesting macroscopic magnetic properties leads to the discovery of new compounds having exotic magnetic behaviour. We can include in this kind of materials those obtained by addition of elements like B, C, Si, Ge, N and P. Such chemical additions can be of crucial importance for producing new compounds with improved magnetic properties. For instance, the compound $Nd_2Fe_{14}B$ is nowadays substituting $SmCo_5$ as material for permanent magnets. The materials to be used as permanent magnets must be characterised by high saturated magnetisation and high magneto-crystalline anisotropy. The field of rare-earth intermetallic magnetism is a good example that can be extended to other subjects in that investigations have a dual purpose; matters of technological as well as fundamental interest are addressed.

Concerning fundamental properties, in rare-earth intermetallics the most exotic magnetic structures and magnetic behaviour have been observed as a function of temperature. Heavy fermions, valence fluctuation and Kondo systems belong to this class of compounds. An illustration of exotic behaviour is provided by CeSb. This compound presents a very complex magnetic phase diagram as a function of temperature, pressure and applied magnetic field. The magnetic structure changes are impressive: below $T_N = 16.2K$ there are at least seven different magnetic phases at low field and pressure. This has served as a model for theoretical predictions of the ANNNI (Anisotropic Next-Nearest-Neighbours Ising) calculations and as an experimental realisation of the "devil's staircase" concept. These investigations could only have been done using single crystal neutron diffraction on samples mounted in a bulky sample environment.

The knowledge of the crystal and magnetic structures of intermetallic compounds is crucial for the synthesis and tailoring of new materials. All subsequent interpretation of bulk magnetic and structural properties as well as microscopic properties rest on the underlying crystal and magnetic structure. In this area, neutron powder diffraction has played a dominant role. This is highlighted by the refinement of the crystal and magnetic structure of $Nd_2Fe_{14}B$ in 1984 by neutron powder diffraction.

There are many examples using constant wavelength and time-of-flight powder diffraction techniques of magnetic structure determinations in intermetallic compounds, we give below two recent illustrative examples.

- The systems RMn_6Ge_6 show re-entrant behaviour as a function of temperature. In particular the compound $TbMn_6Ge_6$ becomes magnetically ordered at 500K with two propagation vectors. The magnetic structure is a triple distorted spiral with a ferromagnetic component in the spiral plane. This ferromagnetic component disappears between RT and 100K. Below 100K a ferromagnetic component appears giving rise to a tripled conical structure.
- Crystallographic structures of intermetallic compounds have been studied with TOF instruments and some magnetic structures have been also solved. Particularly interesting is the study of the AF2 magnetic structure of Mn_5Si_3, the high resolution at high d-spacing (2.5 to 12 Å) obtained on IRIS allowed the discrimination between different magnetic models. The lowering of symmetry of the crystal structure from the paramagnetic ($P6_3/mcm$) to the magnetically ordered state (Ccmm) was easily detected while the crystal structure was refined on HRPD.

The access to the structural magnetic parameters characterising the magnetic ordering of intermetallic compounds is only possible using neutron diffraction. For new materials, neutron powder diffraction is also a technique absolutely essential for crystal structure refinement. This is particularly true for compounds having light elements (like B, C, N, Al, Si and P) in the presence of rare earths. In the future, this subject should offer new areas of study which cannot be predicted at present. Novel compounds of ever increasing structural and magnetic complexity are constantly being synthesised.

4.4 Miscellaneous systems and subjects

4.4.1 Molecular solids and fullerenes

A very promising field for neutron diffraction work is the structural behaviour as a function of temperature of small molecules in the solid state. Plastic crystals undergoing structural phase transitions can be studied in great detail and the derivation of thermal TLS-parameters and/or probability density functions can provide insight into the dynamics of low energy intermolecular modes. Neutron diffraction is superior to X-ray diffraction in the determination of thermal parameters because of their decoupling from the atomic scattering factors.

The recent studies on fullerenes and their intercalated superconducting derivatives have shown clearly the superiority of neutron scattering in obtaining accurate structural information at the molecular level (including bond lengths and angles at a precision level comparable to the most sophisticated *ab initio* calculations) and following the subtle changes accompanying the orientational ordering transitions in these highly disordered solids with remarkable accuracy. Moreover, the case of fullerenes and of the potentially important materials derived from them illustrates a very common theme associated with new solid materials: at first, they are only available as powders and in very small quantities and their rapid structural and electronic characterisation crucially depends on the availability of very powerful, high resolution structural and spectroscopic techniques. The envisaged diffractometers at the ESS will be particularly invaluable in the study of any novel material giving European scientists and industry the edge in materials research. A typical example in current fullerene research is the very recent availability for the first time of heterofullerene solids, namely mononitrogen-substituted fullerenes ($C_{59}N$). These are currently available in very small quantities and given their disordered nature have been only structurally characterised by synchrotron X-ray diffraction. It is virtually impossible to distinguish by X-rays between the two light elements, C and N and hence full structural elucidation of these materials has to await the synthesis of large quantities of samples to be studied by neutron diffraction. The existence of the ESS would have already allowed the application of neutron techniques to these systems.

In this field neutron scattering, as a more precise than and complementary technique to X-ray diffraction, could help to solve problems related to the pharmaceutical industry. Some molecules crystallize in several polymorphs, some of them having no activity (because of differences in solubility for instance). The study of the polymorphic phase transitions and the crystal structure of the polymorphs could be performed by *in situ* neutron powder diffraction. This is possible only if high flux and brilliance is available to study small samples in order to minimise the effect of incoherent scattering of hydrogen.

4.4.2 Composite and technological materials: ceramics, zeolites, catalysts

- *Studies of mixed or composite materials.* Many industrially and technologically important materials are not single phase. A structural material like concrete is a typical example. The bulk-probe nature of neutron diffraction makes the studies of these materials very attractive if analysis of several phases in the same sample in a reasonable time period (not longer that ~12 h) can be carried out. It is also very interesting to study the response of these composite materials to changes in chemical and physical environment: liquid-solid reactions, hydrocarbon pollution, etc.
- *Solution and refinement of new, very complex structures.* Many materials of practical interest have very complex structures, for example zeolites (aluminosilicates and aluminophosphates), High T_c superconductors, super-alloys, drugs and pharmaceutical compounds, etc. In many cases it is very difficult to grow single crystals and hence powder diffraction has to be used to extract the structural information. The strong peak overlapping in the powder diffraction pattern for compounds with large unit cells ($V > 3000$ Å^3) implies that resolution has to be increased. However, there is always a compromise between resolution and intensity and furthermore, below an approximate instrumental resolution limit ($\Delta d/d \sim 0.04$ %), sample broadening is so important that higher resolution cannot help further in the structural investigation. Alternatively, line broadening analysis can be undertaken as many materials of technological importance show this effect either from fabrication or use. There is state-of-the-art software that allows

combined structural studies of complex materials using several powder data sets (neutron and X-rays, including the anomalous scattering if a wavelength just below an absorption edge is chosen in a synchrotron source), and this will result in a very detailed structural picture. In these cases, for example, guest-host interaction can be determined and understood at an atomic resolution level that will have a tremendous impact in the catalysts and drugs industries.

4.4.3 Coordination chemistry

Even though the difficulties in obtaining single crystals of appropriate size for neutron diffraction (due to the "limited" neutron fluxes at the existing sources) have limited the number of structural refinements of coordination and organometallics compounds, the impact of neutron diffraction in these fields cannot be overemphasized.

Indeed, the most important single advance in inorganic Chemistry in the last few years, i.e. Greg Kubas' discovery in 1985 that H_2 molecules can coordinate to transition metal atoms, was unambiguously confirmed only by single crystal neutron diffraction. It is now possible, using the structural data obtained by neutron diffraction on complexes containing molecular hydrogen, to map the reaction path of the oxidative addition of hydrogen to transition metal atoms. This is a very important achievement as it sheds light on the mechanism of catalytic hydrogenation, a reaction of great practical importance. Moreover, the study of the nature of the M-H interaction is still a field in expansion. Very recently, the discovery of new weak M..H bonds and M_H...H interactions, similar to "hydrogen bonds", has opened a new field of research, both in coordination chemistry and in molecular engineering.

It would have been impossible to achieve all these results without the use of single crystal neutron diffraction. With the advent of very intense neutron sources it will be possible to obtain useful data from much smaller crystals, easier to prepare, and thus open up new fields of investigations such as the role of hydrogen in biological systems.

The complexity of most of the organometallic compounds has prevented the use powder diffraction both for the refinement and for the *ab initio* determination of their structures (when no single crystal is available). The combination of very high resolution neutron powder diffraction with SR data may extend the applicability of these methods to structural determinations of these compounds.

4.4.4 Supramolecular magnetic solids

Supramolecular magnetism is a relatively new field, which will develop in the near future. The corresponding chemical structures are rather complex, and single crystals presently have only sizes suitable for X-ray work. However checks concerning phase transitions and in particular studies of magnetic ordering are possible (and have been successfully started) with neutrons using long wavelengths. The improved cold sources in the future ESS should make it possible to study the magnetism of these complex systems on a routine basis.

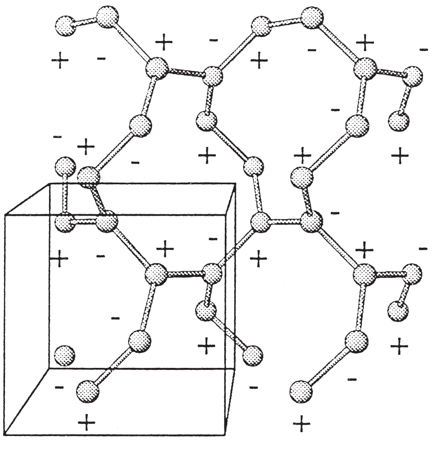

Figure 2: The antiferromagnetic collinear spin configuration of the Mn^{2+} ions that constitute the 3D chiral network of the supramolecular compound $[Fe^{II}(d_8\text{-}bpy)_3]^{2+}n[Mn^{II}_2(ox)_3]_n^{2n-}$ [after S Decurtins et al, to be published in Advanced Materials].

4.4.5 Chemical reactions: solid-solid, liquid-solid, gas-solid

To determine the stable phases and to characterise structurally crystalline materials under relevant industrial conditions is of great importance to improve chemical processes on a large scale. Among the most important chemical conditions to which a solid material is subjected we can mention the presence of reactive liquids and/or gases. The study of the structural behaviour of the sample in such conditions can help to understand catalysts, ionic conductors and sensors. To this kind of studies the technique of *in situ* neutron powder diffraction in reaction vessels and bulky sample environment is of the utmost importance.

4.4.6 Ionic conductors, solid electrolytes

Ionic conductivity is a field in which the techniques of crystallography and the methods used for studying disordered materials can be combined. Neutron diffraction is preferable to X-ray diffraction mainly because the ionic species are normally light elements (like alkali metals and oxygen) diffusing in a heavier matrix. Total scattering experiments should improve the picture obtained by crystallographic methods. In applying the total scattering methods better precision in absolute intensities is needed, so the high flux and low intrinsic background of the ESS are vital to this kind of research.

4.4.7 Aperiodic materials: quasicrystals, modulated structures

This is also a field in which neutron scattering is providing crucial results. Contrast between close elements in the periodic table provides an enormous advantage to neutrons in the structural analysis of quasicrystals and related systems. The recent advances in data analysis using the framework of high dimensional crystallography combined with traditional analysis on disordered systems are giving a new insight into the complex structures of these materials.

Modulated and intergrowth structures are quite common in inorganic materials. To characterize structurally these materials, neutron diffraction has played a very important role. The intrinsic features of the neutron-matter interaction are the basis for a higher precision and accuracy in structural parameters obtained from neutron diffraction. Neutron diffraction is complementary to the use of X-rays in this field. The increase in neutron flux and resolution should permit the study of smaller and more homogeneous samples, as well as the temperature dependence of the modulation wave vector(s) keeping the measurement of intensities reliable.

4.4.8 Diluted magnetic semiconductors

The determination of the cation distribution in diluted magnetic semiconductors (DMS) is essential in the understanding of their structural and magnetic properties. Due to the proximity in atomic number of some of the chemical elements in a large number of DMS, neutron diffraction experiments are more appropriate than X-ray scattering processes. Crystal growth of quaternary DMS usually gives very small crystals which require high flux neutron sources. Moreover, for a given concentration of the paramagnetic cation, small quantities of powdered samples are available since it is not possible to add samples coming from various chemical syntheses. The reason is that the quantity of paramagnetic cation entering the sample is hardly controlled during the process of chemical synthesis.

5. What cannot be done with present neutron sources. The need for the ESS

With the improvement of today's instrumentation on present neutron sources we can gain more than one order of magnitude flux in some cases: Be-monochromators, focusing, multidetectors, area detectors, supermirror guides, ^{3}He polarisers. This is a field where continuous effort must be put. However, qualitative improvement of the neutron scattering data, making possible new science, can be obtained only with more flux in a very intense Spallation Neutron Source (SNS). There are important experiments which cannot be undertaken with the current neutron sources or, if they can, the experiments demand an unfeasible amount of time. The list of such experiments includes:

- *Very small sample studies.* Some materials can only be obtained in very small amounts for various reasons. For example, some superconductors have recently been obtained at very high pressures as tiny samples. Very small samples under extreme exotic conditions of temperature, pressure and chemical gradient, can be studied. Diffractometers at a very intense SNS will also be used for the study of small samples with very expensive isotopes to avoid elements with high absorption cross section, although materials of considerable technological importance with such elements can be studied in this high intensity source by increasing statistics of the appropriate-size samples. 50-60 mg compounds can be studied in existing SNS counting over a day. In the new facility, samples of the order of milligrams can be investigated to extract structural information by counting over a day and alternatively, samples of about 50-60 mg can be studied in one or two hours. The size of the samples at this source will be approximately that needed in conventional X-ray diffraction studies but the sensitivity of neutrons to light elements and magnetic fields, relative to X-rays, results in a very clear advantage.

- The use of *very small single crystals* (well below 0.01 mm^3) in a very intense SNS would permit the study of really small chemical and magnetic single domain crystals, such as is often the case for magnetoelectric single domain monocrystals, thus yielding unambiguous magnetic structures with the corresponding chirality.

- *Partially hydrogenated materials.* Location of hydrogen in new materials and samples of biological interest is an outstanding problem still not solved. Neutron incoherent scattering from hydrogen makes the patterns, in existing neutron sources, unusable for many purposes, even if the statistics is improved. X-rays cannot be used unless high-quality single crystals of simple structures can be grown, which is not generally the case. This problem has been partially avoided through isotopic substitution of hydrogen by deuterium. However, for some samples the deuterating process is very complex (and very expensive), while sometimes it is impossible to deuterate to a satisfactory level. In the new SNS, optimum-size samples can be studied although statistics would have to be very much increased. A state-of-the-art example of studies in the new ESS source will be routine research on metal hydrides as they represent a very efficient way of storing hydrogen.

- Experiments involving *proton transferring* are of strong current interest because of their implications in the understanding of biological processes. There have been recently found solid state materials that may be used as model systems. To understand these materials, very precise structural determinations of the hydrogen positions, above and below the hopping process that occurs at about room temperature, is required.

- *Subtle structural changes.* Higher accuracy in the measurement of intensities and higher resolution will allow the study of subtle structural changes accompanying electronic processes, magnetic ordering, spin-Peierls transitions, charge ordering, etc. Some organic and metal-organic molecular conductors develop spin-Peierls transitions and others order as antiferromagnets. In both cases a transition to a superconducting state is inhibited. The structural behaviour and differences in these three types of compounds are very difficult to describe precisely because they involve tiny displacements in the positions of light atoms.
- *Magnetisation densities in complex systems.* Using polarisation analysis and polarised neutrons (^{3}He polariser) higher accuracy and more complex systems could be studied to obtain magnetisation densities, fine details of magnetic structures, and form factors. The magnetic structures of antiferromagnets should include the contribution of spin densities delocalized in organic molecules.
- *In situ* measurements of surface reactions. This is of primary importance in catalysis. One important problem is the study of intermediate states in H-catalysts.
- *Magnetic structures of molecular materials.* The determination of magnetic structures in magnetic molecular materials is a difficult or impossible task with the state-of-the-art technology since, in general, they have large unit cells, light atoms, magnetic moments delocalized in organic ligands or in free radicals, the size of crystals is much less than 1 mm^3 and deuteration is extremely complicated.
- *Very high pressure.* High pressure studies are of tremendous interest. High intensity sources would permit us to increase the range of pressures available. This will qualitatively benefit research in many areas of condensed matter for structural, magnetic and technological reasons. If higher fluxes are available, it will be possible to extend neutron measurements to higher pressures (on smaller samples) in an opposed-anvil type cell reaching ~50 GPa. Experiments of this nature (even for higher pressures) are already under investigation in synchrotron sources, but improved and complementary information can be extracted from neutron diffraction.
- *Below-one-second resolution kinetics.* Studies of chemical kinetic processes occurring during synthesis in the solid state by using high resolution in time is also another exciting type of experiment ideal to be performed in a high flux neutron source.
- *Near surface structures.* Structure near surfaces (melting process) and the study of nanocrystalline materials and grain boundaries need higher resolution and flux.

6. Industrial, energy, and health applications

The impact on industrial research of the ESS could be very important. In modern society new materials play an increasingly important role in daily life. The quality of life in our society is, in many cases, related to the availability of objects and devices made of such materials. A very important application of neutrons to applied research is the study of residual stresses and texture of structural materials. This is an engineering use of neutrons that is not considered here.

The understanding of chemical and physical properties of new materials requires the knowledge of their crystalline structures as well as the nature of their defects and the mechanisms of their possible reactions with the environment. These problems fall directly into the field of SSC. For solving problems relevant to applied research a panoply of techniques is to be used. In particular, neutron diffraction is extremely powerful for structural and *in situ* reactions analysis. The possibility of using neutrons for applied research is largely increased due to the very high flux expected for the ESS and the consequent reduction of time for making a diffraction experiment. Most of technological materials present also a fundamental interest, so that strong links between applied and fundamental research can be established.

The number of technological materials is so large that here we give just some examples relevant to the SSC field. Particularly, in relation with the use of neutrons in chemical applied research.

- Structural materials such as concrete, ceramics and composites, magnetic materials, electro-optical materials, catalysts and superconductors are very important to industry. Neutron diffraction is a technique for obtaining the crystal structure, and the relative amount of the different crystalline phases existing in a complex material, with a better precision than X-ray diffraction. The magnetic structure, and its behaviour as a function of external magnetic fields, of materials used for permanent magnets provides a fundamental information for improving the properties by chemical substitutions. In this respect neutron diffraction is an unique tool to obtain the microscopic spin configuration in solids.
- New materials for health include pharmaceuticals compounds and bio-compatible materials. The structural determination, and the survey of polymorphic transitions, in small organic molecules is of great importance to pharmacy industry in order to understand the biological activity of the polymorphs of a single compound. Among bio-compatible materials the fluoro-phosphates, apatites and composite resins used in dentistry are being improved using different synthetic procedures. The application of neutron diffraction to study the synthesis reactions should help to understand the reaction mechanisms and, ultimately, understand the relations between the physico-chemical properties and the crystal structures and microstructures.
- In this field, the study of hydrogen storage in solid matrices is one of the subjects to which neutron diffraction is absolutely essential due to the relative high scattering power of hydrogen. The understanding of the microscopic mechanisms underlying the capacity of certain metallic solids to trap high amounts of hydrogen, needs an extensive use of neutron powder diffraction in both high resolution and high flux modes. The same comments can be made extensive to the study of chemical processes in solid state batteries a is, for instance, the reduction of Mn-oxides.
- The degradation of structural materials under pollution conditions is one of the problems to which neutron diffraction can be applied as complementary to other techniques. The study of the cement-water and related reactions is an example of such a subject.

The presence of very efficient diffractometers in the future ESS should improve the study of the technological materials made directly by industrial institutions. The ESS should provide a service for industrial or technical purposes: for instance, powder diffraction quantitative phase analysis for industry and/or geological problems can be performed routinely in the ESS. If high flux is available this can be done by distributing properly the beamtime between industrial and academic research.

7. Conclusions

We have identified many areas of SSC for which the availability of a very intense SNS should make a breakthrough in our understanding of structural problems at an atomic level. The European Spallation Source Project is presently the only long term alternative to the present neutron sources. The improvement of neutron instrumentation in the latter sources should be developed in parallel with the ESS and should benefit the future ESS during the installation period.

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This a list of representative references corresponding to some of the topics that have been treated in this document. No explicit references have been given in the text in order to facilitate readability. The reader can find the relevant references just looking at the title of the corresponding section.

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Vibrational spectroscopy

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1. Introduction

Vibrational spectroscopy is a frequently used technique in fundamental and applied research. Infrared and Raman instruments are routinely available in many laboratories and companies, whilst inelastic neutron scattering (INS) can only be carried out at a very limited number of neutron sources. Vibration frequencies depend on the chemical bonds linking atoms and the interactions between molecules. Intensities depend on interactions between the incident radiation and the sample. These are quite different for the infrared, Raman and INS techniques. 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 which is still far from being fully understood. The ultimate purpose of fundamental research in this field is to achieve a realistic representation of vibrational dynamics. These are governed by forces, or potentials, due to manifolds of interactions between atoms and molecules. Theoretical approaches (e.g., quantum chemistry) are not yet able to account precisely for the observations, and experimental vibrational spectra are still the only means to obtain a detailed view of these interactions.

2. Major advantages of INS

2.1 Intensities

For optical techniques, intensities are related either to derivatives of the dipolar moment in the infrared, or to components of the polarizability tensor in Raman. In the most general case, these quantities are largely unknown : they cannot be measured directly and quantum calculations are not yet able to provide reliable values. They cannot be transferred from one system to another since they are very sensitive to the hybridization state of valence electrons. Therefore, the measured intensities cannot be fully exploited. With INS, the neutron scattering process is entirely attributable to nuclear interactions. Each atom is characterized by its nuclear cross section which is independent of its chemical bonding. Therefore, transition moments can be calculated accurately and measured intensities can be directly compared to calculations.

2.2 Contrast

The cross section of the proton for neutron scattering is about 10 times greater than that for any other atom. Therefore, proton dynamics can be studied in many different non-hydrogenous environments. Even for concentrations as low as ~ 1 wt.% in protonic species, the non-hydrogenous matrix can be considered to be virtually transparent. This proton selectivity can be further exploited because the deuterium atom (2H or D) has a very much smaller cross section than the proton. For a system with several protons, specific deuteration of some sites therefore simplifies the observed signals. As a result, INS intensities provide information on proton dynamics that can be analyzed with greater confidence than the corresponding infrared and Raman spectra.

2.3 Momentum transfer

INS spectroscopy offers the unique opportunity to measure vibrational spectra over a broad range of energy and momentum transfer $\mathbf{Q}$. In contrast, for optical spectra $\mathbf{Q} \sim 0$. The full scattering function, $S(\mathbf{Q},\omega)$, contains spatial information of the wave functions for the corresponding vibrations. We can then use the $\mathbf{Q}$ dependence of the INS intensity to obtain the shape of the potential functions and the effective oscillator mass for the various vibrations. The $\mathbf{Q}$ dependence provides a straightforward distinction between single and double minimum potentials (tunnelling).

2.4 Penetration depth

In many cases, electromagnetic radiation over a wide range of frequencies are strongly absorbed or refracted. In this situation, optical spectroscopy is limited to an extremely thin layer of sample at the surface. Neutrons can penetrate most media and, therefore, probe the bulk. Only a relatively few specific isotopes absorb neutrons to an extent which may preclude INS measurements.

3. Fields of application

Vibrational spectroscopy with neutrons already has achieved results of interest across most of the classic disciplines of **chemistry** (e.g., organic, mineral, metals, surfaces, hydrides, organo-metallic, polymers, materials, conductors, catalysts…), **physics** (e.g., lattice dynamics, phase transitions, superconductors, magnetism in bulks or clusters, mechanical properties of solids …) and **biology** (hydrogen bonds, dynamics in small molecules, water, polypeptides, DNA bases, drugs, …). INS has proved its ability to reveal new and important aspects of vibrational dynamics of great impact to fundamental and applied research. It appears more and more as complementary to optical techniques. New results obtained with INS allow for a better understanding, and consequently a more effective use, of infrared and Raman. In certain cases, INS imposes dramatic re-assignments of the optical spectra.

However, because the INS technique is much younger than infrared and Raman; because it can be used only at a very limited number of places through rather complex application procedures – some times intimidating for potential users – to oversubscribed spectrometers; and because it requires rather large amounts of samples (typically several grams), the number of problems which has been tackled is still rather modest compared to the huge knowledge accumulated with the infrared and Raman techniques over several decades. Furthermore, INS is only used for analytical and process control problems in exceptional circumstances. Even though it is not realistic to suppose that INS will ever become a routine technique like infrared and Raman, it is clear that more INS spectrometers are needed to fill the gap between the relatively small number of experiments which can be performed today and the enormous potential of the relevant scientific communities. At the same time, limitations imposed by the performances of the available spectrometers (flux, resolution, energy and momentum transfer range) should be overcome for further investigations. Therefore, we need both more quantity and more quality.

4. INS spectrometers and neutron sources

An ideal spectrometer should cover the whole energy-transfer range of vibrational modes (at least from 0 to 4000 cm^{-1} for comparison with infrared and Raman), and a large momentum transfer range in order to measure the intensity maxima for oscillators with heavy 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 …, smaller than ~ 10^{-4}. At the same time, higher energy resolution, better than ~ 1 cm^{-1}, is necessary to achieve reliable spectral profile analyses in condensed matter. Such spectrometers are not currently available and are not expected for the immediate future. However, any step toward this prospect should provide new insight into vibrational dynamics.

A prerequisite for vibrational spectroscopy with neutrons is a source providing a high flux of neutrons with incident energies (E_i) greater than vibrational transitions to be investigated. Pioneering work of great significance has been done at nuclear reactors, either at relatively modest energy transfer (below ~ 500 cm^{-1}) or even at larger energy transfer (e.g., the very important studies performed on IN1B at ILL).

Advanced pulsed neutron sources providing intense fluxes of epithermal neutrons are well suited to vibrational spectroscopy at high energy transfer. Indisputably, spectrometers like TFXA and MARI at ISIS cover greater energy or/and momentum transfer range, with better resolution and lower background than their homologues at reactor sources (e.g., IN1B and IN4 at ILL). They have provided unique results in the field of vibrational spectroscopy and given a glimpse of the potential of the method. 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.

The TFXA-type spectrometer could at this moment be significantly improved with MODES which would have detected fluxes 10 times greater and energy resolution 3 times better. Extrapolated to the ESS source, the following performances are likely:

- a resolution of six-fold better than TFXA ($\Delta E/E \sim 0.3\%$)
- a detected flux ~ 100-fold that of TFXA.

The use of the MARI spectrometer suffers from rather long counting times to obtain $S(\mathbf{Q},\omega)$ maps with statistics and resolution which enable detailed profile analyses. Detected fluxes need to be significantly increased with an increased number of detectors. This extension of vibrational spectroscopy shows tremendous promise but it is still in its infancy and both the quality and quantity of experiments must be increased to achieve this promise.

A significant increase in the neutron source flux (by a factor of ~ 30) used either to improve statistics and/or resolution should allow many outstanding problems to be pursued and to open up new fields of investigation:

- More complicated spectra would be resolvable and, therefore, larger molecules could be more effectively analysed.
- Band-shape analysis could be performed at higher momentum and energy transfers. Combinations and overtones would be better distinguished. Auto-correlation functions could be derived from band-shapes.
- Band origins would become sharper and clearly identified to much higher energies, or for softer materials, or at higher temperature.
- Weak features of non-hydrogenous atoms would become observable. This is of great consequence to force-field simulations and would represent a major advance in the use and applicability of the INS technique.

5. Fundamental problems and prospects

5.1 Force-fields

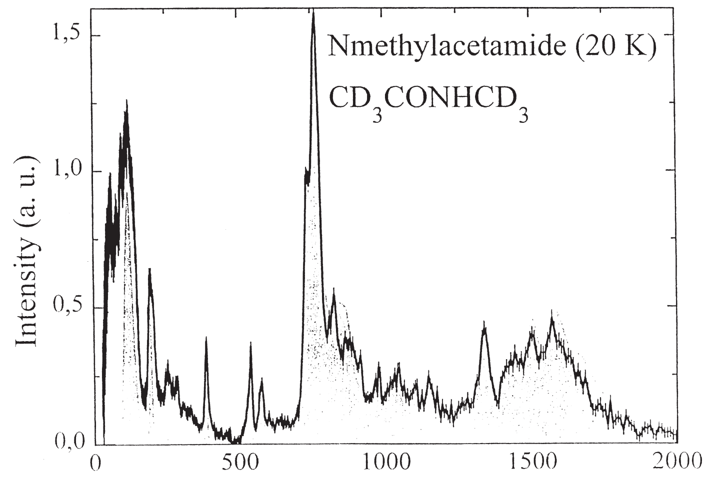
The objective for the interpretation of vibrational spectra is to determine atomic displacements for each observed vibration. A molecule can be represented by point masses (atoms) linked by springs (bonds or interactions) forming harmonic oscillators. For an isolated non-linear molecule containing N atoms, there are 3N-6 internal degrees of freedom corresponding to internal vibrations of the molecule. The dynamics are then determined with force fields (e.g., valence-bond, Urey-Bradley, ...) which contain (3N-6)(3N-5)/2 force constants. The eigenvalues of the (3N-6)x(3N-6) dynamical matrix give the vibrational frequencies and the eigenvectors give the atomic displacements for each of the (3N-6) normal modes.

For optical techniques, intensities cannot be exploited. Therefore, force fields derived from optical spectra are largely arbitrary since they are based almost exclusively on normal mode frequencies. Eigenvectors related to the effective oscillator masses and spectral intensities 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 exist). All of them are in accord with the observed infrared and Raman spectra!

Some of the difficulties encountered in the analysis of infrared and Raman spectra can be overcome with INS spectroscopy. The intensity for any transition is simply related to the atomic displacements scaled by scattering cross sections. It is thus possible to simulate spectra and a comparison with the observation provides a rigorous evaluation of the quality of any model (fig. 1). Although examples of force-field calculations including INS intensities are still quite limited in what is still a novel technique, they have provided a much more focused picture than that obtained previously from optical techniques.

Nevertheless, force-fields consistent with INS intensities are not totally free of arbitrariness, even though they represent conclusions which are the most firmly based on experimental data. This is because INS spectra are dominated by protonic modes, and because the majority of these spectra were measured over only a very narrow slice of (**Q**,ω) space. Consequently, normal modes with negligible proton displacements are still beyond quantitative analysis. Future force-fields based on full S(**Q**,ω) maps including weak bands at large momentum transfer values due to normal modes with large effective masses will truly raise vibrational spectroscopy to the state of "Science".

Figure 1: Comparison of the observed (error bars) and calculated (gray) spectra for the methyl deuterated Nmethylacetamide molecule at 20 K ($CD_3CONHCD_3$).



5.1.1 Valence-bond force-fields

Some molecular crystals (e.g., **benzene, imidazole, thiophene, model bases in DNA**, ...) are rather well represented with valence-bond force-field models. In some cases, relevant force-fields are significantly at variance with those obtained earlier from optical data. Comparison vibrational spectra calculated with the most advanced methods of quantum chemistry provides an important yardstick of the quality of the theory.

5.1.2 Localised modes

In some cases, the valence bond approach fails completely. This is the case for many hydrogen bonded systems : **carbonates** $MHCO_3$ (M = Na, K, Rb, Cs), **disulphates** $M_3H(SO_4)_2$ (M = K, Rb), **trifluoroacetates** $MH(CF_3COO)_2$ (M = K,Cs), **N-methylacetamide** (NMA, $CD_3CONHCD_3$), **polyglycines** (PG) $(\text{-CO-CD}_2\text{-NH-})_n$... In every cases, irrespective of the ionic or molecular nature of the systems, the dynamics of those protons involved in hydrogen bonds are almost totally decoupled from the dynamics of the other atoms and must be described in terms of localized modes, rather than normal modes. This is clearly revealed on the $S(\mathbf{Q},\omega)$ maps of intensity (fig. 2). This dynamical behaviour could not have been anticipated from optical data. So far, such dynamics are beyond the capabilities of quantum chemistry. It is worthwhile stressing that this decoupling does not in fact occur for much weaker hydrogen bonds such as in ice.

5.1.3 New assignment schemes

In some cases (e.g., the NMA molecule and PG), INS intensities reveal that previous assignments based on optical data are largely in error. New assignment schemes must be proposed for infrared and Raman spectra. Consequently, a new view of hydrogen bonding in peptides emerges. Again, these results emphasize the limitations of quantum chemistry.

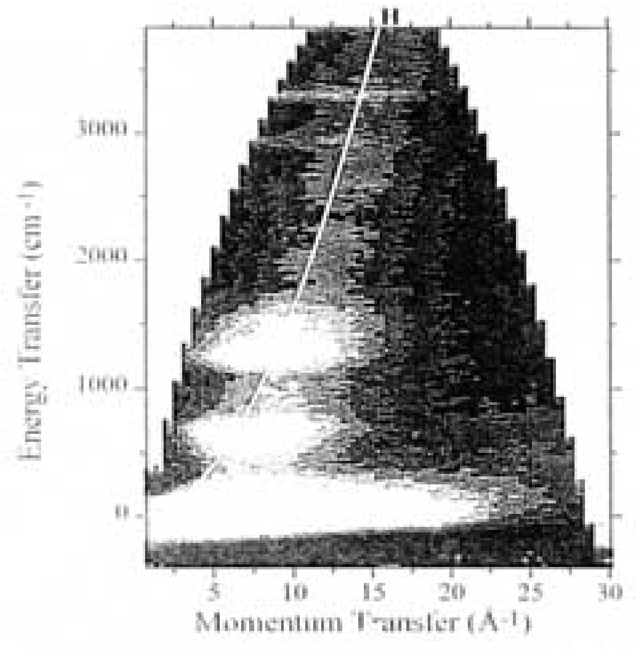


Figure 2: $S(Q,\omega)$ map of intensity for the anti-parallel rippled-sheet form of partially deuterated polyglycine $(\text{-CO-CD}_2\text{-NH-})_n$ at 20 K. The maximums of intensity are on the theoretical line for effective oscillator mass of 1 amu. This confirms that the proton vibrations are localized modes virtually independent of the other atoms.

5.2 Proton transfer along hydrogen bonds

Proton transfer is of considerable importance to much of chemistry, physics and biology. The transfer frequently occurs along an existing hydrogen bond (AH...B). In this case, it is thought to be governed by a double-minimum potential. Quantum tunnelling is most dramatic when the potential has a symmetric double minimum and a low potential barrier. Previous studies of proton transfer with NMR and quasi-elastic neutron-scattering (QENS) have been hampered by quantum effects and strong interactions with the motions of surrounding atoms. The "**vibration assisted tunnelling**" model was proposed. Consequently, it was thought that tunnelling transitions in hydrogen bonds should be extremely broad and difficult to distinguish from the background.

Vibrational spectroscopy is the only technique that measures atomic oscillations on a time scale comparable with proton dynamics (i.e., 10^{-12} to 10^{-15}s). Unfortunately, optical spectroscopy has disadvantages for the study of proton transfer that preclude a complete characterisation of the potential : *viz.* the nonspecific sensitivity for proton vibrations and the lack of a rigorous theoretical framework for the interpretation of band shapes and intensities. With hindsight, it is not surprising that the characterisation of proton transfer mechanisms with optical techniques has been the source of some long-standing controversies. INS enables us to measure quantum tunnelling directly and reveals that strong interactions have been overestimated in the past.

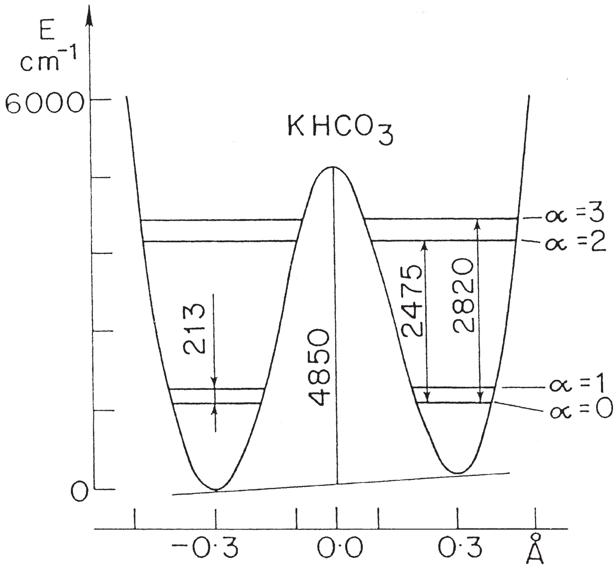
5.2.1 Proton transfer in ionic crystals

Potassium hydrogen carbonate ($KHCO_3$) is a prototype system for proton dynamics and proton transfer studies in hydrogen bonds. The crystal contains centrosymmetric dimer entities $(HCO_3^-)_2$ linked by moderately strong hydrogen bonds. The transition associated with quantum proton transfer within a quasi-symmetric double-minimum potential was predicted to be at 213 cm^{-1} (fig. 3). It could be observed unambiguously only with INS, at 216 cm^{-1}. Further INS studies have revealed tunnelling transitions for similar systems : at 57 cm^{-1} for $K_3H(SO_4)_2$, at 44 cm^{-1} for $Rb_3H(SO_4)_2$ and at 87 cm^{-1} for $KH(CF_3COO)_2$.

These observations are seriously in conflict with the "vibration assisted tunnelling" model. It transpires that vibrational spectroscopy with INS and NMR techniques, which probe proton dynamics at totally different wavelengths and time-scales, do not look at the same processes. Further theoretical and experimental works are required to reconcile the different approaches.

5.2.2 Proton transfer in amides and polypeptides

One of the recent highlights of INS in vibrational spectroscopy has been the study of **N-methylacetamide** and **polyglycine**, and their partially deuterated analogues.



Figue 3: Quasi-symmetric double minimum potential for proton transfer along the hydrogen bond in $KHCO_3$.
The $a = 0 \rightarrow a = 1$ transition can be observed only with INS.

These molecules are simple models for the peptide unit, which is of central importance to many biological structures and processes.

The S(**Q**,ω) map of the tunnelling transition of the stretching mode has been measured for the triple helix structure 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 thus emerges : hydrogen bonds form a network with the protons being delocalized between two equivalent sites. Therefore, proton transfer, an essential process in biology, is achieved naturally as a result of the hydrogen bond.

Symmetric double minimum potentials for formally asymmetric hydrogen bonds is in conflict with the Born-Oppenheimer approximation. This represents a new challenge for quantum chemistry.

5.3 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 measurements have been performed on potassium dihydrogen phosphate (**KH_2PO_4** or **KDP**) and **$KHCO_3$**. $S(Q_i,Q_j, \omega)$ maps with momentum transfer parallel to the plane defined by two of the three degrees of freedom : νOH, δOH and γOH, respectively, are the Fourier transform of the proton autocorrelation function (fig. 4). Such maps provide the most detailed information ever obtained. Long-standing problems like vibrational coupling, Fermi resonance, coherent tunnelling ..., can now be resolved. However, the necessary theoretical framework is not yet totally developed.

These experiments require large single crystals and time-consuming measurements for many different orientations, each data set having excellent statistics and resolution. For the time being, it is not possible to resolve finer band structures, nor to obtain maps for non-protonic modes.

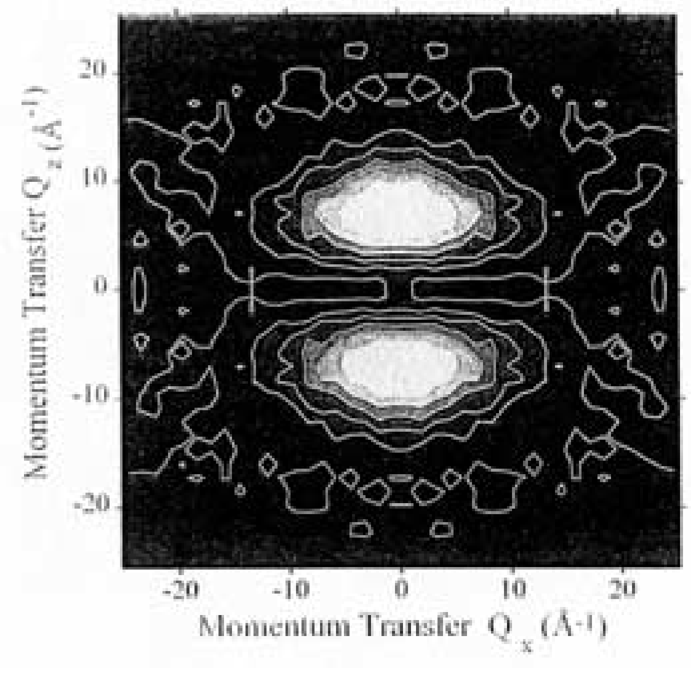


Figure 4: $S(Q_x,Q_z)$ map of intensity in KDP at energy transfer of 960 cm^{-1}. Momentum transfer vectors Q_x and Q_z are parallel to stretching and out-of-plane bending OH vibrations, respectively. This Fourier trans-formation of the proton auto-correlation functions reflects the shape of the proton wave-functions.

5.4 Free protons in solids

The existence of free protons in solids has been a matter of speculation for a long time, but no experimental evidence has been obtained, until recently, thanks to INS. The corresponding S(**Q**,ω) map is characterised by a ridge of intensity along the recoil line. Such maps have been observed for the first time for **coal** (fig. 5) and **manganese dioxide** (γ-MnO_2). They reveal the existence of free bare protons (with effective mass of ~ 1 amu). The physics of free protons in such systems is not yet totally understood.

Since recoil of free protons in solids gives rather broad signals, the limiting factor in this case is not resolution, but mainly statistics.

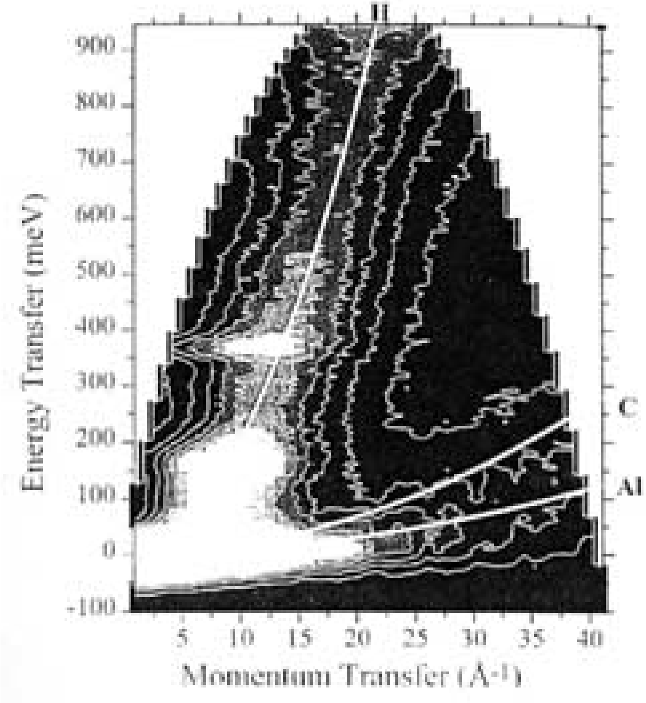


Figure 5: Free protons in coal at 20 K give a continuum of intensity which is a maximum along the theoretical line for effective mass of 1 amu.

5.5 New protonic species

5.5.1 $(H^+)_4$ entities

For γ MnO_2, it has been speculated that charge compensating entities such as $(H^+)_4$ should be located near by Mn^{4+} vacancies. INS reveals that these entities effectively exist. They behave like freely rotating tetrahedra at the centre of the oxygen octahedra surrounding Mn^{4+} vacancies. The radius of gyration is 0.5 Å. The tetrahedron inversion is observed at 40 cm^{-1}.

A complete characterisation of these entities should be furnished by the S(**Q**,ω) 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.

5.5.2 Tetrahedral oxonium ions H_3O^+

In hydrated protonic conductors, mobile entities are proton hydrated species: H_3O^+, $H_5O_2^+$, *etc*. Optical spectra are dominated by signals caused by the matrix stabilizing 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 reveals a tetrahedral symmetry for H_3O^+ entities, instead of the trigonal symmetry assumed up to now.

The remarkable capability of INS to reveal new protonic species in proton conductors is a very strong incentive for many more studies. Because the concentration of some mobile charge carriers can be very small, their identification requires intense flux and excellent statistics.

5.6 Hydrogen in metals *(R.Hempelmann)*

Proton dynamics in metals can be studied exclusively with INS which allows fundamentals (between 500 and 1500 cm^{-1}) and overtones to be observed. These dynamics are related to the symmetry of the interstitial sites, the depth and shape of the potential wells and, in some cases, reveal proton jumps between adjacent sites (tunnelling). Much better resolution is required for a more precise analysis of band shapes which could reveal finer structure due to tunnel splitting in the vibrational excited states.

5.7 Catalysts *(H.Jobic, P C H Mitchell)*

INS provides unique information on catalysts and adsorbed molecules. Many catalyzed reactions involve hydrogen in the catalyst or reactant molecules. INS is uniquely suited to study hydrogenic species in catalysis with rather little background interference which causes problems in infrared and Raman studies. Catalysts are usually opaque or totally black so that only very limited frequency windows can be investigated with infrared. Catalysts may also decompose or fluoresce in the laser beam used for Raman. INS enables identification of adsorbed species, their geometry, and the strength of bonding at the surface to be ascertained. INS has been used mostly to study **hydrogen and reactant molecules chemisorbed** on **metals**, **sulphides** and **oxides**.

A large increase of neutron flux would allow new catalysts to be studied where the number of hydrogen atoms on the surface is small : supported catalysts, post-combustion automotive catalysts, fuel cell catalysts ... In these cases, scattering signals are at the limit of sensitivity of current instruments. Some catalysts cannot be obtained in the necessary amounts required for INS experiments (e.g. 10 - 100 g). A more intense source would allow measurements to be performed with much less sample. Similarly, CAT converters in cars involve surface chemistry at concentrations just below the capabilities of present instrumentation. Finally, kinetics could be studied. The possibility of working at non-cryogenic temperatures is also interesting in this context.

5.8 C_{60}

INS has provided a remarkable insight into the vibrational dynamics of C_{60}. This molecule has such a high symmetry that only very few vibrational modes are active in infrared or Raman. In spite of the very small scattering cross section of C atoms, all the vibrational modes anticipated have been observed with TFXA. Moreover, small perturbations can be observed in intercalated or doped derivatives. In this case, INS is the only technique which allows vibrational dynamics to be fully understood.

6. 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. The contrast advantage is fully exploited and tunnelling transitions give extremely intense bands. There is no other technique to observe such tunnelling frequencies. In this respect, INS provides crucial evidence for fundamental aspects of quantum mechanics.

6.1 Single particle

Pioneering works using spectrometers with limited resolution emphasized the single particle character of the rotational dynamics. These dynamics are then represented as isolated rigid rotors experiencing periodic potentials. The observed tunnelling transition is then directly related to the potential barrier height. Because the tunnelling frequency depends almost exponentially on the barrier height, this spectroscopy is an extremely sensitive probe of the local potential experienced by the top. This has been used to study **small molecules** (CH_4, NH_3) adsorbed on **surfaces** (graphite, MgO), or **isolated** in cryogenic "inert gas" **matrices**, or molecules in complex **intercalates** ($C_{28}Cs(NH_3)_x$) and **clathrates** (toluene in calix[4]arenes, Hoffmann clathrates). Tunnelling transitions can also reveal very slightly different dynamics for non equivalent molecules in complex structures (**N-oxy-picoline**, **mesitylene**, **dimethylpyrazine**). The rotational dynamics of hydrogen molecules in organo-metallic complexes provides a very detailed insight on the **H-H** distances and, therefore, the degree of molecular dissociation. This is of great impact to catalysis in the liquid state.

Because tunnelling frequencies may vary over several orders of magnitude upon tiny changes of the environment, they provide a crucial test for molecular dynamic simulations. Unfortunately, only in a few simple cases where pair interaction potentials and crystal structures are well established a crude estimate of tunnel frequencies is possible.

6.2 Coupled rotors

Experiments with better resolving power spectrometers have revealed in some cases more complex energy level schemes which were attributed to coupling between rotors. Two prototypical systems have been thoroughly investigated and interpreted in totally different ways.

Rotational dynamics in the **lithium acetate** crystal ($CH_3CO_2Li.2H_2O$), on the one hand, have been represented by isolated pairs of tops coupled to each other. The fundamental concept of tunnelling transition is the same as in the single particle approach. The coupling term merely introduces more complexity in the energy level scheme.

On the other hand, models of the rotational dynamics in infinite chains of coupled rotors have been used for the **4-methylpyridine** crystal ($C_5H_4N\text{-}CH_3$ or γ-picoline) and for the **2,6-dimethylpyridine** crystal ($C_5H_3N\text{-}(CH_3)_2$ or lutidine). The quantum sine-Gordon model has been proposed. This approach is quite divergent in nature from the tunnelling concept : in this case INS spectra are dominated by translational motions of nonlinear excitations (solitons). These two models are obviously incompatible. However, it is not yet clear that this conflict reflects irreconcilable physical realities, and new experiments are worthwhile.

6.3 Temperature effects

Tunnelling transitions are best observed at very low temperature and vanish rapidly as the temperature is increased. This is related to the transition from quantum to classical regimes.

Dynamical coupling with phonons and spin conversion are the most important mechanisms to account for temperature effects and time evolution of tunnelling transitions. Advanced crystallographic works show increasing interest in rotational dynamics. They are not limited to low temperature and, therefore, they should be able to fill the gap between the two regimes.

6.4 Fields of application

Tunnelling spectroscopy has a major impact on fundamental research : quantum mechanics and pair potential estimates. To this respect, INS has been and is still a prestigious technique widely recognized. It is largely complementary to NMR, NQR, diffraction and calorimetric measurements. The matrix isolation technique is of great interest for the evaluation of pair potentials. Molecule adsorbed on surfaces and clathrates are of great relevance in chemistry.

6.5 Prospects

Tunnelling spectroscopy requires more detected flux to observe more diluted samples, or weaker scatterers (e.g., D, F...) or smaller samples (e.g., pressure). More intensity is also required for better time-resolved measurements (spin conversion).

Increased resolution is needed to observe tunnelling transitions at low frequency (higher potential barriers or smaller rotational constants : N_2, CF_3...). Simultaneously, more fine structure could be resolved for the tunnelling bands.

Simultaneous studies of structural and dynamical aspects of complex samples can now just be achieved on today's white beam spectrometers. This is particularly powerful when studying uniquely prepared samples like **intercalates** where direct correlation between structure and dynamics can be observed. This kind of work will be greatly advantaged with more intense sources.

7. New fields of application

A significant increase of detected fluxes should allow to apply INS to fields of interest which are beyond the present source/instrument capabilities.

7.1 Matrix isolation

Molecules trapped at low concentration in "inert" cryogenic matrices are only very slightly perturbed by their environment. This technique has been recognized for a long time as a very good approach to molecules in vacuo and to offer the best overlap to quantum chemistry. Moreover, species unstable under normal conditions can be studied.

So far, INS spectra of matrix-isolated species have been obtained essentially for quantum rotational tunnelling of small molecules (**CH_4, NH_3**). In principle, increased fluxes will allow internal molecular vibrations to be observed (e.g., with a TFXA-like spectrometer with a detected flux ~ 100 times greater).

7.2 High pressure

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 in 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. A spectrometer with rather modest resolution but with a highly collimated neutron beam could offer this new field a great impetus.

7.3 Better statistics

For proton-containing systems, studies have been focused so far on proton dynamics, which are most easily observed. Consequently, the dynamics of the other atoms remains largely unknown, inasmuch as it is not revealed by dynamical coupling to protons or riding effects. It would be necessary to improve statistics by orders of magnitude to be able to observe simultaneously the heavy atom dynamics.

The observation and characterization of new protonic species is also one of the most challenging prospect of advanced neutron sources and spectrometers.

The situation for **non hydrogenous** or **fully deuterated** systems is slightly better, since the contrast between the strongly scattering protons and the weakly scattering heavier atoms is largely suppressed. Previous measurements with TFXA and MARI on non-hydrogenous systems (**C_{60}**, **graphite**, **PTFE**, **glass** ...) demonstrate that such measurements would in fact be feasible. An important aspect is that **coherent scatterers** provide further information on vibrational dynamics which have been very little exploited so far. Progress in this field would remove further ambiguities in our knowledge of vibrational dynamics. Vibrational spectroscopy would then become a well-established technique, comparable to the most advanced diffraction, NMR..., techniques and would play the role of a calibrant for theoretical methods.

7.4 Increasing momentum transfer range and energy resolution

The ability of INS to measure wave functions directly is surely the most promising prospect for further developments of vibrational spectroscopy : force-fields including all atoms, tunnelling, Fermi resonance, ...

7.5 Neutron Compton scattering

For very large energy and momentum transfer, neutron Compton scattering should provide insight into the vibrational dynamics of a great variety of systems. This technique allows the kinetic momentum distribution for each atom in the ground state to be measured (e.g., H, D, C, ... are well separated). This is complementary to the normal vibrational spectroscopy. This technique has been used very little so far, although early results are very encouraging. It is being developed currently to study hydrogen and other atoms in catalysts. To be really quantitatively reliable the method requires high flux of neutrons at high energy and an improvement of a factor 4 in resolution.

8. “Flagship” experiments

Vibrational spectroscopy

1. High resolution $S(Q_x,Q_y,Q_z,\omega)$ maps of intensity on single crystals : $KHCO_3$,KH_2PO_4, partially deuterated Nmethylacetamide $CD_3CONHCD_3$.
2. $S(\mathbf{Q},\omega)$ map of intensity for proton quantum tunnelling in polyglycine $(\text{-CO-CD}_2\text{-NH-})_n$ with high resolution and large momentum transfer.
3. $S(\mathbf{Q},\omega)$ map of intensity for $(H^+)_4$ entities in γ-MnO_2 and H_3O^+ entities in β-alumina.
4. Proton transfer under high pressure (anvil cells).

5. Hydrogen in precious-metal alloy catalysts for fundamental understanding of the role of the catalyst in hydrogen dissociative chemisorption.

Tunnelling spectroscopy

1. High resolution $S(Q_x, Q_y, Q_z, \omega)$ maps of intensity on single crystals : 4-methylpyridine
2. Tunnelling under high pressure (anvil cells).

Biology, biotechnology and biomedical applications

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1. Introduction

Neutrons have many properties that are uniquely useful for molecular biology structural studies, in general:

- a choice of wavelength from below 1Å to more than 10Å associated with "soft" energies and negligible absorption in most matter
- isotope (especially hydrogen-deuterium) effects
- scattering amplitudes independent of atomic mass
- a negative coherent amplitude and large incoherent cross-section for ^{1}H.
- because of their weak interaction with matter they cause no significant radiation damage.

Furthermore, the energies of neutrons of the appropriate wave-lengths for structural studies correspond to thermal energies for temperatures between a few degrees K to well above room temperature. In fact, neutrons produced in a reactor or spallation source have their wavelengths "adjusted" by equilibration at a given temperature; thus "cold" neutrons have wavelengths of several Å, "hot" neutrons have wavelengths of a fraction of an Ångstrom and "thermal" neutrons have wavelengths close to 1 Å. Because of this wavelength-energy link, neutron inelastic scattering allows the simultaneous study of spatial structure, on the one hand, and dynamics, on the other, at the atomic and molecular levels—motions in proteins, for example, that have been shown to be associated with biological function.

The above properties of neutrons allow them to be used in a wide variety of different ways in the investigation of the structure and dynamics of biological systems. Thus for structural studies, solutions of macromolecules or disordered gels may be investigated by small angle neutron scattering (SANS). Ordered systems can be investigated using crystallographic techniques on one, two or three-dimensionally ordered systems. Even here we can distinguish two different methods: high resolution crystallography (similar to that carried out by X-rays but exploiting the relatively greater scattering length of hydrogen or deuterium to locate precisely these atoms) or low resolution crystallography exploiting the contrast variation method. A currently rapidly expanding technique is neutron reflectometry which allows the investigation of surface structures and which is thus of great potential in studying membranes. Macromolecular dynamics is currently studied using quasi-elastic, inelastic or spin-echo techniques, each of them being suitable for a particular energy resolution and spatial range.

The provision of a higher intensity source would open up the prospect of carrying out experiments on structure and dynamics simultaneously.

In this report we wish to place an emphasis on the importance of the biological systems which can be investigated and the ways in which the different neutron scattering techniques can contribute to our understanding of the biological functions at the molecular level which in sum make up life. It is only in throwing light upon function that we can justify the investigation of structure and dynamics. In the following chapters we will therefore outline how neutron scattering has and will continue and expand in the investigation of the fundamental components of living systems but also in biotechnology and the medical field.

It is clear that in many fields of molecular biology other physical techniques are of wider application but in many cases neutrons produce information which is unique and complementary to that obtained from other techniques. Biological systems are by their nature complex and one technique alone will never be sufficient to elucidate their functions.

2. Proteins

Proteins provide the widest variety of macromolecules in the living cell. It is estimated that in a simple prokaryotic cell such as *E. Coli* there are 10 000 different proteins each encoded in the cellular DNA. In general, each protein takes up a single (or a number of closely related) conformation determined by its amino-acid sequence which is in turn specified in its DNA gene sequence. The field of high resolution neutron protein crystallography has to date been rather unproductive compared with X-ray and NMR techniques. This has been due principally to the lack of flux on neutron diffractometers. The combination of a higher flux pulsed source and the quasi-Laue technique will make such experiments much more tractable in the future. It should be noted that the problem of incoherent background (due mainly to hydrogen atoms) can also be radically reduced by producing perdeuterated proteins using modern molecular biological techniques. The first experiments using perdeuterated samples have recently been carried out and show great promise (1). Neutron crystallography will allow the determination of proton positions and the orientation of water molecules at the surface of proteins to be determined with high accuracy. As almost all enzyme mechanisms involve the making and breaking of hydrogen bonds such information is clearly of vital importance. Another important feature of such detailed structural information is that it enables the determination of better potentials for use in theoretical studies of protein conformation. The **"protein folding"** problem, or the prediction of how a particular amino acid sequence will fold to give a final tertiary structure, is one of the major general problems being tackled in modern structural molecular biology. Despite the knowledge of more than 1000 different amino acid sequences and their associated tertiary structures the solution to this problem still seems some way off. One of the reasons for this may well be the absence of understanding of the role of water around proteins and an often invoked theory is the role of the hydrophobic interaction. In an exhaustive review paper (2), Blokzijl and Engberts have proposed a key experiment where neutrons should be used. They argue that in order to resolve the nature of hydrophobic interactions, neutrons should be used to elucidate the structure of water near interfaces. This could be done using isotopic labelling in a way similar to that used for investigating aqueous solutions of simple salts. Apart from the folding problem this technique could be of great interest in the food industry for investigating the protein and other gels and surfactants which up many foods. **Food gels and emulsions** are usually opaque and therefore light scattering is less suitable. The application of X-rays is limited because of the length scales to be probed and more seriously by the small contrast between various hydrocarbons and water. Neutrons are therefore the choice to be made for studying gels and emulsions. It would be of great scientific and practical interest to study the aggregation processes involved in the preparation of foodstuffs. Specific examples taken from a recent Faraday Discussions (3) on "Gels" are whey protein, gelatine, starch, polysaccharide, casein, soy protein and combinations thereof. Such experiments would naturally fit to similar questions put forward on the structure and behaviour of surfactants (e.g. proteins, phosphoproteins, polysaccharides) at surfaces. Another key experiment here would be the structure/conformation of proteins at surfaces under dynamical (expanding/compressing) conditions. This property is related to the formation and (in)stability of emulsions and foams. The behaviour of proteins under pressure has to date received very little attention, although the application of pressure to foods is often used as a means of inactivating bacteria and other agents harmful for conservation.

Another important aspect of protein folding is **chaperone-mediated protein folding.** Chaperones are molecules which assist other proteins, termed substrate proteins, in the process of correct folding. Understanding of the chaperone function has (i) biological, (ii) medical and (iii) biotechnological significance:

(i) Chaperones play a role in the maturation process of nascent protein (folding into the active conformation) after synthesis by ribosomes.

(ii) Chaperones are used to renature proteins after stress, for example heat-induced denaturation. The enhanced production of chaperones after infection with concomitant fever suggests that these molecules might play a role in stabilizing proteins under heat stress.

(iii) Recombinant expressed proteins are often prone to aggregation. Chaperones can dissolve precipitated proteins. It would be of great bio-technological significance if chaperones could be used in the activation process of recombinant proteins.

Neutron small-angle scattering can contribute to the understanding of the folding process by analysing the structure of D-labelled substrate proteins in the presence of contrast matched chaperone molecules. Static measurements are already being performed using a high flux neutron source such as that at ILL. However, since folding is a dynamic process, **kinetic studies** are also necessary. These measurements are only possible if a neutron source considerably higher intensity is available, such as the planned ESS.

3. Protein-nucleic interactions

It is characteristic for biological systems that a variety of individual proteins and nucleic acid components work together to maintain a certain function important for the survival of the cell. In order to analyse a particular function, e.g. transcription, sub-assemblies of the transcription apparatus are isolated from cells and analysed *in vitro*. It is the aim of this kind of study to mimic the *in vivo* situation as closely as possible. This is achieved by simultaneously studying the largest possible number of components involved in the process under study. Neutron small angle scattering is a unique method for obtaining 3-D structural information about such large complex arrangements. This is done by highlighting single components by means of deuteration and matching of the residual part of the complex by adding D_2O to the solution buffer. In the case of protein-nucleic acid complexes the natural neutron contrast between components is high and specific deuteration unnecessary. Such experiments could be seen as bridging the gap between molecular and cell biology.

This method has been applied successfully for example to the analysis of, *inter alia*, the internal *E. Coli* ribosome structure (4), the HIV-1 reverse transcriptase sub-unit arrangement (5) and the spatial arrangement of *E. Coli* RNA polymerase bound to DNA with and without transcription factors (6). Extension of the approaches described above to the corresponding eukaryotic systems has not yet been done. The number of components participating in such a process as transcription is, however, much larger in eukaryotes than in the previously analysed bacterial (prokaryotic) systems. Improvement of the neutron flux will help to extend the applicability of the neutron scattering approach to very large eukaryotic complexes having biological and biotechnological significance, such as the regulated transcription complex in eukaryotic cells. analysis of large protein-nucleic acid complexes is important for the mechanism of gene regulation and processes such as cell development and differentiation and de-differentiation in malign cells.

A higher neutron flux would allow **kinetic distance measurements** of proteins to be made as they move along the DNA. An example would be the translocation of DNA dependent RNA polymerase along the DNA during RNA synthesis in real time. DNA dependent RNA polymerase is the enzyme which catalyzes the transcription of genetic information of DNA into RNA. How this enzyme translocates along the DNA during RNA synthesis is not yet understood. By using a DNA-bound deuterated protein as reference point, the movement of D-labelled RNA polymerase relative to the reference point could be measured directly. Static distance measurements using this system have already been successfully performed. Kinetic distance measurements in this system require much higher neutron intensities. Virus particles are another form of complex which serves as a paradigm for a multitude of cellular functions. In recent years there have been dramatic advances in the understanding of virus structure through X-ray crystallography. These advances have however been limited to examples of non-enveloped icosahedral viruses which can be fairly readily crystallised. Even in these cases information is usually obtained only about the protein coat as the nucleic acid genome is at least partially disordered and consequently has very low contrast for X-rays. Through low resolution crystallography neutrons have allowed the nucleic acid to be located and its interaction with the protein coat to be studied (7). In the future a combination of high resolution X-ray crystallography, low resolution neutron crystallography and electron microscopy will be able to provide a full picture of the organisation of such particles. In the case of the enveloped viruses (which are surrounded by a fluid cell membrane-derived lipid bilayer) it has not yet been possible to obtain crystals and quite possibly never will be possible. Here small angle scattering with contrast variation allied with electron microscopy can be a very powerful tool for determining the overall organisation of the particle. The small amounts of material and low concentrations sometimes available often require higher fluxes than are presently available.

The ribosome is the protein factory of the cell and is a complex structure composed of two subunits, one containing 21 proteins and 1 piece of RNA, the other 32 proteins and 2 pieces of RNA. Over the past 20 years the overall structure of this particle has been determined at low resolution by neutron scattering from deuterium labelled particles and by electron microscopy. In recent years the sub-particles have been crystallized and are being studied by high resolution crystallography but there exists as yet no way to determine the phases of the X-ray structure factors. Here again further neutron crystallographic data could be of help in defining a particle envelope or intersub-unit boundaries. Other molecular complexes, often more labile, are continually being discovered, for example the signal recognition particle (SRP). These will require a high neutron flux to provide important structural information. The study by neutron scattering of particles whose components have been studied at near atomic resolution by X-ray crystallography will become more and more common particularly in cases where a complex is unstable and is only present under well defined narrow conditions in solution. The existence of a known crystal structure reduces vastly the number of unknown parameters and will allow the modelling of complex interactions in solution and under realistic physiological conditions.

4. Membranes and transport

From a reductionist point of view, a biological membrane can be considered to be made up of (i) an organised lipid component that contributes mainly to the membrane's physical properties (semi-permeability, electrical insulation, visco-elasticity, etc.) and (ii) membrane proteins that are mainly responsible for biological function (as receptors, pores, pumps, transporters, energy transducers, etc.). It is therefore useful to divide such studies into two classes: those on model systems (usually lipid bilayers) and those on native membranes or membrane components.

4.1 Model systems and transport devices

Diffraction from specifically deuterated stacked bilayers was among the first neutron scattering techniques successfully applied in model membrane research. A milestone represents the work of Büldt et al. (8) which demonstrated the advantages of selective deuteration for the determination of phospholipid multilayer structure. Furthermore, this work provided evidence that the average orientation of the dipolar headgroup of lecithin is nearly perpendicular to the membrane normal in both the fluid and the gel phase of the bilayer. Other authors used a combination of SANS and diffraction methods for the elucidation of phospholipid structure in bilayers and multilayers at a resolution of 1-2 Å (9).

Since the early days of model membrane research a number of central questions have been addressed : (i) whether the large number of chemically different lipid molecules in biomembranes is a present necessity or an evolutionary left-over and (ii) whether this complex composition is essential for the formation of functional enzyme complexes, the maintenance of lateral heterogeneity and of the asymmetry of the membranes. Such an active role would certainly be associated with processes of lateral and transverse phase separation of lipids and selective lipid/protein interactions. Since the working state of biomembranes is the liquid crystalline (L_α) phase, phase separation in this phase is of prime interest. SANS in combination with contrast variation is a very powerful technique for determining phase diagrams in thermodynamic equilibrium states and which evaluates simultaneously the detailed structure of the membrane undergoing phase instabilities. So far, SANS has been applied for the study of binary lipid mixtures and provided very detailed information about mixing behaviour, molecular volumes, cholesterol-lipid interaction and on the critical demixing process in the two-phase coexistence region (10).

Neutron reflection is a relatively new technique for measuring interfacial structure of model membranes. It is an exceptionally sensitive method, requiring only nano moles of sample, which makes it method very attractive for the study of the interaction between membranes and highly purified proteins. The methodological approach is essentially similar to well established X-ray reflectivity measurements, but with the advantage of deuterium/hydrogen substitution. Thus, by selective deuteration of a lipid, one can probe different interfaces in a lipid bilayer. Similarly, variation of the bulk water contrast around the membrane by mixing normal water and heavy water, or substituting one species by the other, provides information about the hydration properties of the membrane head groups and the penetration depth of water into the membrane interior. Moreover, the relatively high neutron transparency of crystals like silicon enables the use of such solids as a planar support for the membrane in reflectivity studies.

The first model membrane systems studied by this method were (one component) phospholipid monolayers at the air water interface (11), but it is only a matter of a year or two since the first reports were published with detailed studies of the interaction of monolayers with a second component, be it proteins (12) or other amphiphiles (13). One of the key features here is the potential of neutron reflection to differentiate clearly between an intercalation of parts of the adsorbing molecules into the model membrane from a mere adsorption. This opens up new possibilities for the exploration of the role of so called hydrophobic loops of proteins in the process of a functional coupling to a membrane. The next step was the study of the bilayers adsorbed to quartz or silicon crystals (so called supported bilayers) which provide the basis for detailed bilayer - protein interaction studies . In the design and development of effective **drug delivery systems**, the neutron data can supply information which cannot be obtained by any other means. The level of detail provided, for example, by neutron reflection studies of adsorbed surfactant monolayers (14) and supported bilayers (15), can greatly facilitate the process of designing *novel* surfactants for use in the delivery of drugs **(and also pesticides)** - a task likely to assume increasing importance in future years, not only because of the world-wide ban on the use of chlorofluorocarbon propellants in aerosol devices, but also because of the greater efforts likely to be demanded in the production of non-toxic, biodegradable, environmentally-friendly surfactants. In the area of polymer science, the neutron reflection experiments can provide the same valuable contribution (16), yielding detailed structural information to facilitate the **design of novel polymer-based drug delivery systems**. To complement the reflectivity studies, neutron small angle scattering experiments can be performed to provide direct information on the structures of all of the commonly used types of drug delivery systems, including macro- and micro-emulsions (17), micelles and vesicles. The structure of biological membranes is also of fundamental importance in pharmaceutical formulations' research, because all drugs administered to patients are required to traverse innumerable biomembranes *en route* to their target site. Neutron reflectivity studies presently provide the only means to obtain the required level of detail on membrane structure, and can also be used in determining the likely beneficial and detrimental influences of putative drug penetration enhancers.

It would lead to a proliferation and elaboration of the kinds of detailed studies already undertaken for systems involving non-natural surfactants, and would provide the first opportunity to carry out the same types of experiments on systems involving biological lipids. From the knowledge thence gained on the relationship between the covalent structures of amphiphilic molecules and the structures and properties of their interfacial aggregates, it could thus be hoped that there would be greater understanding achieved on the structure and properties of biological membranes, and that significant progress could be made in using molecular management in membrane engineering. For biological applications, for example, it could become possible to engineer **artificial cells with predetermined size**, shape, permeability and elasticity, affording real opportunities for the rational design of synthetic erythrocytes and microscopically-dimensioned devices for controlled drug delivery. In the wider context, these efforts would provide widespread opportunities for wealth creation, greatly facilitating the synthesis of novel amphiphiles and polymers, giving concomitant benefits not only to pharmaceuticals research, but also to pesticides, cosmetics, detergents, petrochemicals, and agrochemicals research.

An important experiment to be carried out using a new high flux source could be to **determine the detailed molecular architecture of synthetic erythrocyte membranes** using the technique of neutron specular reflection in conjunction with isotopic labelling of the component membrane lipids.

Membrane function is closely related to the **lipid bilayer dynamics** which is determined by a whole hierarchy of motional processes. It involves (i) conformational transitions of the hydrocarbon chains, (ii) locally restricted rotational diffusion, as well as in-plane and out-of-plane translational diffusion, (iii) long range lateral diffusion of the lipid molecules, (iv) collective undulatory excitations of the bilayer (membrane flickering). The chain dynamics provides the fluctuating thermal forces for the excitation of the conformational states of the membrane proteins, which is essential for enzymatic function. The lateral diffusion controls the formation of functional enzyme complexes (e.g. in the electron transfer chain of mitochondria or during the association of the receptor-adenylatecylase-G-protein complex). For these processes the two-dimensionality of the membranes is essential. Finally, the undulatory excitations may provide an essential contribution to the repulsive forces between membranes.

Despite this importance of all aspects of lipid dynamics for biomembrane processes our knowledge in this field is still rudimentary and contradictory. Quasi-elastic neutron scattering (QENS) offers outstanding advantages for the exploration of lipid membrane dynamics. Its particular features are:

(i) The molecular motions may be studied by incoherent QENS. Therefore the motion of parts of the lipid molecules (e.g. of the head groups) may be filtered out by deuteration of the residual parts (e.g. chain and glycerol backbone).

(ii) By selection of the instrument resolution, motional processes at different time scales may be distinguished (e.g. the chain dynamics from the lateral diffusion).

(iii) Collective and molecular motional processes may be evaluated by simultaneous measurements with backscattering and/or time of flight instruments and neutron spin echo instruments.

(iv) Most importantly, in-plane and out-of-plane motional process may be evaluated by variation of the scattering angle with respect to the membrane normal.

Besides the spin echo technique, which has been successfully applied for the study of membrane undulatory motion, scattering with ultracold neutrons is a promising technique to study the dynamics in the slow time (ca. 10^{-7} s) regime. Incoherent QENS is the only method available which can provide simultaneous information on the correlation times and the geometry of membrane molecular motion in the GHz - THz frequency regime. This is a particularly interesting regime since virtually all molecular dynamics of biomolecules can be assigned to frequencies in this region.

4.2 Natural membranes and membrane proteins

Two types of protein organisation are likely to be encountered in the plane of the membrane: (i) disordered or liquid-like; (ii) well-ordered two-dimensional crystalline patches.

Bacteriorhodopsin (BR) in purple membranes is the paradigm of the second type. Complementary structural methods for its structural study have been electron microscopy (EM), atomic force microscopy (AFM) and synchrotron radiation (SR) diffraction. Single two-dimensional crystal membrane patches can only be examined by EM or AFM. For neutron and SR diffraction to be observed, on the other hand, samples of stacked membranes are required - samples that give powder diffraction lines. The structure of BR is now known to a few Å resolution from cryo-EM, in which diffraction reflections were phased by image reconstruction. Only certain features of the density map could be attributed unambiguously, however, e.g. those arising from aromatic side chains, and independent information on the location of various parts of the structure obtained from deuterium labelling and neutron diffraction was very useful (18). Exchangeable protons and water molecules play important functional roles in various membrane proteins and neutron diffraction from crystals is presently unique in being able to provide information on their location. Furthermore, the ease with which special sample environments (temperature, pressure, salt conditions...) can be built for neutron diffraction allows studies of different functional states in membranes.

There have been few studies of the liquid type of protein in-plane organisation in natural membranes. These would not be easy experiments. Large samples are required and most probably specific deuteration will be essential to separate contributions to the scattering curve. On the other hand, knowing the lateral organisation of large protein complexes in membranes is likely to be essential for understanding functional mechanisms.

For both types of in-plane organisation, samples for neutron or X-ray diffraction studies are made up of stacked membrane patches. These usually have regular spacing depending on conditions such as water and salt content, and can be considered as 1-d crystals. They allow the study of the membrane profile, i.e. the scattering density distribution along the normal to the membrane surface, which contains information on depth of protein insertion, associations to the membrane surfaces and the location of deuterium labelled groups.

The strong incoherent scattering from H in proteins, lipids and water has made possible the study of membrane dynamics by neutron inelastic scattering in the ns to ps time scale (19). The field of functional dynamics in biological membranes is relatively new and has exciting potential. In principle, ordered samples are not necessary for these studies, although, in stacked membranes, information can be derived on motions perpendicular and parallel to the membrane surfaces by appropriately choosing the orientation of the scattering vector. Here too, neutrons are unique in the study of global motions in the thermal range. Specific deuterium labelling allows to focus on the motions of different parts of a structure (the incoherent scattering cross-section of D is 40 times smaller than that of H).

Membrane proteins can be extracted and purified in biologically active form by using various detergent molecules. The detergent-protein complex can be studied in the same way as a soluble protein. In particular, its molecular mass (and hence stoichiometry when many proteins are associated - as is often the case for membrane proteins), radius of gyration and extended scattering curve can be measured by SANS, which, compared to SAXS, has the important advantage of contrast variation to account for the contribution of bound detergent. The low resolution neutron crystallography approach developed for the study of complex structures such as viruses is particularly suited to membrane protein-detergent crystals. Protein and detergent components are separated in the scattering density maps by contrast variation (20). The method can be extended to separate protein components that have been specifically deuterium labelled. Because of the low resolution and long wavelengths used, neutron diffraction is relatively strong and the limitations on minimum crystal size are considerably relaxed compared to atomic resolution studies. In fact, because of the importance of water and exchangeable protons in the biological function of many membrane proteins, high resolution neutron crystallography studies would be of paramount interest. Crystals are usually small, however, and unit cells, too large for even the best instrumentation available at present. But the study of membrane protein-detergent crystals should profit from progress in neutron crystallography, in general, e.g. through the development of more powerful detector systems and quasi-Laue methods.

5. Polysaccharides

Polysaccharides represent, with proteins, lipids and nucleic acids one of the four main classes of constituents that make up living matter. They have been the object of extensive studies for a long time due to their **economic importance**. **Industrial processing of high polymers of vegetal origin** (starch, cellulose, pectins), or of **animal origin** (chitin) was developed quite early. More recently a more specific biological interest has developed due to the discovery of saccharide structures of high complexity, which play an essential role in the life of cells, and can play therefore a key role in a variety of biomedical applications. The most important class of compounds is that of glycoconjugates (21); they are present as essential elements of all the biological membranes. Furthermore they can be responsible for serious metabolic diseases. Consequently two new disciplines have developed recently: glycobiology (22) and glycopathology. Glycoconjugates result from the association of a saccharide subunit either with a protein (in glycoproteins), or with a lipid in glycolipids. Among glycoproteins lectins deserve special attention. These are oligomeric glycoproteins present in cellular membranes. Their importance originates from the observation that they undergo drastic modifications in cancer cells. Such molecular modifications can on the one hand favour diffusion of metastasis, and on the other also trigger the onset of immune reactions against neoplastic cells. The concept of biological specificity of glycans is substantiated by various findings: they increase protein solubility, they are essential in keeping peptide chains in a biologically active conformation, glycans control to a large extent membrane permeability and can in this way have a leading role in controlling cellular metabolism, modest chemical modifications make glycoproteins, which are usually weakly antigenic, strongly immunogenic, they also influence the mechanisms of recognition and adhesion of micro-organisms to the cells. The structure of glycans is less known than that of nucleic acids or of polypeptides. Sugar chemistry is extremely complex since it deals with multifunctional compounds with extremely variable reactivity. **Glycoconjugates are well-adapted to study by contrast variation** which can distinguish clearly the role played by the often highly hydrated polysaccharide in this two-component system. It will be vital to study the **dynamics of the water** which also plays a key role in the stabilisation of polysaccharide structures. This may be of particular impact in the **food industry**, e.g. in pasta production. In the biomedical field an other important topic involving saccharides is that of bacterial polysaccharides. Their potential for the preparation of new vaccines was already recognised long time ago. Classical work on capsule polysaccharides has provided the basis for fundamental research on the protein nature of antibodies, and on the transformation processes of bacteria, thus contributing significantly to the development of modern immunology and molecular biology. However only in the late seventies and in the eighties practical applications in the field of vaccines became possible owing both to improvements in non-denaturing purification processes, and also to a better understanding of the mechanisms of immune response. Nowadays they are gaining more importance while the traditional antibiotic therapies are reaching their limits. **Polysaccharide based vaccines** are very well tolerated because polysaccharides do not play any active role in the viral action, they do not have a direct toxic effect, and just prevent the bacteria from being 'eliminated' by the immune system. The route initiated many years ago which is now leading to effective polysaccharide based vaccines is a clear example of the benefits and achievements which may result from a combined effort on basic and applied biochemical research, and provides a valid model for future research efforts in similar fields.

6. Biotechnology, biocompatible materials

6.1 Biosensors

This term is used interchangeably for two different classes of devices (23): those that measure biological macromolecules and those that use biomolecules as part of the sensing mechanisms. The basic conceptual design implies a biological receptor (usually an enzyme for selective catalysis or an antibody for selective binding) coupled to an electronic transducer. Biosensors are particularly attractive : they are small, simple to use, sensitive and highly specific, with a wide range of applications to monitor a variety of processes from those inside the human body, to those in on-line industrial streams. Part of the tremendous potential for applying these technologies lies in the medical field. For instance integrated biosensors capable of measuring substrate concentrations in blood *in situ* could effectively replace conventional techniques which are not only costly, but have also turnaround times exceeding 24 hours. Even more important is that new kinds of measurements will become possible, for instance measurements of substrates which are too unstable for storage. Just to give a concrete example: constructing a device to deliver insulin to diabetics based on blood parameters could be a major achievement in the years to come. To understand the nature of the interface between biomolecules and there substrates neutron reflectometry will an important technique whilst inelastic and quasi-elastic scattering will be of importance in studying the dynamics.

6.2 Bioseparation media (24)

Preparative electrophoresis is today one of the fastest growing bioseparation business. Designers of protein pharmaceutical purification processes have to tackle the goal of improving separation technologies at the preparative (milligram to multigram) and at the pilot (gram to kilogram) level. This can be achieved by enhancing the quality of the separations and therefore reducing the number of processing steps. For this purpose innovative matrices are required together with improved methodologies in order to combine high loading capacities with high resolving power. Problems which are still to some extent to be solved involve thermal effects within the matrices, solute-capillary wall interactions, bubble and clot problems, exploitation of new electrochemical detectors. Biosensors coupled with miniaturised components may in the future enable construction of systems that could separate and analyse substances of clinical significance from body fluids, for example. Small angle scattering is vital to the study of the structure of these matrices. Moreover the higher intensity available from a next generation source could allow one to perform kinetic experiments *in situ*, where DNA fragments or proteins are monitored as they diffuse through a contrast-matched gel. Quasi-elastic scattering will be useful for characterising the microviscosity parameters of the matrix and relating them to the macroscopic mobility of the diffusing molecules.

6.3 Biocatalysts

Organic chemicals are mostly produced by classic synthetic routes but the interest in using biocatalysts is increasing (25). Some unique features of biocatalysts make them particularly attractive : they work under mild conditions (temperature, pH, pressure); they exhibit a high level of regio- and enantio-selectivity and specificity, moreover they raise fewer safety and pollution issues. Biocatalysts have always had their drawbacks (limited stability relatively limited conversion yield and specificity). New technological developments including molecular modelling could significantly extend the range of commercial applications. As an example we may consider that of enzymes. By their nature they work in aqueous environments. This has presented a serious limitation for systems that consist of hydrophobic substrates and/or products. In the past few years it has been demonstrated that enzymes in a hydrophobic environment display substantially different properties both in stability and in substrate specificity; the potential applications of enzymes in non-aqueous environments could be very significant. Neutron scattering could play an important role in determining the structure of proteins in such environments.

6.4 Biomaterials in cosmetics industry

There is a large overlap between drugs and cosmetics: skin ‘rejuvenation’ creams are considered cosmetics even though their labels claim that they alter cell function. With the advance of biotechnology it may become possible to improve appearance by directly altering skin and hair function (26). For example products could be developed that darken skin by stimulating the production of natural pigments. Similarly it might be possible to impart a darker, natural colour to grey hair. Both small angle scattering and quasi-elastic scattering will contribute to the understanding of skin structure and permeability.

6.5 Tissue engineering

Tissue engineering combines the principles and methods of the life sciences with those of engineering to elucidate fundamental understanding of structure-function relationships in normal and diseased tissues, to develop materials and methods to repair damaged or diseased tissues (27). Biomaterials play important roles in this context, for example serving as matrices to guide tissue regeneration, and in implants to support cell transplantation. Protein and polysaccharide-based materials have a major role in this context. Collagen is an important structural protein, often present in fibrillar form. It can be present in solution at warm temperatures and as a gel below ~37° C, and the pore size in the material may influence markedly cell behaviour. Biopolymer gels of polysaccharides are also useful materials in tissue engineering. Hyaluronic acid is an important example. Dilute solutions of this anionic polysaccharide form a viscous solution, which is being explored as a coating on tissue surfaces to minimise damage induced by handling during surgery. The properties of hyaluronic acid may be widely modified by chemical modification For example extensive esterification generates materials that form water-insoluble films. Slow hydrolysis of the ester leads to slow dissolution of the film over time.

Amorphous protein polymers have also been used to produce biologically derived materials. Elastin is a naturally occurring amorphous protein; it is both intra- and inter-molecularly cross-linked, and it has elastomeric properties. By incorporating redox-sensitive species or pH sensitive amino acids into the protein polymer in hydrogel form it is then possible to prepare hydrogels that swell or de-swell in response to changes in the environment of the gel (pH, temperature, chemical and/or electrical potential) thus enabling the material to serve as a thermomechanical or chemomechanical transducer. An other important property for several bioapplications is the ability of a material to resorb over time thus avoiding risks of complications that can be associated with the long term presence in the body of a foreign material. Many of the advances in biomaterials have been key in enabling novel approaches to therapy, and this role will certainly be enhanced in the future. The investigation of the gel structure of all these materials will depend heavily on the sensitivity of neutron scattering.

7. Laboratory support facilities

It is widely acknowledged that major facilities such as neutron or synchrotron X-ray sources must be accompanied by equally sophisticated sample environment equipment if their full potential is to be recognised. Hence major investments in cryogenic, high temperature or high pressure facilities are rightly considered an essential part of such centres. The equivalent investment is imperative for biology but in this case it is the particular complexity and sensitivity of the sample which is the issue. Facilities for on-site preparation and characterisation are absolutely essential. Such a large part of neutron scattering applies relies on deuteration that a new source would appear to be the natural site for an in vivo deuteration laboratory for producing partially or fully deuterated proteins, nucleic acids or polysaccharides. Another major obstacle often encountered is the difficulty of obtaining *selectively deuterated* polymers, lipids, surfactants. This restriction severely limits the current possibilities for studies on complex lipids of biological origin, and also makes it difficult to conduct probing investigations of the aggregates and adsorbed layers formed from non-natural surfactants and polymers; in both cases the restriction necessitates that the required compounds must be synthesized in the laboratory. The chemical syntheses of such molecules are in principle simple but rarely straightforward (particularly if stereoisomerism is important), which means that it is often difficult to obtain significant yields of pure compound even when preparing the normal protonated materials. There is then the added complication that the same synthetic routes may not be appropriate for producing the selectively deuterated forms of the compounds, either because the required deuterated starting materials are not available commercially, or because they are available but prohibitively expensive. Under a variety of circumstances, therefore, it is necessary to devise novel schemes of synthesis for the compounds of interest, combining guaranteed high yield and purity with cost-effectiveness and versatility. In the establishment of the proposed ESS, therefore, it would be highly desirable to set up a 'service' facility specializing in the chemical synthesis of *deuterated* lipids, surfactants and polymers. The success in development of such a facility would have an immediate bearing on the investigations of surfactant monolayers and bilayers undertaken using contrast variation in conjunction with neutron specular reflection (and also those employing surface optical spectroscopy and proton/deuterium NMR).

8. Conclusions

Neutron scattering has played an significant role over the last 20 years in the understanding of the structure and dynamics and hence the functioning of biological macromolecules. Its limitations have been due to a lack of facilities and inadequate flux. In particular the wide availability of equipment to try new exciting, at times speculative, experiments has reduced the impact that neutron scattering might have had on biological problems. Molecular biology requires not only test experiments but also systematic studies over a large range of similar molecules. For much of biology it is the small differences between closely related systems which is of importance. The availability of a new, more intense source is vital in the coming decade if the promises of the past are to come to fruition. Molecular cell biology will clearly be one of the major growth areas in the coming decades and a battery of methods including neutron scattering will be required to understand the functioning of the cell at the molecular level. This understanding is vital in our ability to control disease, improve materials or preserve our natural environment for future generations.

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Neutron scattering in the Earth and environmental sciences

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1. Introduction

The use of neutron scattering by the Earth Sciences community has only a short history, but it is now clear is that the potential of neutron scattering methods for the solution of Earth Sciences problems, including many environmental problems, is enormous. Many of the problems encountered in Earth Sciences have, until recently, simply been too complicated for earlier neutron sources and instrumentation. For example, the crystal structures of many important and interesting minerals have been too complicated for routine analysis by conventional medium-resolution neutron powder diffractometers. Only with the advent of the high resolution powder diffractometer at ISIS has it become possible to study the crystal structures of minerals as a function of temperature with sufficient accuracy (both in terms of resolution and counting statistics) to be really useful. There are many problems in the Earth and environmental sciences for which the present sources and instrumentation are still inadequate. Examples include measurements of the structural changes in minerals at high pressures and high temperatures, locations of light elements in complex structures, and studies of the dynamical properties (neutron spectroscopy). This information will enable the modelling of fundamental processes in the Earth, ranging from large scale phenomena such as deep-focus earthquakes and volcanic activity, through to the transport of pollutants in the Earth's crust.

However, recent experience with the new state-of-the-art sources such as ISIS has shown that the outlook for applications of neutron scattering in Earth Sciences is extremely promising. There are many features of neutron scattering that find ready application to the study of natural materials. One clear example is that many natural materials contain hydrogen. Hydrogen is virtually invisible to X-rays, but it will scatter neutrons reasonably strongly. Moreover, the fact that neutrons can be scattered both coherently and incoherently means that they can probe both long-range and short-range order. Hydrogen is central to so many problems in geology and the environment that there are likely to be countless exciting applications of neutron scattering to hydrogenous minerals, and to minerals containing other light elements, as the facilities for collecting high-quality data are developed.

The ESS will enable us to tackle many new problems related to geological and environmental processes. The ability to construct sample environments that will reproduce the temperature and pressure conditions of the deep Earth will allow us to perform many *in situ* studies of mineral behaviour, which will greatly increase our understanding of the behaviour of the constituent materials of the Earth. The ability to probe the structures and motions of relatively-complicated minerals will provide many new insights and allow us to understand the complex interactions that govern the behaviour of Earth materials in their natural environment. We anticipate being able to study both solids and fluids, as well as the interfaces between these two phases, for the first time by neutron techniques.

2. The value of neutron scattering to Earth and environmental sciences

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 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, whether as a major constituent as in minerals such as Mg(OH)2, or as a minor or trace element, such as molecular water in framework silicates or as hydroxyl defects in silicates, it is essential that there be 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 not possible 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 the complicated crystal structures of many minerals, it gives a significant increase in the amount of information available in a diffraction pattern. Second, to obtain accurate information about thermal motion a wide range of scattering vectors 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. These reasons are relevant to crystalline Bragg-diffraction. However, in crystals with considerable disorder, or in amorphous materials or liquids, there is a lot of information about short-range order contained within the total scattering, S(Q). The Fourier transform of S(Q) provides information about the pair distribution function g(r). The resolution on g(r) will depend directly on the range of the scattering vector in the data. Thus it is possible to obtain better data for g(r) from neutron scattering than from X-ray scattering alone (although it is often profitable to have data from both techniques).
- The fact that the neutron 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 two reasons. First, it allows studies of materials containing 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, including oxygen. Neutron scattering is frequently used to overcome this problem. Second, many problems in geological materials involve site-ordering of isoelectronic cations, 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 cations.
- Because neutrons have a magnetic dipole moment they can be scattered by magnetic ions, which enables 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 diffuse or critical scattering from the surface can give results that

are significantly different to those obtained from in the bulk. With the new availability of high energy X-rays from synchrotron sources this particular advantage of neutrons is not as significant as it once was, although with high energy X-rays it is difficult to obtain the same resolution as can be achieved by neutron scattering, and which is essential for spectroscopic studies. Very often high-energy X-rays also pose severe problems of heat load on the sample.

- 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. Also, in measurements of critical scattering, where the important quantity is the scattering at any wave vector integrated over all energies, the higher energies of X-ray beams can be an advantage over neutrons unless there is a concern about the effects of surface scattering.

3. Science that can be done only with the ESS

3.1 Diffraction studies

Many properties of minerals can be addressed by studying the response of their crystal structures to changes in temperature or pressure. With present sources it is possible to study the temperature evolution of relatively complicated minerals, and the pressure evolution of relatively simple ones. What we need to aim at is to study the evolution of complex minerals, for these are the constituents of the Earth, under conditions of high temperatures and pressures simultaneously. With existing sources there are two (related) obstacles to such studies. First, the small volumes required for high-pressure work means that long counting times are required and signal-to-noise ratios are not high. Second, existing sources are not powerful enough to allow for measurements at many pressure-temperature points in a single experiment, since the data acquisition times for single scans are too long. With the ESS and a powder diffractometer with good resolution to allow measurements of complex minerals, and a wide detector coverage to increase the intensity of the measured signals, measurements over regions of pressure-temperature space that are of geological interest will become routine. Indeed, the ESS will be extremely good for high-pressure studies, because, as with any spallation source, neutrons are measured at a fixed scattering angle, which facilitates the building of high-pressure apparatus.

Other perspectives opened by the ESS include, for example, the study of phase transitions, and the study of equilibrium and kinetic behaviour of order/disorder processes under geological conditions, kinetics of reconstructive phase transitions, and *in situ* equilibrium phase diagrams. A big new area of work will be the study of hydrous minerals at high temperatures and high pressures. These materials are essential in understanding the circulation of water through the Earth's crust and into the deep interior of the Earth, and their effects on potentially catastrophic Earth processes. At the moment we cannot say what happens to water in minerals as they are taken to the conditions found in the Earth's Mantle. Neutrons are essential for this problem since hydrogen is almost invisible to X-rays, and the flux offered by the ESS will be required before neutrons can have the required impact. Some of the hydrous minerals that may be found at considerable depth inside the Earth are dense hydrated silicates that do not naturally occur on the Earth's surface and can only be produced in quantities that are too small for present-day neutron sources. The ESS will enable detailed crystallographic studies of these materials for the first time. A related topic is that of water in nominally anhydrous phases. It is believed that vast quantities of water can be stored as trace amounts in this form, but it is not yet possible to undertake crystallographic studies of these minerals with present neutron sources. The ESS will provide the possibility to collect data of sufficient quality to allow trace amounts of water to be seen in the final crystal structure extracted from the diffraction patterns: this cannot be achieved with present-day facilities.

It should also be noted that neutron diffraction gives the only reliable means to separate purely vibrational effects from the charge density distribution, since these effects are completely overlapping in X-ray diffraction. Furthermore, the anharmonic vibrational behaviour of atoms in crystal structures can only be unambiguously measured by neutron diffraction, and this contribution may be crucial for understanding the behaviour of crystal structures at high temperatures.

3.2 Strain and texture studies

The ESS will open up the study of rock as well as mineral processes. Thus, for example, observations of the geometry and organisation of crack networks in both naturally and artificially deformed rocks show clearly that the strain associated with brittle deformation is not homogeneously distributed throughout the rock, but becomes progressively localised into narrow zones of intense deformation. Yet, whilst the nucleation and propagation of stress-induced cracking in rocks has been studied thoroughly in recent years, the fundamental process of crack linkage and strain localisation that precedes brittle failure remains poorly understood. One of the primary reasons for this gap in our knowledge is the difficulty of experimental observation and measurement of heterogeneous strain distributions and strain localisation in rock samples during deformation. Conventionally, strain in rock mechanics tests has been measured using either displacement transducers mounted across the sample, or by means of strain gauges bonded to the sample surface. Both techniques measure only the average strain across their length. This is an important restriction when the strain may be localised to only a few per-cent of the sample volume, as is often the case for compressive shear faulting. What is required is a technique that can measure the strain distribution within the interior of the sample volume, specifically away from any of the free surfaces. Because of the penetrating nature of the radiation, neutron diffraction is the ideal, and perhaps the only technique available. Pilot tomographic studies have mapped the macro-strain by means of lattice parameter measurements from volumes of deforming rock, but the enhanced intensity of the ESS will enable high resolution studies of in situ deformation to be carried out for the first time.

3.3 Total scattering measurements

Whereas the Bragg peaks contain information about the average structure, the complete diffraction pattern including the diffuse scattering contains information about the short-range order as well. In many cases the short-range order may differ significantly from the average structure. For example, in high-temperature phases of many silicates there is considerable disorder in the orientations of SiO_4 tetrahedra. Short-range order in crystalline materials can therefore be studied using neutron scattering measurements of the whole diffraction pattern. Pulsed sources are particularly good for this work since they allow data to be collected up to high values of Q, essential if good resolution is required for bond lengths. There have been many developments in the analysis of total scattering measurements, which will extract information about three-body correlations and correlations over larger distances. The problem with these methods is that they require very accurate data, since even very small errors in the data can throw up quite spurious results. The accuracy in the data can be improved by two orders of magnitude in the count rate, a large part of which will be achieved simply with the projected flux of the ESS. But to develop what will become a common theme, there will be considerable interest in obtaining information about short-range order over a range of temperatures and pressures. At the moment no total scattering measurements are performed as a function of pressure, because the samples are so small and the corrections to the data will not be sufficiently accurate to allow for good analysis. These experiments are out of the range of present sources, but certainly will be viable with the ESS and a suitably designed instrument.

Traditionally, most total scattering experiments are performed on fluids. For Earth Sciences there are two important types of fluids. One type consists of silicate melts. These are complicated fluids, containing several major atomic components (silicon, oxygen and metallic cations) and many minor components. Actually, the minor components can have a dramatic effect on the behaviour of the silicate melt as it is thrust through the Earth's outer layers. As a result there will be considerable interest in studying the behaviour of silicate melts with their complicated chemical composition under geological conditions, and in particular to study the local coordination about the trace constituents. These studies will be extremely difficult, because a large number of measurements will be required if isotopic substitutions are to be used, because the use of high temperatures and pressures will require the use of small samples, and because the complexity will require data of very high quality. The second type of fluid will be water with trace quantities of dissolved constituents. In order to be able to measure the structure associated with trace elements data of extremely high quality will be required. The demands of these studies can only be faced with the ESS.

3.4 Vibrational properties

Atoms move in solids on a wide range of time scales, from the time scales associated with phonon vibrations up to slow diffusion. All time scales can be important for Earth Sciences, but for a number of reasons vibrational spectroscopy with neutrons has not yet become a routine tool in the Earth Sciences. We again encounter the problem of obtaining vibrational spectra as functions of temperature and pressure, and we will again need the beam flux of the ESS to study small samples with high accuracy, and to perform many measurements under different conditions of pressure and temperature in a reasonable time.

First we consider measurements of phonon frequencies. Single-crystal measurements have usually been performed on relatively simple materials to obtain phonon dispersion curves, or to measure phonon frequencies as a function of temperature. Only limited information has so far been obtained on measurements as a function of pressure. The equation of state of Earth materials is determined in part by the pressure and temperature dependence of phonon frequencies, since the vibrational enthalpy and entropy are important components of the free energy. These measurements are essential for modelling the properties of the inner Earth. Measurements of phonon dispersion curves for complex silicates can be extremely difficult because of the large number of phonon branches. To be able to undertake these measurements on the ESS we will require an instrument that allows data to be collected for a wide range of scattering vectors with good energy resolution. There will be considerable advantages in using instrumentation that allows many spectra to be collected simultaneously. New instruments at ISIS allow this possibility, but will require the flux of the ESS to overcome problems associated with poor counting statistics.

There has been recent interest in performing measurements of the phonon density of states, particularly with materials containing hydrogen where there is large incoherent scattering cross section. These measurements can provide information about hydrogen bonding, for example. Studies of this sort are ideally suited to spallation sources such as ISIS and the ESS, where good resolution can be coupled with measurements to high and low energies. Measurements performed over a range of temperature can show clear evidence for changes in bonding. These measurements are not sufficiently rapid at the moment to allow for non-equilibrium studies, but with sufficient beam flux and suitably designed instrumentation it should be possible to measure the phonon density of states during kinetically-controlled changes in the crystal structure, for example through a phase transition or during dehydration. It should be noted that dehydration is one of the most important industrial and geological processes involving hydrogen, and the use of neutron spectroscopy in the study of the kinetics of dehydration is not possible with present neutron fluxes. Whilst fast reaction kinetics (processes with time scales of order 100 s or less) are likely to remain the domain of synchrotron X-rays, there are a number of transformation processes with time scales of the order of minutes or slower that will fully take advantage of neutron studies.

Incoherent neutron scattering can also be used to study the slow motions of hydrogen in minerals, although this technique has only been used so far in preliminary studies. There are two types of study, both of which require very high energy resolution down to low energies. The first is the study of slow rotational motions of water molecules. The problems with these studies at the present time are that the quasielastic signal is weak compared to the elastic signal, and of very low energy width. Moreover, the O-H bond is relatively short (just less than 0.1 nm), leading to a very small radius of gyration, which requires relatively large scattering vectors to adequately resolve the real-space motions (actually the problem can be compounded by having only some molecules in motion at the same time, which leads to an even shorter average radius of gyration and the need for even larger scattering vectors). At present sources it is not possible to satisfy both high energy resolution and large scattering vector, which effectively limits the use of incoherent neutron scattering to study reorientational dynamics of water molecules and hydroxyl groups in minerals. A problem that has not really been tackled is that of diffusion of hydrogen in minerals, whether as water molecules, hydroxyl ions, or free protons. It is foreseen that signals will be small and of very low energy, requiring good energy resolution. Since the motion of hydrogen in minerals is as important as the chemical bonding, studies of diffusion of hydrogen will become extremely important for the understanding of the chemical processes in the Earth and environmental sciences.

3.5 Mesoscopic structures

Very little neutron scattering work has yet been performed on mesoscopic structures in minerals, such as the textures that arise as a result of phase transitions and phase separation processes, and the structures of mineral surfaces. Indeed, surface neutron spectroscopy and reflectometry is still a relatively new technique in chemistry and physics. Many of the important geological and environmental processes obviously occur at mineral surfaces, whether surfaces that are open to the atmosphere but contaminated by adsorbed molecules and ions, or in contact with a fluid. In the coming years the studies of mineral surfaces by neutron scattering will become very important. We envisage studies of the interactions of organic molecules (e.g. PCB's) on surfaces, whether as pollutants or as deliberate inhibitors (e.g. to prevent crystal growth in scaling problems). The adsorption of heavy metal ions on clay surfaces is an obvious environmental concern that will be studied by neutrons. The interface of a fluid and solid will lead to modifications in the fluid structure, and it will only be possible to study this with a bulk probe such as neutron scattering.

Small-angle neutron scattering has been used only occasionally in studies of growth and phase-separation textures in minerals (e.g. pore structures). We envisage that this will be an area of investigation that will grow in the near future, but the complicated textures found in minerals, and the relatively low contrast of many of the important processes, will call for enhanced measurement techniques that will be possible only with the ESS. In common with other problems discussed in this document the essential problems will necessitate in situ studies, at high pressures and temperatures, which cannot be tackled with present neutron sources.

4. Summary

A number of common themes are found in the discussion of different applications of neutron scattering to problems in Earth Sciences.

First is the need to be able to perform measurements over a wide range of conditions of pressure and temperature, in contrast to many investigations where one of these conditions is held fixed. The two-dimensional coverage of pressure-temperature conditions demands a fast throughput of measurements, which is not available with present sources nor will be even with upgraded instrumentation. It will be essential for an extremely large increase in usable beam flux coupled with maximum detector coverage. With the ESS we will be able to gain almost two orders of magnitude in usable beam flux over ISIS in its present configuration. Only then will we be able to perform the exciting experimental programmes outlined above.

The second common theme is that with high pressures or high spatial resolution tomographic studies it is necessary to work with small volumes. Such work is still very much in its development stages. At the present time the necessarily-small sample volumes effectively limit the complexity of the problem to be studied, yet many minerals that are of significance in the Earth Sciences are rather more complicated. The technical difficulties will require the beam flux of the ESS to allow these measurements to be routine for Earth Sciences applications.

The third common theme is that many processes of interest are controlled by trace constituents. These could be studied using neutrons, but the necessary accuracy required means that a source of the power of the ESS is essential.

The fourth common theme is the importance of the use of neutrons to study hydrogen in Earth materials. Many properties of minerals and rocks, from the microscopic level to the real geological level, are determined by the behaviour of hydrogen and water. Neutron scattering is a unique tool for the study of hydrogen, operating in energy and momentum windows that are relevant for the structural and dynamic properties of hydrogen in minerals which are not accessible to conventional spectroscopic tools, and these are helped by the specially high incoherent cross section for scattering of neutrons from hydrogen.The other three common themes will be particularly focused on the behaviour of hydrogen in minerals, whether as a major or minor constituent.

With a significantly more powerful new source of neutrons, there will be a major expansion of the use of neutron scattering in Earth Sciences, as many new programmes of work will be tackled for the first time, continuing the rapid growth that is presently being seen at neutron scattering centres throughout the world.

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1. Introduction

The engineering problems which can be tackled by a next-generation pulsed neutron spallation source are considerable and go well beyond what is currently achievable. Only four pulsed instruments for engineering measurements currently exist world-wide, and the potential for improvements in flux and instrumental efficiency is great. One of the major differences which distinguish engineering applications of neutrons from more fundamental studies is the need to study complex systems, (e.g. oils, welds, engines and complex components) often experiencing harsh environments (chemical, mechanical, thermal or processing). Because of their high penetrating power (centimetres of steel), neutrons are particularly well suited to non-destructive studies of real materials and components in their as-fabricated or in-service condition. In most cases, an experiment centres around a component or a process defined by the end use, rather than on an idealised specimen geometry designed to conform to the constraints of the neutron spectrometer, but this puts stringent demands on the design of the spectrometer, the sample environment and on data analysis.

It cannot be over stated how important increases in flux and throughput will be to the engineering community. Currently many experiments take over a week to complete and are thus simply too expensive. If the engineering community are catered for in terms of instrument design, the European Spallation Source will greatly increase the range of experiments which will become commercially or practically feasible.

Areas in which very significant advances may be expected are:

- **in situ *studies*** e.g. fatigue behaviour, thermal cycling stresses, stresses in rotating machinery (e.g. aeroengine components), oxidation of surfaces – often these experiments require complex environments and fast data acquisition times
- ***real time studies*** e.g. dynamics of aggregation and coalescence of aerosols, suspensions, paints and petrochemicals, ageing of alloys, and the design of stress relief procedures – currently data acquisition times are too slow
- ***process monitoring***, e.g. powder processing, sintering, welding, cutting, wear, hardening, carburizing – currently it is difficult to simulate process conditions within the constraints of a diffractometer
- ***3D maps of stresses and textures*** within engineering components – currently such experiments take too long and are thus too expensive
- ***neutron tomography*** to produce 3D images of, for example, the behaviour of lubricants inside working engines, isotope specific radiography – improvements in detectors and optics as well as improved flux are required.

The last area is a good example of the potential for exploitation of neutron methods for engineering ends. In medical diagnostics, 3D nuclear magnetic resonance imaging has recently come of age, largely through improved data analysis and detector design. As a result, it is now commonplace to see 3D physiological representations produced by NMR. Neutrons, given their exceptional penetrating power, clearly have the potential for a parallel development in the engineering world, but the opportunity has yet to be realised. The development of 3D high resolution Computed Neutron Tomography (CNT) is reliant upon the provision of high intensity parallel beams, high spatial definition detectors and complex data analysis procedures, but in principle it is possible to carry out very applied studies, such as monitoring the performance and temperature of engine oil within an operating car engine.

For all the opportunities listed above, three important issues need to be answered first, namely those of current slow turn arounds, high experimental costs and access to the expertise. It is believed that these can only be met through the development of a radically new kind of engineering centre.

The realisation of the ESS will give Europe the opportunity of establishing the world's first Engineering Research, Development and Test Centre for the cost-effective utilisation of neutron beams. This flagship facility will house the engineering and neutron facilities as well as provide the technical expertise for Europe's engineers and materials' developers to measure stresses, observe microstructures and monitor behaviour during processing or in-service.

2. Background to the basic techniques

2.1 Strain

Nearly all engineering components experience mechanical or thermal stressing in-service. In the majority of cases these stresses, when superimposed upon any process induced residual stresses, are either not life limiting or give rise to a failure rate which is acceptable, both from a financial and safety viewpoint. However, in an increasingly significant number of cases, the drive for improved performance means that materials utilisation and design must become less conservative. In addition, in industries such as aerospace and nuclear power component failure is simply unacceptable. In these cases finite element modelling approaches are pivotal in the move towards more intelligent component development. At present it is very difficult to test the reliability of these models against direct measurements of stress deep within components. This is especially true in cases such as welding for which the process conditions are very complex, difficult to measure, and for which reliable constitutive equations to establish. Neutron diffraction provides a unique means of establishing the state of stress deep within complex components, and as such is a powerful tool for refining finite element models, optimising processing technologies for improved production and for highlighting stress-related problems when they arise.

The principle of strain measurement is simple, Bragg's equation is used to determine changes in lattice strain via shifts in the diffraction peak positions. At a spallation source rather than scan q, the time-of-flight (TOF) of the arriving neutrons is recorded which can be related directly to the incident wavelength. The faster more energetic (short wavelength) neutrons arrive first, the slower (longer wavelength) neutrons later, producing a spectrum containing many hkl peaks as a function of the time of flight. The shift in the time of flight (Δt) of the peaks is then simply related to the lattice strain (ε_{hkl}):

$$\lambda = 2d \sin\theta \quad \text{where} \lambda \text{ is proportional to t giving:} \quad \varepsilon_{hkl} = \Delta t_{hkl} / t_{hkl}$$

In other words, the crystalline grains are used as internal strain gauges. While it is possible to determine the state of strain within a single grain; in practice it is more common for the beam to be defined by slits or collimators to give a gauge volume of 1 mm^3 or greater, and thus the strain measured is an average taken over all similarly oriented grains within the gauge volume. The state of strain can then be evaluated either as a function of position within the component, by scanning the sample through the sampling volume, and/or as a function of the external conditions (e.g. temperature or applied loading conditions). Spallation sources have the advantage over constant flux sources that they provide many peaks simultaneously, increasing the engineering confidence in the results over those made on the basis of a single peak. Complementary to conventional diffraction, use of Bragg edge studies in transmission[1] may lead to very fast data acquisition times (~10msec) and high lateral spatial resolution.

Europe has been in the vanguard of the development of neutron diffraction to measure strain and hence stress distributions within engineering components. This work has centred on improving the reliability of interpretation of the technique, refinement of the measurement procedures, and has lead to the commercial application of the technique. Naturally, this work began on neutron diffractometers optimised for basic physics and chemistry research, and great advances have been made on such instruments at reactor sources, most notably in Canada and Denmark. Recently, a BRITE EuRam funded programme has enabled the building of a spallation source instrument (ENGIN) on a test beamline at ISIS at the Rutherford Appleton Laboratory (RAL), which has proven that spallation sources can also be used to make strain measurements for industry. These programmes have demonstrated the opportunities for applied research, development of the technique, and its value as a trouble shooting tool for the European engineering industry. However, they have also highlighted key hurdles inhibiting greater application of the technique. The major problems centre upon the cost of making measurements, access to the instruments and the availability of expertise in the technique. In this context it is important to bear in mind that industry is usually only prepared to spend a small fraction of the financial cost of a problem in finding its solution. At the present time this means that neutron strain measurement is only generally accessible to the large aeroengine, aerospace and power generation companies with major safety critical problems. It is therefore crucial to lower the cost per measurement and to reduce the expertise threshold, for the full benefit of neutron strain measurement to be fulfilled for Europe's engineering industry as a whole.

2.2 Texture

Few materials comprise perfectly randomly oriented grains. In most cases the tendency for grains to be preferentially oriented (textured) in specific directions is not particularly important, but in many others it can be of crucial importance. Important examples range from uneven drawing (earring) during the deep drawing of beverage cans, to the optimising of the superconducting properties of high T_c superconducting ceramics.

The variation of diffraction peak intensity as the sample is rotated allows the degree of texturing to be quantified quickly and non-destructively. The high neutron penetration reduces the problem of absorption corrections and allows in situ experiments to be carried out. In this respect, one area in which neutrons have made a significant contribution is in the real time monitoring of recrystallisation kinetics, where the evolution of texture with time is monitored continuously at elevated temperature. In future it will be possible to go a step further to produce 3D maps showing the variation in texture in engineering components, produced for example by forging or rolling.

2.3 Microstructure

Few engineering materials are truly homogeneous. Small angle scattering can provide a range of information important to materials designers as well as process engineers, from 1nm to 1µm. As above, the basic governing equation is Bragg's equation, but in this case the scattering is from objects (e.g. precipitates, voids, colloidal particles) with a representative structural dimension d (diameter, length, etc.), which is very much larger than a lattice spacing, and hence is recorded as low angle scattering. The accessible structural range, d_{min} to d_{max}, is dependent on the Q-range[2] of the instrument and ranges from precipitates in metallic alloys, defects in semi-conductors, to particle size and dispersity in colloids and aerosols.

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[1] in this technique, sharp edges in the transmitted intensity are used to deduce changes in lattice parameter; the high transmitted intensity means that measurements times can be very fast (<<1sec).

[2] Q is equal to $2\pi/d$ ($=4\pi\sin\theta/\lambda$), where d is the structural length that is measured; because spallation sources provide a large range of wavelengths (λ) they naturally have a large Q-range; constant flux sources scan θ and need to use a number of separate λ to achieve the same range.

2.4 Surfaces and layers

Neutron reflectometry[3] has exploded onto the scene for the study of surfaces, thin coatings and multilayers. Whereas the Brewster angles for internal reflection of electromagnetic waves can be large (for example, preventing a goldfish seeing out of his goldfish bowl!) for neutrons the angles are very small. But the technique offers very high surface specificity. Most of the applications to date lie within other scientific themes (biology, polymer science, solid state physics and magnetism, etc.), but it has already proven has proven invaluable to chemical engineers for the study of surfactant behaviour, providing information from the 1-100nm level. The technique has yet to be fully exploited for the study of protective layers and coatings and other engineering applications.

2.5 Radiology

Neutron radiology is a general term recently introduced by ASTM to describe the science and applications of imaging and inspecting with neutrons. It encompasses various methods such as neutron gaging, neutron radiography and radioscopy, computed neutron tomography, scanning PGAA, NCA, NRA and neutron activation and neutron capture- autoradiographic techniques.

At present most of the work in NR can be classified as static or quasi-static, i.e. inspections of stationary objects and studies of time independent processes or processes which are slow in comparison with the neutron exposure time. However, in the last decade interest in the applications of dynamic "real time" neutron radiological methods (RTNR i.e. neutron radioscopy and cineradiography, flash or pulsed neutron radiography-PNR, neutron stroboscopy) has increased. RTNR techniques can been applied to various problems in diverse fields:

- tribology (wear) and lubrication;
- studies of two-phase flow, phase transitions and dynamics of liquids;
- studies of fast chemical processes, (e.g. in pyrotechnics and aerospace technology, in the tobacco industry for the improvement of cigarette filters);
- studies of castings, solidification and segregation processes in metallurgy and materials science;
- studies of transport phenomena of water and hydrogenous liquids in porous materials, such as ceramics, building materials, sand, soil and rocks.

Two newer radiology techniques which are also seeing increasing importance are prompt-gamma activation analysis (PGAA) and neutron depth profiling (NDP).

PGAA: This method is particularly useful for non-destructively determining elements which absorb neutrons, but do not produce radioactive products. The PGAA method analyses the entire sample, including any substrate or container by which it is supported in the beam. The values of the nuclear parameters and the abundances of the elements in common materials are such that PGAA finds its greatest applicability in the determination of non-metals that form the major and minor elements of geological and biological materials (H, C, N, Si, P, S), or trace elements with high thermal capture cross sections (B, Cd, Gd) that are not readily determinable by other techniques.

NDP: The development of the neutron depth profiling technique has been motivated by the importance of light elements in optical, polymer, metal alloy and especially micro-electronic materials. Boron is widely used as a p-type dopant in semiconductor device fabrication and

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[3] neutron reflectometery involves the reflection of neutrons at very low angles from external or internal surfaces; it gives information about the refractive index, from which it is possible to deduce the structure of the surface (<1000Å).

in the insulating passivation barriers applied either as an organometallic or a vapour phase deposition of glass. NDP has both good sensitivity for boron and good spatial resolution to a depth of a few micrometers. It is used both as a stand alone technique and in a complementary role with a variety of other analytical methods. Recently NDP has been used to certify the concentration and confirm the profile of boron in silicon for a NITS Standard Reference Material primarily for the use of secondary ion mass spectroscopy (SIMS) calibration.

3. The Engineering Research, Development and Test Centre

While existing neutron instruments have been designed specifically to meet the needs of physicists and chemists, engineers have not been so well catered for. This centre will be the first at a neutron source containing instruments designed to meet their needs from the start. There are essentially three barriers to the use of neutron beams for solving engineering problems:

- expertise
- access
- cost effectiveness

The instruments and the facilities that the Centre will provide will revolutionise engineering measurements, bringing cost-effective measurements to a much wider range of industries for the first time. In this context it is important to remember that the geometry of the component or of the manufacturing process to be studied is determined by engineering constraints and the spectrometers must be sufficiently flexible to reflect this.

The **Centre** will be sufficiently spacious to allow the mounting of large engineering components or systems upon the instrument and to allow in-service observation. Easy access to the instruments is essential and sufficient space will be provided to allow for complex ancillary equipment or services without interfering with other experiments. While it may not be possible to run a jet engine on site - measurements on a car-sized engine should be practical! Direct access will be possible from outside to aid the introduction of equipment and for the provision of services. Two metres of space will be available below the beam for the insertion of large components and translation stages. In view of current interest in studying active samples, the provision of shielded zones may also be necessary.

Expertise will be provided in the form of an Engineering Liaison Section aimed at advising companies of the potential of the technique, designing experiments or trials, helping to carry out and analyse the experiments. This is essential if engineers are to be able to use this resource cost-effectively and without significant expertise in the area. At the moment there exists a barrier in that neutron facilities don’t function easily in service mode; local scientists are in place to advice in the carrying out of experiments, rather than to provide a measuring service. In this respect, it is probably important to follow the lead in the X-ray measurement field where companies (e.g. Lambda in the US) will undertake measurements for a fee providing a service to industry.

Access will be achieved by a balanced programme between scheduled peer reviewed research programmes and industrially resourced, commercially sensitive, contracts. The peer review process will have a 3-6 month turn-around, but commercial access will be on a much faster basis. This will enable measurements to be made rapidly, reliably and, if necessary, in a proprietary manner using standardised methods of measurement and interpretation.

Cost-effectiveness will be attained by a dramatic increase in the rate of data collection hence reducing the amount of time necessary to undertake an engineering experiment. This will be achieved partly through increased flux at the specimen (x30), but also through greater neutron collection efficiency and instrument optimisation. As a result measurement times will reduce to minutes rather than hours. The present beam time cost of around £5000 per day is simply too great for solving all but the most expensive (and thus usually safety critical) problems. Around 15 measurements can be made per day; a cost which can be compared with hole drilling, which provides shallow depth measurements at around £50-100 per hole. Increases in measurement efficiency of around 30 times would bring the cost down to around £20 per measurement, opening up the technique to a very much wider engineering community for the first time.

Because the centre would be a permanent facility run by a dedicated team, fast turn arounds would be possible. In addition, digital component definition by laser on an off-line simulator will reduce set-up times and allow automatic control of the scanning processes.

3.1 Instruments within the Engineering Centre

Strain instrument: Measurements of strain will be possible to 0.1mm linear resolution, although 1-0.5mm will be more common, accuracy will be 50 microstrain. Great attention will be focused on the monitoring of performance under in-service conditions: the high penetrative power of neutrons allows the investigation of individual components within assemblies or under severe conditions of temperature or atmosphere. The instrument will be very much easier to use than existing diffractometers, with the option of automatic peak analysis, specimen scanning and rotation, and stress tensor calculation. At the present time, the scientist must ensure that awkwardly shaped components are manoeuvred so as not to strike the detectors or collimators. In the future, prior digital component definition off line will open up the opportunity for intelligent component manipulation by computer, drastically reducing the skill level required for operation of the spectrometer. This instrument will also be able to extract basic texture information at the same time as the strain measurements are made. This is very important because strong textures can affect interpretation of the strain results as well as influence component behaviour. Resolution will be intermediate, but at very high intensity.

A range of focusing collimators of the type developed for ISIS may be used to define the sampling volume at a distance (~150mm) without the need for defining slits in close proximity to the specimen. Strain resolution needs to be $50\mu\varepsilon$ using a 15m flight path for high intensity. Recent advances in multi-layered super-mirrors mean that it is now possible to build tapered guides which will concentrate the incident beam onto a small region of the sample. Given this, it is anticipated that the flux over a 1mm cross-section will be 30 times that already achieved at ENGIN, this taken together with an increase in detector coverage will lead to gains of around 100 dramatically increasing the range of studies which will be economically feasible.

Texture instrument: Two texture facilities are required; one will be an dedicated instrument capable of measuring textures quickly and accurately, both for standard experiments and for dynamic studies, the other facility would run on the strain spectrometer allowing simultaneous measurement of texture and strain. Both instruments would use whole diffraction profiles measured at differently positioned detectors, rather than rely upon the repeated rotation of the specimen using a fixed detector measuring a single diffraction peak. This would also allow the construction of texture maps in much the same way as strain maps are produced, say within forged or other deformation processed components.

SANS instrument: From a resolution viewpoint, small angle scattering instruments are well optimised nowadays, but a weak point is represented by 'detectors'. They should be larger (up to 1m diameter) in order to collect data in a wider Q range. Pulsed sources are naturally suited to extended Q studies. In a spallation source instrument operating with neutron wavelengths between 2 and 10 Å, metallurgical studies are always a problem since more than 50% of the neutrons (those with short wavelengths) cannot be used because of double Bragg scattering; for this reason a cold source with the maximum of the flux centred around 5 or 6 Å is recommended. With the experience made on LOQ at ISIS, the new SANS instrument should have the possibility of moving the detector away from the sample. If possible the instrument should have no window in the beam path; this implies that the sample chamber is in vacuum and two valves have to be installed between the sample chamber and the detector and the collimation case. Such a feature reduces drastically the background and allows the measurements of very weak scatterers such as samples with transmissions of about 99%.

From an engineering viewpoint it is preferable to have one SANS spectrometer on each of the low and high repetition rate targets, giving one with a shorter path length (up to 6m), but equipped with a larger detector in order to collect neutrons at higher Q values (up to 0.6-0.7Å^{-1}) and one with higher resolution with a maximum sample-to-detector distance up to 20m. In addition to the ancillary equipment producing electric and magnetic fields of variable intensity; we believe that a low temperature cryostat and high temperature furnace have also to be considered. Naturally it is important to build the instruments in an uniform way (where possible) in order to facilitate use of the same ancillary equipment on all instruments. The SANS instruments need not necessarily lie within the Engineering Test Centre.

Reflectometry instrument: While there are many important engineering problems which require the use of reflectometry it is felt that the general reflectometry instruments will be suitable.

Radiology: The majority of the reported work in Real Time Neutron Radiology has been carried using stationary neutron (thermal, cold) beams and employing video-real time neutron imaging technology with a time frame resolution typically between 1/20 to 1/30 of a second. For very fast time dependent examinations or studies of fast phenomena the time resolution of conventional RTNR techniques is not sufficient and strong pulsed neutron sources, in combination with more sophisticated stroboscopic neutron imaging techniques are required.

It is recommended that the following methods using thermal, cold and epithermal neutron beams should be implemented at the ESS facility, although for logistical reasons not all would lie within the Engineering Research, Development & Test Centre:
1. Static neutron radiography;
2. Real time and pulsed, stroboscopic imaging techniques;
3. High resolution Computed Neutron Tomography;
4. Scanning TOF neutron transmission measurements using epithermal neutron beams;
5. SANS radiography;
6. Scanning methods of chemical analysis: PGAA, NCA and NRA.

For the experiments and routine commercial applications 2 - 4 neutron beams are needed fitted with suitable collimators, nuclear shielding, detectors (neutron imaging, gamma spectroscopy) and object handling equipment. Two of the beams should be installed at the storage moderator and two at the "leakage, decoupled" moderator. The basic characteristics (e.g. L/D ratio and maximum available time averaged and peak neutron flux at the image plane, useful neutron beam diameter at the image plane, maximum dimensions of the object to be inspected of the ESS NR facilities should be designed to extend the existing relevant state-of-the-art NR facilities at the powerful research reactors such as ORPHEE at Saclay, HFR and LFR at JRC in Petten and the spallation sources in Europe (SINQ) & the US (IPNS-1).

4. The engineering case for the future

As discussed in section 2, the development of a new, more intense neutron source will enable many engineering problems to be tackled that are, at present, intractable. Nevertheless, many important engineering problems have already been solved using the technique. World-wide there are at least six instruments (in Canada, France, Denmark, Sweden, UK and the USA) that are used predominantly for engineering purposes, and many others (in Germany, France, USA, the Czech Republic) have significant engineering programmes. A study sponsored by the European Science Foundation and chaired by Dr T. Holden to investigate the status of neutron-based engineering research and development has documented its vibrancy, as well as highlighted the even greater potential for future growth into new areas of industrial application. In view of this, the purpose of the current document is not to establish the health of current research, but to look to the future.

4.1 Industrial

Residual stresses are responsible for a great deal of unexpected failures in industry, especially in fatigue or stress corrosion environments. These failures are expensive to investigate, and difficult to put right. With a much more intense source the tremendous benefits of neutron measurements over more limited traditional methods will enable a wider range of engineering problems to be solved. As the more traditional sectors of industry drive to reduce their margins they will need the high level of information that neutron diffraction can provide. Consequently, there is a need to transfer the technology currently developed for high value added applications. The Engineering Research, Development and Test Centre will be instrumental in bringing this about by bringing down the cost of measurements and providing the necessary expertise on site.

Heat treatment procedures are an essential part of many fabrication processes, reducing potentially fatal residual stresses to more acceptable levels. The ***definition of effective stress relief treatments*** is often made by a combination of experience and trial and error, success, in many cases, being judged by the number of subsequent failures! More scientific approaches involve expensive sectioning or hole drilling procedures to give limited, but important insights into the state of stress which, when combined with theoretical investigations, can lead to substantial improvements in performance. What is uncertain is the relative relaxation rates of the hydrostatic and deviatoric stresses. The ability to study in real time the evolution of stress non-destructively would lead to large gains in our understanding. Neutron diffraction not only offers an unambiguous way of evaluating the performance of stress relief procedures, and for identifying dangerous ‘hotspots’, but for studying stress relief in real time opening up the opportunity for intelligent definition of cost-effective stress-relief procedures. New stress-relief procedures can be evaluated quickly; for example, most strain measurements on vibrationally stress relieved samples have shown no significant change in macro-residual stresses. In certain cases however changes of the order of 25% have been seen; further investigations are necessary to identify whether this is related to the exact method of vibrational excitation. In addition there is a need to study behaviour in high temperature environments, especially where the decay of residual stresses is important (e.g. reheat creep cracking, type IV zone cracking, stress relief cracking, etc.), such as in the application of pressure vessel steels.

It will be possible to study case hardening/carburizing quantifying residual stress distributions and phase contents and their effect on fatigue crack growth under surface stresses. It will also be possible to monitor the retention of ***life extending residual stressing treatments*** such as peening, prestretching, etc. during service. By exploiting the pulsed nature of the beam it will be possible to study stress changes taking place during fatigue cycling (<10Hz) and to map how they evolve with component life.

Recently, as a result of the increased industrial activity in the area of strain measurement by neutron diffraction, VAMAS has set up a Technical Working Group (TWA 20) to ***develop standards*** for the neutron measurement of residual stress. Industries rely on standards to maintain quality and reproducibility world-wide and so this is a very important step in the developing maturity of the technique and will lead to uniformity of approach and proven levels of confidence. However, without the Engineering Research, Development and Test Centre cost and access limitations will continue to limit the level of industrial take up.

SANS has found use in the study of creep cavitation cracking, allowing the quantification of voiding as a function of component thermal and mechanical history. In-service ageing as quantified by SANS can also be used as a means to assess remnant life of components, as well as changes in their performance characteristics with temperature. Once again the opportunity for real time studies would be of tremendous benefit.

Neutron radiology finds broad utilisation in industry, in the R&D of new technologies and the development of new materials, as well as in bio/medical sciences, agriculture, forensics and in the conservation of objects of art.

A new spallation source would facilitate routine commercial work in the radiological following areas:

- Corrosion and moisture detection in Al aircraft structures and inspections of adhesively bonded metal/composite parts;
- Inspections of precision cast parts, such as turbine blades of aircraft engines for the remnants of core material;
- Inspections of pyrotechnical devices in aerospace industry, in the production of explosives, in the Q/C of car airbag gas initiators;
- Examination of paintings, objects of art and archaeological objects.

Very high time averaged thermal and cold neutron fluxes will enable to undertaking of high resolution **computed neutron tomography** (CNT) in quasi-real time conditions, which will extend the applicability of 3-D neutron imaging. High resolution CNT will find applications in industry and materials science, for example, in the examination of objects with complicated internal structures, as well as for studying reciprocating engines. In this respect the sensitivity of neutrons to hydrogen make it possible to monitor the performance of lubricants.

Neutron analytical methods as **Prompt Gamma Activation Analysis (PGAA), Neutron Capture Analysis** and **Neutron Depth Profiling** (for boron and lithium) would enable fast and non-destructive chemical analysis for a series of elements in various objects. For instance, using cold neutron PGAA it is feasible to measure hydrogen concentrations in titanium-alloy jet engine turbine blades at the concentration levels of about 100 μg/g Ti.

4.2 Chemical engineering

SANS already finds considerable use in chemical engineering for studying ***aggregation phenomena*** in colloids and aerosols. Industrial users need detailed chemical and microstructural information for complex materials and processes providing 0.1% phase sensitivity, under conditions of extreme pressure (~100kbar) and temperature (~2000K), with collection times of a few minutes. The ability to change the contrast by substituting deuterium for hydrogen also provides an invaluable tool for interpreting the experimental data. Because of the very large parameter space which controls colloid stability (e.g. pressure, temperature, pH, relative concentration, polymer structure and degree of polymerisation, particle size, use of surfactants and stabilisers, etc.), it has so far proven difficult to explore the multi-dimensional space, inhibiting improvements in colloidal performance. Increases in flux will also open up dynamical studies of coagulation, aggregation and sedimentation.

Measurements on industrial colloids with a view to process control or stabilisation control are in their infancy. The requirements of industry is for information on aggregation and dispersity as a function of the parameters listed above. This requires an instrument allowing good environmental control combined with a Q range of $5\cdot10^{-4}$ Å^{-1} to access μm length scales. SANS has the advantage over SAXS of phase contrast mapping of H and D. At the present time data acquisition times of several hours is typical, for useful kinetic studies gains of 1000 are required. Improved understandings will lead to enhanced oil-recovery, better control of aerosol dispersions, paints and inks.

SANS can greatly improve our knowledge of the stability of petroleum industry colloids. For example, understanding fluid flow is of crucial importance to the petroleum industry, where the interactions between rock and brine/hydrocarbon mixtures are especially important. Dynamics of fluid behaviour could also be investigated, in near surface regions using reflectometry and deeper using SANS. In cyclic experiments, such as those which might mimic lubricant behaviour in reciprocating engines experiments, one could exploit the pulsed nature of the beam to provide information about in-cycle fluctuations. In addition, **neutron reflectometry** has potential for probing oil, water and surfactant interactions with quartz and clay surfaces at temperatures and pressures representative of oil collection conditions and the development of new lubricants.

One area yet to reach maturity is that of **neutron resonance radiography**. Here resonances characteristic of particular elements can be used for elemental identification or as a means determining the local temperature very accurately. Recent experiments involving the measurement of temperature within the active elements of a catalytic converter have proven the feasibility of such studies.

PGAA has been used alone to measure up to 21 elements in standard rocks, and in combination with conventional instrumental neutron activation analysis- (INAA) to measure as many as 48 elements in coal without chemical separation. These two complementary techniques have been extensively used in the study of natural and manmade atmospheric aerosols. Currently, irradiation times of at least several hours are required for most multi-element analysis, hence the throughput is low because only one sample can be irradiated and measured at a time.

4.3 Process engineering

Neutron scattering can help with the definition of ***new processing strategies*** in areas such as powder metallurgy, mechanical alloying, molecular beam epitaxy, sputtering, recrystallisation and heat treatment, and rapid solidification. One example is the exploitation of SANS to monitor the extent of sintering of metals and ceramics as a function of heat treatment temperature, providing information about the number, size and shape of the voids. Here the future is very exciting since the ESS with its higher flux will open the way for time resolved processing experiments, while at the same time providing the space necessary to allow the staging of more complex processing simulations.

Pulsed and real time radiological techniques using strong cold, thermal and selective epithermal neutron beams offer powerful techniques to inspect running engines and other machine parts, or to study fast time dependent phenomena. Very short source pulse widths of less than 1s and very high peak neutron fluxes greater than 10^{17} n/cm^2/s enable flash or stroboscopic neutron imaging opening up new application possibilities for the inspection moving objects or to study fast time dependent phenomena. Areas particularly suited to dynamic radiology studies include:

- the distribution and transport of oil in car and other engines, lubrication of bearings, etc.;
- studies of evaporation processes and transport of coolants in R&D of cooling technology, improvements in the operation of pumps, valves, visco-clutches, carburettors and of whole engines in the car and aircraft industry, in the petrochemical industry, improvements of coffee machines or fire extinguishers in the industry of house-hold appliances;
- studies of castings, solidification and segregation processes in metallurgy and materials science;
- the development of hydrophobic treatments and coatings in civil engineering, optimisation of crude oil extraction from oil wells, optimisation of contaminated soil cleaning procedures using surfactants, procedures to convert desert sand into arable soil etc.

4.4 Materials science

Materials science is primarily concerned with the enhancement of performance through ***microstructural control***. Interest is therefore often focused on the role of point defects, line defects (dislocations), two dimensional defects (e.g. grain boundaries, interphase boundaries, multilayers) and three dimensional defects (e.g. cavities, dispersoids, microcracks, fibres). **SANS** can provide information about many of these features in combination with complementary techniques such as X-ray scattering, transmission electron microscopy, etc. Neutron techniques have already made many important contributions in increasing our understanding of novel and conventional materials (e.g. alloys, composites, semi-conductors, superconductors, ceramics, polymers, fuel cells, catalysts, fibres, natural materials).

Neutron diffraction will play a key role in the ***design*** of new materials and components. For example, in the development of metal matrix composites the ability to measure the response of each phase separately has been crucial. To date, performance limiting ***thermal stresses*** have been monitored. These are especially important under thermal cycling conditions, because the different thermal expansion coefficients regenerate large stresses each cycle. The evolution of these stresses can be measured during the cycle. In the future, the effect of thermal stresses between dissimilar materials in assemblies will also be evaluated during conditions of varying temperature or externally applied stress, leading to improved designs, minimising thermal distortion or stress.

One area where neutrons have been invaluable already is in the understanding of ***recrystallisation textures*** and their evolution; for example one can use neutrons to monitor recrystallisation of small samples in-situ, gaining insight into the kinetics of the process. Textures caused as a result of deformation processing by forging, rolling, extrusion can be spatially variant and a need exists to be able to map these variations non-destructively. Reliable models are some way off, but the development of the ESS will enable the scanning of the component across the beam to provide ***texture maps*** throughout components, both immediately after forming and as a function of recrystallisation heat treatments. This will provide valuable information to designers, especially in the aeroengine industry where expensive trials and microstructure studies are required to optimise component microstructure. It may also be possible to make kinetic measurements (on a local scale) looking at recrystallisation or grain growth and possibly even during deformation. For example, concerning recrystallisation, there is a need to be able to study the growth of single grains to learn more about the fundamental growth processes. At the present time only average measurements are possible, from which it is very hard to deduce single grain/grain boundary behaviour.

Another area of interest is in the study of ***layers and coatings***. In this context **neutron reflectometry** is an important tool having high sensitivity to elements such as carbon, hydrogen and oxygen relative to synchrotron radiation. As a result the technique has potential for studying corrosion and stress corrosion phenomena and has already been used to study scale formation on magnetic materials. With oxidation, corrosion and wear costing billions of dollars each year this is an area ripe for further development. This will be stimulated by increased intensity since this will allow in situ monitoring of the growth of such films.

Higher neutron fluxes are needed to increase the spatial resolution (now about 0.3 mm) in order to investigate interesting stress problems through interfaces, and in particular in protection coatings, such as the thermal barrier coatings used to protect turbine blades.

The ***development of new materials*** such as aluminides and ceramics for high temperature applications has brought problems of harnessing brittle materials. Processing requires stringent quality control with critical flaw sizes in such materials ranging from 2 to 20µm. Flaws in this size range with densities as low as 10^7cm^{-3} can now be assessed by **SANS** experiments spanning a Q-range of 10^{-4} to 10^{-1} nm^{-1}. It is anticipated that SANS will find increasing application for ***process monitoring and optimisation***. Such techniques will be especially useful for the development of nano and microparticle ceramics and with the new instrument time resolutions of around 1 minute may be possible.

4.5 Health and safety

Design must be particularly conservative in situations where the cost of failure, either financially or in terms of human life is great. As a result, expensive fabrication procedures, stringent quality control and testing, and high levels of non-conformance rejection characterise manufacturing in such cases. Further, replacement of parts or removal of the system from service must be contemplated at the first sign of wear. In this respect, weldment **stresses** present considerable challenges to the design engineer particularly in the nuclear and aerospace industries. The level of residual stress can be reduced by intelligent weld process design, or by subsequent thermal or mechanical treatments. A great deal of investment has been focused on the development of design tools in the form of finite element weld models. However progress is currently hampered by the lack of a reliable measurements of the residual stresses within well characterised welds.

Neutron diffraction is already an important tool as the only means of measuring the stress field deep within welds non-destructively and has found particular application in the aeroengine and nuclear plant industries where safety is especially important. However, in many other cases designers and engineers are not able to exploit the technique because it is expensive and large parts are difficult to examine. The establishment of the Engineering research, Development and Test Centre would allow engineers to gain much more information, quickly and at an acceptable cost, about the state of stress, especially at welded joints and other sites of high stress and low reliability, giving rise to optimised fabrication procedures and lower levels of non-conformance rejection. Other questions such as the extent to which life extending treatments, such as shot-peening, as well as shakedown over the life of the component due to fatiguing could be asked. Potential benefits of quantifying residual stresses lie in reducing life cycle costs and improving safety management of critical components. Further, it would enable more intelligent design based on the actual level of stress across the assembly reducing the chance of unexpected failures, yet at the same time highlighting opportunities for less conservative design.

Another issue of emerging importance especially in the US is that of nuclear stock-pile management. Neutron techniques are finding increasing application in evaluating the longevity of existing stocks.

4.6 Nuclear engineering

Nuclear fission accounts for a large proportion of the energy produced world-wide and fusion reactors are being considered as a source of energy for the future. As a result there is an important need for the investigation of active materials. Future spallation sources will be of great help in investigating irradiation generated degradation which is impossible with the currently available instruments. Engineering instruments at current neutron facilities are simply not equipped to deal with ***highly active samples***. This is not a trivial problem, since existing beamlines are currently too cramped. The introduction of such facilities will lead to better understanding and modelling of structural integrity after exposure and for life-time predictions.

	Fuels	**Cladding**		**Vessels**	**Internals**	**Space Reactors**
		LWR	Adv React			
Fluence	10^{18}-10^{23}	$<10^{22}$	10^{23}	10^{17}-10^{19}	10^{18}-10^{22}	10^{23}
Irradiation volume (cm^3)	>10	10-50	>50	5-1000	5-100	1000
Temp (°C)	350-2800	290	500	50-290	290	>600

Table from Nuclear Radiation & Radiation Effects a paper at the Tech. & Science at a High Power Spallation Source, Workshop Proc. Argonne Nat. Lab, 1993

Experimental studies can be broadly divided into two areas, nuclear engineering and radiation damage. Many of the issues relating to the former area have been covered in the industrial section. These centre around the integrity of pressure vessels, pipes and associated components. Often it is in the heat affected zone surrounding welded joints that fatigue, corrosion cracking or creep fatigue occur driven by the presence of weld induced stresses. In certain cases, because the weld zone is largest at the surface, the parent metal cracks sub-surface and is shielded from external view by the more compliant weld metal. Such cracking is particularly hard to detect and needs to be prevented by modification of the causal residual stress. Commonly such components are 20-100mm thick and neutrons provide the only means of determining the stresses deep within the weld and is an area of major importance for the nuclear power industry. Consequently, most of the large manufacturers are involved in studies of this type. With respect to the latter area, for fission systems, the behaviour of cladding and its interaction with fuel is an important issue. In addition the effects of radiation induced hardening and embrittlement remain a challenge, as well as cracking effects caused by stress corrosion hastened by radiation damage. An important factor in these studies is the fact that there are fundamental differences in the radiation damage caused by electron, light, ion and neutron irradiation, meaning that while other radiations can be used to shed some light on neutron irradiation problems, they cannot be used as a basis for design and lifing considerations. Spallation sources allow us to gain a better understanding about irradiation across a wide neutron energy spectrum and as such have a major role to play. In order to exploit this opportunity, incident flux must be maximised, combined with a large shielded irradiation area.

Under alpha particle radiation He bubbles can form in metals by implantation of the alpha particles and subsequent annealing. This effect can be studied using **SANS**. A pulsed neutron source with a wide wavelength spectrum will allow a precise calculation of the deformation pressures as well as providing information about the size and the dispersity of the He bubbles; combining both the results, it is possible to measure the gas density inside the bubbles.

Magnetic SANS complemented by high resolution TEM has provided insights into fundamental mechanisms leading to radiation-induced embrittlement of ferritic pressure vessel steels in light water fission reactors. In addition neutron scattering has also been used to analyses precipitate microstructures in fusion reactor walls.

Routine **Neutron Radiology** studies are capable of providing basic information of importance to nuclear engineers, e.g.:

- detection of hydrides in steel (hydrogen embrittlement), titanium, zirconium and other metals of technological importance for the production of structural components in the nuclear industry (as well as the aerospace and petrochemical industries and in the future development of materials for hydrogen storage and transportation);
- examination of nuclear fuel rods and assemblies, control rods and shielding materials and irradiation devices;
- dynamic studies of the cooling of nuclear fuel rods in nuclear safety studies.

A related area of increasing importance is that of nuclear stock-pile stewardship. Neutron scattering techniques are finding increasing use in the US for identifying the deterioration of explosives, crevice detection, etc.

4.7 Medical

Neutron diffraction has much to offer in the field of medical implants. For example, it is now not uncommon for hip-joint replacements to need replacing. Neutron diffraction is offering important insights into the failure of current hip-joint designs as well as helping in the design of new implants with improved lives. Cobalt-based and titanium based alloys are frequently used as implant materials in hip and knee joint replacements. However, wear of the implants is a major concern and has prompted the search for biocompatible wear resistant coatings or protective layers. **Neutron reflectometry** and **diffraction techniques** have great potential for assisting in the development of such applications.

5. Relationship to other techniques

Engineers are interested in problem solving rather than in application of any particular experimental technique. For this reason neutrons will always be used alongside other techniques. In the area of **stress measurement**, destructive methods such as hole drilling and layer removal as well as surface sensitive methods such as X-ray diffraction will always be used to provide additional information. In addition finite element models are often used to predict the residual stresses and neutrons represent perhaps the only way of refining and improving the reliability of such models. X-ray synchrotrons have penetrations comparable with neutrons, but the very short wavelengths, (~0.08Å) means that the scattering angles are low, restricting studies to transmission geometries. For many engineering applications this geometry is not suitable.

X-ray synchrotrons are challenging neutrons for the interrogation of interfacial structures, phase separation kinetics. SAXS is an important companion to **SANS** in many polymer and colloidal studies in that they access different regions of Q space. Engineers cannot afford to be one technique specialists and so the level of expertise and advice offered by the facility is crucial to the success of the studies. With the advent of the next generation spallation source the level of information available to engineers and materials scientists will enable much more intelligent design of components, processes and materials.

In the area of **radiography** the high penetration of neutrons mean that they have clear advantages over X-ray or synchrotron X-ray radiography. Furthermore, one of the important properties of NR is the capability to detect and inspect hydrogenous materials and materials containing neutron absorbing elements through walls of most of the technically important metals, which is difficult if not impossible with conventional X- or gamma radiography.

6. Summary

The needs of the engineering community are quite different to those for the more fundamental science. Neutron scattering offers unique insights into the performance of industrial components and industrial processes. Insights that will be ever more necessary if European industry is to compete in increasingly competitive global markets. Increased performance will open up whole new areas, especially in real time and in situ experiments and 3D mapping. Most importantly, however, the building of a new type of centre, an Engineering Research, Development and Test centre, will bring the cost of making measurements within the budget of a much wider range of industries and provide the expertise and facilities to allow them to exploit the next generation source.

Appendix:

Industries known to have made neutron strain measurements, either under contract, or in collaboration with University teams

Advanced Ceramics Corp (USA)
AEA Technology (UK)
AEROSPATIALE (FR)
Air Products & Chemicals (USA)
Alcan (UK)
Allied Signal Inc (USA)
Ansaldo (IT)
Aristech Chem. Corp. (USA)
Armstrong world Industries (USA)
ASEA (SE)
AT&T Ball Labs (USA)
Babcock & Wilcox (USA)
Biotraces Inc. (USA)
BMW (DE)
BNFL (UK)
Boeing (USA)
BP (UK)
Ridon Wire Ropes (UK)
British Aerospace (UK)
British Rail (UK)
British Steel (UK)
Brown Bovary (SE)
CEA/CEN (FR)
CID Tech (USA)
Czech and Slovak Building industry (CR,SV)
Defence Research Agency (UK)
Dornier, DASA (DE)
Dow Chemical (USA)
Dow Corning (USA)
Du Pont (USA)
Eastman Kodak (USA)
EDF (FR)
Elf (FR)
ENEA (IT)
ENEL (IT)
Exxon Chemical Co (USA)
FIAT (IT)
Fokker (NL)
Ford Motor Company (USA)
FRAMATOM (FR)
General Electric (USA)
General Motors (USA)
Goodyear (USA)
IBM (USA)
Intel Corp. (USA)
Kodak (USA)
Magnox (UK)
Mercedes Benz AG (DE)
Moltech Corp (USA)
MTU (DE)
Nanophase Tech. (USA)
NASA (USA)
National Museums (FR, DE)
Nuclear Electric (UK)
Oconics Corp (USA)
Optical Coating Lab (USA)
Parallax Res Labs. (USA)
Pechiney (FR)
Philips Res Lab. (Nl)
Planseewerke (DE)
Pratt & Whitney (USA)
Proctor & Gamble (UK, USA)
Pulp & Paper Res./ Inst. (USA)
RayChem (USA)
Rockwell International (USA)
Rohm & Haas (USA)
Rolls Royce (UK)
Sandoz Co. (USA)
Schott Fiber Optics (USA)
Science Res. Labs, (USA)
SFA Inc. (USA)
Siemens-KWU (DE)
Southwest Res. Inst. (USA)
Stamphal (IT)
T-ProSci Co. (USA)
Taylors bell Co. (UK)
Texaco (USA)
The Welding Institute (UK)
3M Corp (USA)
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Condensed matter physics

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1. Introduction

The contribution of neutron scattering to our present understanding of the physics of condensed matter since the pioneering work of Brockhouse and Shull some fifty years ago is well known and its importance is commonly acknowledged not only since the Nobel prize has been awarded to Brockhouse and Shull. Thus these achievements need not to be repeated in general here. Most of the relevant work has been performed on reactor neutron sources, simply because such sources have been the only ones until recent years, when sufficiently powerful spallation neutron sources came on line, and instrumentation has been developed to the necessary performance. Since these sources, which produce a pulsed neutron beam, do offer specific possibilities for neutron scattering experiments on condensed matter, it is appropriate to mention some outstanding achievements from recent years, which are beyond the reach of reactor sources. A unique feature of such sources is the high flux of high energy neutrons in the energy range between a few hundred meV and several eV. This is not only relevant for the spectroscopy of high energy excitations but also where high momentum transfer is required. Typical examples are the study of the spin dynamics in transition metals and high T_c - superconductors and the study of the momentum distribution in quantum and classical liquids.

The spin dynamics of transition metals and high T_c-superconductors are characterised by the large energy scale of about 1 eV. This corresponds to the high Curie temperature in the transition metals and most likely to the high superconducting transition temperature of the cuprates. The recent experiments at the presently most powerful spallation source ISIS covering the high energy part of the spin dynamics have been fundamental for the understanding of the microscopic phenomena, which determine the extraordinary properties of these materials with their obvious technological importance.

Quantum liquids have different groundstates depending on whether they are Bose- or Fermi-systems. In a Bose- system like ^{4}He superfluidity occurs, which is due to the fact that the He-atoms can condense into one single state with momentum p=0. The number of atoms in this state, n(0), represents thus the fraction of the He- atoms in the superfluid state. This can be measured by neutrons, if the momentum transfer is high enough to be in the impulse approximation. Such measurements have recently shown that n(0) can in principle be measured by the high energy neutrons available at spallation sources.

In what follows, we have chosen the topics, which are and which are expected to remain key topics for the study of the physics of condensed matter by neutrons. These are **magnetism**, **superconductivity and other electronic correlations**, **structural properties** and **liquids**.For these topics we shall extrapolate from our present knowledge, where a new generation spallation source can give us qualitatively new results. We shall discuss as well, where new methodological approaches become conceivable with such a new source. This will include a consideration of the specific properties of such a source, like its pulse structure, which is important for experiments under **extreme conditions**.

2. Magnetism

Magnetism has been in the past, is at present and is expected to be in the future one of the prime topics for neutron scattering: the unique features, easy to interpret cross section, appropriate energy range and the easy separation of magnetic and nuclear cross section through polarized neutron experiments, are the reason for this.

Whereas neutron scattering has provided the key to solving the structures of bulk magnetic materials in the last 30 years, we see an important future in elucidating the atomic scale structure of new magnetic materials based on artificial fabrication techniques. Important amongst these are magnetic nanostructures and magnetic multilayers, new magnetic storage media and novel hard magnets such as the nitride based materials, etc. The thrust of modern materials science and technology is to develop new materials structured on the nanoscale and new uses are expected for increasingly small elements in device and data storage applications. These materials raise new important questions in physics, discussed below.

Ultrathin magnetic structures, in particular determination of the absolute value of the total magnetic moment (not accessed in XMCD (X-ray Magnetic Circular Dichroism)). Important examples are moment formation in low dimensional systems, interface polarisation, exchange coupling. For magnetic multilayers, increased flux may allow form factor measurements to be made revealing the spin density distribution. In the case of thin magnetic layers PNR (Polarized Neutron Reflection) 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 (Neutron Diffraction). In contrast with XMCD, PNR with polarisation analysis (PA) determines the in-plane magnetic vector magnetisation profile. Polarised neutron reflectivity studies are the only method to provide a complete analysis of the magnetic structure, including the coherence length of collinear and non-collinear 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 mechanisms (e.g. interlayer exchange coupling) in the magnetic multilayers and for optimisation of devices such as spin valves. 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 (Giant Magneto Resistance) multilayer structures but also for understanding exchange coupling and testing model predictions directly.

We also see exciting potential for extending polarised neutron reflection (PNR) techniques to high wave-vectors where information on the atomic scale profile of the layer dependent magnetic structure in magnetic multilayers can be probed. PNR provides an example of a recently developed application of neutron scattering which allows very small amounts of magnetic material to be studied. It should also be realised that by carrying out neutron reflectivity studies the typical samples size required has been reduced by a factor of 10^{-6}, or from 1g to about 10^{-6}g. Surface neutron scattering under glancing angles is a new method which is just at the brink of producing results. It will be an increasingly important tool for studying near surface magnetic structures and phase transitions as well as buried magnetic interfaces. In particular, films and multilayers showing perpendicular magnetic anisotropy will benefit from this new technique. For surface neutron scattering more flux from advanced sources would be highly beneficial. A significant development in PNR has been recently reported by Felcher (Nature 1995): the spin dependent birefringence of a cold neutron beam reflected from a magnetic surface due has been observed. It has been proposed that this effect can be used as a probe of surface spin dynamics.

PNR can be used to study magnetic properties *in situ* and in real time, e.g. surface oxidation, provided sufficient flux is available.

It is clear that the study of single layers and in particular the spin dynamics can only be reached by a new quality source. Even then all the neutrons available must be usable simultaneously, which requires the pulse structure to be fully used.

Turning to the more classical field of spin dynamics in bulk samples, it is the high energy excitation which are evidently the most obvious application. But while now „only" nearly ideal and simple model systems can be studied, a new generation source would allow the systematic study of technologically relevant but complicated systems. Such systematics must include the quick study of a large number of different systems. This is presently completely out of scope.

Other fields which are presently under study, but are limited typically by a combination of very weak signal and the need of very high resolution for q and w, are systems which are at some sort of a stability edge like:

- **low moment** systems, correlated electron systems;
- **non-equilibrium processes** involving ordering of structures from the atomic to the macroscopic scale or magnetic relaxation phenomena (e.g. domain relaxation, after effect);
- **molecular magnets** with small magnetic moment;
- **ground state properties** of materials of low dimensional systems, heavy fermions, spin liquids, spin glasses, ferro-liquids;
- study of **electron - phonon interactions**;
- **weak changes** of phonon dispersion, which are expected in connection with magnetic phase transitions such as magnetostriction, magnetoelastic transitions etc.

In most of these investigations the use of polarised neutrons and polarisation analysis is mandatory to identify the magnetic cross-section.

Many systems are inhomogeneous, some by definition like frustrated systems, other accidentally by e.g. domain-formation. In such systems an investigation in reciprocal space is no more appropriate, but real space studies are required. We expect that a new quality source will enable to develop such techniques for local imaging. The information size is at present of the order of $(1\text{mm})^3$, which may be reduced to $(0.5\text{mm})^3$ 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.

One step further would be:

- the **real-time and real-space study of relaxation processes** in magnetic materials including domain dynamics in ferromagnets, domain-wall pinning etc. These are all questions of obvious technological relevance. Again, the flux is the basic limiting factor for this type of measurement.

3. Superconductivity and other electron correlations

Neutron scattering has proved to be an important technique for investigating superconductors in general, but the high temperature superconductors in particular. The arguments presented below apply to many of the currently most interesting materials which form the family of substances which might be used for 'oxide' electronics.

For ‘conventional’ superconductivity neutron scattering has been important in illustrating the role of the electron-phonon interaction and providing detailed information about the flux-line lattice in type II superconductors. Neutron scattering has contributed much more to our understanding of high T_c superconductors.

Such systems in view of technological applications possess large characteristic energy scales and are complex due to the interplay of superconductivity and magnetism, which requires extensive measurements of $S(Q, \omega)$.

High T_c superconductors are oxides which are usually near to structural instabilities and magnetic order as well as developing a superconducting state at low temperatures. To many scientists the ‘normal’ state in these materials is more ‘unusual’ than the superconducting state.

High T_c superconductors are extreme type II materials with large penetration depths and small coherence length. Therefore for magnetic fields greater than H_{c1} and less than H_{c2} a magnetic field can enter a superconducting sample; the flux is quantised in units of h/2e and distributed on a lattice. This flux-line lattice and its ability to move through a material under an applied current is an important consideration in determining the feasibility of using such materials in many forms of device structure.

In studies of the flux-line lattice with an enhanced source it would be possible to examine a range of pinning distributions which would control to an extent the formation of the ‘ordered’ distribution of flux. High quality single crystal samples, (usually small), with well defined pinnig distributions and thin films would be suitable candidates for such studies. The information provided by such experiments would be important for optimising current densities in superconducting materials. In the very anisotropic superconductors, experiments have been restricted to a small corner of the phase diagram in B and T, where a well ordered flux-line lattice exists. Only with greater neutron flux it would be possible to considerably extend this work and examine the regions where the flux-lines have decomposed into ‘pancake’ vortices which are effectively decoupled from layer to layer and the region above the ‘irreversibility’ line where essentially a liquid of flux-lines or pancakes exists. Experiments on the dynamics of the magnetic flux in such superconductors would be feasible with considerably more neutron intensity, allowing the examination of the motion of the flux-line lattice against an applied current or as thermal properties dominate at temperatures above the irreversibility line- Such experiments would probably be performed using the spin echo technique. In addition, the changes of viscosity of the flux-liquid due to the presence of extended pins and their role in the growth of short range order. Such experiments would be of particular interest in terms of practical applications and basic science as they will illuminate the current carrying capacities of these superconductors and the unusual „phase transitions“ which exist in such systems.

It is appropriate to stress that a detailed study of the flux lattice, in particular the dynamics yields access to the topology of the flow of currents in a superconductor, a quantity not accessible by experiments at present sources.

As in magnetism particularly demanding are experiments on systems which just make it into superconductivity or just don’t make it. In such situations, due to competition of different possible groundstates of the electronic system unusual behaviour can be expected like in heavy fermion systems or magnetic superconductors. In such a situation the direct measurement of the different degrees of freedom, for example magnetic, structural and electronic need to be measured in detail with high precision. The long-standing question of the ultimate groundstate of correlated electrons (Fermi liquid, marginal Fermi liquid) could then be addressed in detail. Such investigations, nowadays only just feasible, will definitely yield new insight into the problem of the final groundstate of such systems, if with a qualitatively new source they were possible in detail with high precision and resolution.

4. Structural properties

Phonon dispersions as measured by inelastic neutron scattering are indispensable for an understanding of the mechanical properties of any kind of condensed matter on an atomic scale. This technique has brought new information particularly in the study of structural phase transformations .It is the possibility to scan anywhere in reciprocal space (Q, ω) which makes this method so valuable. The technique has recently been extended to high energies (Compton scattering). This gave new information concerning momentum distributions which are important e.g. for ^{3}He and ^{4}He.

An important area for neutron scattering has been the measurement of structure factors in liquids and solutions. The unique feature of neutrons (in contrast to X-rays) is related to the large values of the scattering vector Q (up to 100 $Å^{-1}$) which can be achieved.

Neutron diffractometry is the key technique to detect positions of light atoms in the presence of heavy atoms as well as to distinguish different isotopes of the same element from each other (e.g. ^{16}O/^{18}O substitution in high-temperature superconductors).

As science and experiments for the future can be identified:

Vibrational excitations of solids and liquids are always central in understanding their behaviour. The future will see vibrational excitations in layered and artificially structured materials which are different from those in normal crystalline solids and are therefore of great fundamental interest. The excitations in amorphous systems, quasi crystals and liquid crystals need to be mentioned here as well. Also, new forms of collective excitations such as fractons must be invoked.

Effects on the phonon dispersion are expected at magnetic phase transitions (magnetostriction, dimer transitions, etc.). The effects are presumably very weak and are therefore detectable only in high-resolution experiments (which are presently flux limited).

Real time experiments at phase transitions will be particularly important (martensitic phase transformations, how do domains behave?) which needs microbeams of neutrons for local investigations. Here the importance of a next generation neutron source is obvious (much more flux). In this context the dynamics of texture should also be mentioned.

While the phonon dispersion $E(q)$ probes the strength and range of interatomic forces, different information is contained in the line width which is a measure of the lifetime of the excitation (e.g. information on the electron-phonon interaction in high-temperature superconductors). Such measurements need an order of magnitude better resolution which can only be achieved on a next generation neutron source.

Diffusion processes are important in liquids as well as in solids (diffusion of oxygen in high-temperature superconducting cuprates, diffusion processes in biomaterials, H-diffusion in connection with H-storage etc.). Polarized neutrons as a tool to separate coherent from incoherent scattering will be essential in the future. There is also a need to study diffusion processes on thin films (catalysis), which is clearly an area where more flux is needed, in particular if such processes are to be studied in real time.

As the structure forms the basis of all further investigations and applications of a material, very often an overall information about the phonons is required before proceeding in the use of a material. This is presently done mostly through a measurement of the heat capacity. The other technique yielding much more of the desired information is the determination of the density of states (DOS) by inelastic neutron scattering. Due to the presently necessary effort and time for such measurements this is done only on selected systems like HTC superconductors. A new generation source, however, and a pulsed one is particularly suited, could make such measurements over a large Q and w range so fast that the DOS can be measured as simply as heat capacity.

An important subject is the area of non-equilibrium physics. Non-equilibrium can be achieved in many ways, e.g. by pulsed fields (magnetic and electric), pressure shocks, temperature gradients, light irradiation, etc. A prominent example is the generation of excited-state phonons by optical excitation through spin-lattice relaxation which has already been realised for ruby in a Raman experiment. This mechanism is of utmost importance in the understanding of the photosynthetic process, i.e. light conversion into mechanical (and subsequently chemical) energy in biological systems (proton pump in photosynthetic materials such as pseudomonas viridis). Such measurements (spectroscopy in real time during the relaxation of the excited states) obviously require a new quality source.

As mentioned in the beginning, spallation neutron sources are the source of choice to study liquids. From what we know now, the forecast is quite safe, that a new generation of such a source will bring us a fundamental step forward toward the understanding of the simple quantum liquids which are models for correlated electrons. Here it is the combination of weak cross-section and the required high resolution, where a large flux increase is the basis for better experiments. Naturally the complex liquids relevant for technology (detergents etc.) are with present sources accessible on a very limited scale and a new source would open up the study of new technological questions for neutrons.

5. Extreme conditions

Recently we have seen an ever increasing demand for neutron experiments under extreme conditions: very high and very low temperatures, high pressure and high magnetic fields. Also complex sample environment including all of the above and something else like a high intensity laser pulse are required. Such extreme conditions generally restrict experimental conditions significantly: available for short times only, beam geometry not variable, small samples possible only. Magnetic fields beyond 15T can be obtained effectively as pulses only and mechanical stability requires a fixed neutron flight path; very high pressure 25 GPa and beyond can be obtained with very small samples and with very restricted beam geometry only. With the recent development in such technologies it becomes increasingly clear that new and exciting physics can be expected with extreme conditions. The restrictions mentioned above can be overcome with a new generation pulsed source: this yields the flux necessary to perform experiments with the low duty cycle of a pulsed high magnetic field or with the small samples at high pressure. The restricted scattering geometries is no problem for a pulsed source as wavelength dispersive measurements can be performed. Similarly will additional options as simultaneous laser irradiation become a promising option since a high flux pulsed beam is flexible enough to incorporate it. An example is:

In certain compounds laser irradiation changes the spin state of transition metal- or rare earth-ions. This happens especially in octahedrally co-ordinated Fe^{2+}-complexes where the ligand molecules produce strong enough crystal electric field effects. Through thermal or optical switching a high spin-low spin transition is accomplished. In certain Eu-compounds similar effects occur through changing the number of 4f-electrons.

Neutron spectroscopy could be helpful in elucidating the spin and charge states of the magnetic ions under these extreme thermal or optical conditions. It would be particularly interesting to investigate whether dispersion effects exist in such compounds, whether exchange interactions are different in ground and excited states. Pulsed laser irradiation synchronised to the pulsed neutron beam is the only way to study such dispersive and relaxation effects.

6. Conclusion

In conclusion, we see in many areas of condensed matter physics the possibility of a qualitative step forward with a new generation spallation neutron source. These areas include magnetism, in particular thin films, superconductivity, in particular the flux lattice, and structural properties, in particular real time experiments and nonequilibrium situations. Given the observation, that future studies in basic and applied condensed matter research will move towards intrinsically smaller and smaller and more and more complex systems, the possibility to measure small cross-sections over large ranges of Q and ω by neutrons is fundamental. Only a new generation neutron source can ensure that the contributions to our understanding of these systems, which neutrons can provide, will become available in the future. Such studies can be performed by a pulsed beam technique at a pulsed source most effectively and the high flux will make small cross-sections measurable.

It is evident that in the future the study of kinetics will become more and more important. Consequently we find it very important, that a new generation neutron source will make such measurements feasible. A high intensity pulsed source is ideally suited and needed for a real time measurement of $S(Q,\omega)$. More speculative is making neutrons a 'local' probe to investigate $S(Q,\omega)$ of inhomogeneous samples. Such studies, however, would solve problems like the 'random field antiferromagnet', which can not be solved by present neutron sources and techniques.

Last but not least a new generation spallation source as the ESS would make experiments under extreme conditions like very high pulsed magnetic fields on very high pressure presently out of range feasible and by doing so, open up areas where up to now microscopic information as provided by neutrons was not available.

Particle and nuclear physics and their industrial application at the ESS

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At the planned European Spallation Source (ESS), neutrons in the energy range from 10^{-7} eV to 10^{+9} eV will be available. Further, different types of other secondary particles will be produced. With the ESS facility, a number of unique experiments can be performed which will help, firstly, to determine the basic structure of the elementary interactions of nature, secondly, to elucidate the history of the universe, and, thirdly, to study various questions from the field of quantum and measurement theory. Also, a number of important new nuclear physics applications in industrial sciences and engineering will become feasible with ESS.

In a recent survey to the European Science Foundation, the impact and potential of neutron particle and neutron nuclear physics in the near and far future was covered. In the present report, we shall assume that this survey is known to the reader. Here, we shall discuss, one by one, the various beams at ESS required for the particle and nuclear physics programme.

For each beamline, we give a number of examples of experimental uses. In particular, the following experimental highlights will be discussed in more detail:

- Neutron decay into a hydrogen atom, and the question of the handedness of nature;
- Free neutron-neutron scattering, and the question of isotopic-spin invariance;
- Time reversal symmetry violation in neutron optics, and the question of the baryon asymmetry of the universe;
- Element-sensitive neutron 3D-tomography for industry;
- Temperature-sensitive neutron 3D-tomography for industry;
- Element-sensitive neutron autoradiography for materials testing.

1. High-intensity cold guide for particle physics

In neutron-particle physics there is and, for many years, there will be a high demand for a high intensity polarized cold neutron beam at the end position of a neutron guide. If possible, this guide should be made from supermirrors, and there should be no interruption of the guide upstream.

One of the uses of this guide will be free neutron decay. As was discussed in the ESF survey, about one dozen different observables can be measured in neutron decay. About half of them have, by now, been addressed by experiment, and only few with high precision. Neutron decay data can be used to answer about one dozen of different physic questions, ranging from cosmology and astrophysics to the present standard model of particle physics, and beyond. Most of these physics questions have come up only during the eighties.

Another main topic on this beam will be the measurement of the weak interaction between nucleons. This interaction can be isolated by its unique property of complete left-handedness. In the past, many beautiful demonstrations of this left handedness have been done with the help of neutrons. An unpolarized neutron beam, for instance, when interacting with any kind of "unpolarized" matter, will pick up a measurable non-zero polarization. One big challenge for the future is to measure this effect on a sample of hydrogen or helium.

As a **flagship** experiment for this beam, the following topic has been chosen, and will be described in some more detail.

1.1 Neutron decay into a hydrogen atom, and the question of the handedness of nature

For a long time, it had been taken for granted that the fundamental interactions in nature do not distinguish between left and right. Then, in the late fifties, it was recognized that one of the four known forces, namely the weak interaction, is exclusively left-handed. Neutrinos, for instance, which can interact only weakly, exist, to our knowledge, only as left-polarized particles. This state of affairs is well described by the so-called Standard Model of particle physics.

However, for various reasons, the Standard Model cannot be the ultimate theory of particles, and there exist beautiful, yet unproven Grand Unified Theories, most of which start with a left-right symmetric universe. In these models the evident left-handedness of nature is due to a spontaneous symmetry breaking at a certain intermediate critical energy. If this scenario is true, then the neutrino should still today, where energy has dropped to three Kelvin, carry a small right-handed component. The size of this component depends on the size of the critical energy, and could still be as much as five percent. Limits on this right-handed component have been derived from free neutron and muon decay experiments. There, by angular momentum conservation, the angular distribution of the decay products depends on their "handedness", and recent years have seen some progress in this field.

What really is needed, however, is a clear-cut *Yes* or *No* experiment. Beta-decay of (unpolarized) neutrons into hydrogen could be such an experiment. In this allowed decay-mode, the emitted beta particle is captured into a Bohr orbit about the proton. The hydrogen atom thus formed has a kinetic energy of 352 eV, due to the recoil received from the quasi-monoenergetic (783 keV) antineutrino. The branching ratio for this decay is $4.2 \cdot 10^{-6}$, relative to ordinary free neutron beta decay. What makes this decay so interesting is that one of the four hydrogen hyperfine states cannot be populated at all if the neutrino is completely left-handed (i.e., the antineutrino completely right-handed), again by simple angular momentum conservation. A non-zero population of this substate would be a direct measure of a right-handed component of the weak current.

The hydrogen substate populations can be measured in the first excited 2S-state of hydrogen. This state is populated in 10.5% of all neutron to hydrogen decays. Substate population exchanges by radio frequency transitions and subsequent level-crossing depopulation via Lyman-alpha photon emission from the 2P-state are standard techniques to measure the populations of the individual hyperfine states.

If the time average of the pulsed neutron flux of ESS reaches the flux of ILL, then one expects from a 100 liter interaction volume (e.g. $0.2 \cdot 0.2 \cdot 2.5$ m^3) a time average rate of ten allowed hydrogen-2S events per minute. The event signature is a fast hydrogen atom in coincidence with a Lyman-alpha photon. Hydrogen atoms of several hundred eV are routinely measured in secondary electron detectors with 70% efficiency. These detectors are completely insensitive to thermal atoms. Lyman-alpha photons are transformed to the visible region in large area plastic wavelength shifters with a measured 40% efficiency, and subsequently detected in phototubes with 25% quantum efficiency. This gives a coincidence event rate of about one every hundred seconds. With polarized neutrons, there will be a strong left-right asymmetry in the hydrogen emission probability. A single event background rate of ten per second each is permitted in the hydrogen and photon detectors, for a signal to noise ratio of ten.

Under these severe background requirements the pulsed structure of ESS is a necessary ingredient for background suppression. Thus, with ESS it may be possible to prove for the first time that, firstly, nature does not possess an intrinsic handedness, and, secondly, that there is exciting new physics beyond today's Standard Model.

2. Ultra-cold neutron source

At present, there are five different types of ultracold neutron (UNC) sources existing or under active development:

1. The ultracold neutron turbine is presently the best working UCN source, although not the one with the highest possible potential, as it does not enhance the phase space density of UCN.
2. The so-called superthermal UCN source does not have this phase space limitation. At present this line is been pursued Germany, USA and in Japan.
3. The so-called thin-film source is an extension of the superthermal UCN concept, and can be operated in-pile. This concept is being developed in Berlin.
4. The frozen deuterium source was recently put into operation in St. Petersburg. A large increase in UCN-density was observed when temperature was lowered below 10 K.
5. The rotating crystal UCN source is being developed in the United States.

At present, it cannot be decided which source will be best a decade from now. But, most certainly, ultracold neutrons will stay in high demand also during the decades to come.

One main use of ultracold neutrons is in **neutron-particle physics**. One very long-term project is the search for an electric dipole moment of the neutron. With this experiment, one hopes to solve the following problems:

- Why, after the big bang, more particles have survived than antiparticles?
- Can the forces and particles of nature be grand-unified?
- What is the origin of time reversal violation?

Another long-term project is free neutron decay. The best neutron lifetime measurements have been done with UCN, and the measurement of some of the other neutron decay parameters with UCN is in preparation.

There are many more uses of ultracold neutrons in **general physics**. In addition, very cold neutrons (VCN) in the energy range between 1 and 100 μeV find increasing use. In order to give an impression of the programme in this field, some recent or presently running experiments on UCN or VCN are listed below.

- Weak and strong localization of UCN in disordered media
- Optical pumping of UCN
- Chaotic billiard
- Tunnelling times
- Phase topography
- Neutrons with " $\langle\sigma_z\rangle >> 1$ "
- Anomalous Larmor precession
- Dressed neutrons
- Berry phases

- Tidal forces
- Coriolis forces
- Inertial versus gravitational mass
- UCN-microscopy

A third use of ultracold neutron is in **condensed matter physics**. The potential of this field has been explored in a recent review (Review of Modern Physics, in press). The topics investigated were, among others, UCN reflectometry, UCN elastic scattering, and UCN inelastic scattering. For instance, by studying UCN upscattering in superfluid ^{4}He, the liquid-helium excitation spectrum can be measured. In UCN reflection from surfaces, energy changes smaller than 10^{-11} eV per bounce have been resolved. But we shall not go deeper into this matter.

3. High-resolution, under-moderated neutron beam for particle, nuclear and applied physics

On this beam, many experiments can be done which are out of range at reactor neutron sources. In the domain of **particle physics**, interesting question can be posed, such as:

- What happens when one pulls on a quark inside the neutron? The answer to this question, which is the electric polarizability of the neutron, gives us unique information on the slope of the quark-quark potential. This potential goes to infinity for large quark separations ("quark confinement").
- Is negative charge concentrated more in the centre of the neutron or more in its halo? This question is answered by a measurement of the neutron-electron scattering length, which depends on the mean squared charge radius of the neutron.

Among the many other experiments possible with this beam, two have been selected as **flagship** experiments, which again will be described in more detail.

3.1 Free neutron-neutron scattering, and the question of isotopic-spin invariance

It is believed that the strong nuclear force is essentially the same for protons and neutrons or, more generally, for up quarks and down quarks. In other words, protons and neutrons are identical particles with respect to the strong force. This assumption leads to the concept of isotopic spin as a conserved quantity.

Isotopic-spin invariance can best be tested by measurements of the proton-proton, proton-neutron, and neutron-neutron nuclear singlet scattering lengths at low energies. Among these, most accurately known today is the neutron-proton scattering length $a_{np} = -23.817(13)$ fm. The actual value of the strong proton-proton scattering length $a_{pp} = -17.1(2)$ fm, on the other hand, is more doubtful because, at low energies, the scattering process is dominated by the Coulomb interaction. In order to subtract the Coulomb interaction, phenomenological nuclear potentials must be used, and there are major uncertainties concerning for instance the size of nonlocal contributions to the nuclear potential. The neutron-neutron scattering length, a_{nn}=-18.5(5) fm, finally, is even more doubtful as it is obtained only indirectly from deuteron breakup reactions like $d + n \rightarrow p + n + n$, where a_{nn} is derived from the neutron-neutron interaction which takes place in the three body final state.

Therefore, it cannot be answered with certainty whether the difference a_{nn} - a_{np} = 5 fm or a_{pp} - a_{np} = 6 fm really signals a breakdown of isotopic-spin invariance. The best way to check this would be a direct measurement of a_{nn} via the scattering between free neutrons. As the interaction rate for this process scales with the square of the momentary neutron flux density, a spallation source like ESS has in this case a huge advantage over a continuous neutron source.

The central idea is to let a fast, i.e. epithermal neutron beam impinge onto a group of slow, i.e. cold neutrons, and to register both outgoing neutrons in large position-sensitive detectors. This simple process has an interesting signature: both outgoing neutrons always are registered "downstream" relative to their point of interaction, and both hit the detectors at points which are coplanar with the neutron beam axis. The opening angle of the outgoing neutron trajectories always is 90°. This angle can be resolved if the detectors have a sufficient distance to the interaction zone. Next, the magnitudes of the velocity component perpendicular to the beam axis are equal for both outgoing neutrons. This has the important consequence that both neutrons always hit the detectors at the same time, no matter what the initial velocity of the incoming or what the scattering angle of the outgoing neutrons, provided the neutron detectors are arranged parallel and at equal and sufficiently large distance to the beam axis. Further, the faster outgoing neutrons go to the detectors more downstream, the slower ones stay more upstream, and detector efficiencies may, to some extent, be adapted to this. Finally, the overall angular distribution of the outgoing neutrons is Lambertian.

To realise such an experiment at ESS, one lets the fast neutrons of one pulse hit the slow neutrons of a preceding pulse. The slow pulse comes from a wide but focusing cold guide system, the fast pulse comes from a narrow, straight thermal guide which is concentric with the cold guide. [An alternative to this setup could be an ultracold neutron (UCN) target, because next generation UCN sources promise UCN densities of the same order as the cold neutron density assumed here (10^5 cm^{-3})].

If the time average of the pulsed neutron flux of ESS reaches the flux of ILL, then one expects from a 100 liter interaction volume (e.g. $0.2 \cdot 0.2 \cdot 2.5$ m^3) a time average coincidence count rate of two per minute. The background induced by neutron scattering on the residual gas in the interaction volume is negligible (below one per hour) when the pressure is 10^{-9} mbar. In the partial detector volume where a coincident event is expected, the permitted random single-neutron background rate is three per second, for a signal to noise ratio of ten. Of special interest should be the use of fully polarized neutrons: in this case, neutron-neutron scattering should be completely suppressed, due to the Pauli principle.

In summary, with the ESS a neutron-neutron free-scattering experiment will become well feasible with a carefully designed instrument, and will make a significant contribution to the understanding of one of the four known forces of nature.

3.2 Time reversal symmetry violation in neutron optics, and the question of the baryon asymmetry of the universe

In the big bang, initially, an equal amount of matter and antimatter was produced. As, subsequently, matter and antimatter could annihilate each other, only very few heavy particles ("baryons"), and a roughly equal amount of antiparticles, should have escaped from this early period. But our mere existence contradicts this expectation: there remained about 10^8 times more baryons in the universe than predicted, and almost no antibaryons survived.

The so far only viable solution to this "baryon asymmetry problem" was proposed in the sixties by the late A. Sakharov: the violation of CP-symmetry, which leads to a baryon asymmetry in the partial decay rates of some heavy particles. CP-violation is, in all reasonable contexts, equivalent to a violation of T-symmetry. This latter symmetry describes the invariance of all basic interactions of nature under a reversal of the "arrow of time". Violation of CP-symmetry has been observed long ago in the decay of Kaons. But this one positive result is not sufficient to verify Sakharov's conjecture, nor to identify the origin of CP- or T-violation. Therefore, searches for CP- and T-violation have been done in several other systems. Among the most sensitive searches are those involving neutrons (electric dipole moment of the neutron, neutron optics, neutron induced reactions, free neutron decay). Both, the Grand Unified Theories and Sakharov´s conjecture, require T-violating amplitudes that are orders of magnitude larger than what can be accommodated in the present Standard Model of particle physics. But, still, it seems that another generation of experiments is needed to obtain a decisive answer.

In recent years, neutron optics has provided us with powerful new methods to test various basic symmetries with high accuracy. In the case of P (= Parity) - symmetry it was found that at certain neutron-nuclear resonances there exist very efficient enhancement mechanisms within the nucleus which increase the weak P-violating amplitudes by several orders of magnitude. For instance, in the case of the 0.73 eV neutron p-wave resonance of ^{139}La, the P-violating neutron-optical dichroism effect amounts to several percent, while only a 10^{-7} effect is expected from naive weak interaction theory. There are good reasons to believe that the same enhancement mechanisms are effective for T-violating amplitudes, should there be any.

A new method is proposed to search for both P and T-violating amplitudes in such resonances. This method tests whether, within matter, changes in neutron polarisation from positive to negative helicity are the same as changes from negative to positive helicity, when these operations are performed on neutrons in resonance with the nuclei. This experiment can only be done at a source like ESS with an under-moderated pulsed epithermal neutron beam of high peak intensity, with widely tunable energy, and with sharp timing (< 20 µs time width at 50 Hz repetition rate). With such a source, the present sensibility for T-violating amplitudes can be increased by orders of magnitude, and there is good hope that both the question of the matter-antimatter asymmetry of the universe and the question of grand unification can get a decisive answer.

So far the description of possible particle physics experiments on the undermoderated beam line. The potential of **nuclear physics** with epithermal and high energy neutrons was explored in a recent three volume investigation by a Los Alamos group. A number of very interesting problems was addressed in this work, some of which are listed below.

As was already pointed out in the ESF survey, one of the main goals of nuclear physics is of very general interest, and is in no way limited to the strong nuclear force: This goal is the description of a mesoscopic quantum system with an intermediate number of a strongly interacting particles. This is one of the most difficult theoretical problems in physics. Nuclear physics is best suited to contribute to the solution of this problems, as it provides many tools and is able to extract copious and readily detectable signals. Some of the nuclear physics questions that can be addressed with a fast neutron beam are the following:

- What is the signature of a mesoscopic quantum system whose classical counterpart is chaotic? In the field of quantum chaos, a number of very interesting but so far unproven conjectures have been proposed, whose validity still waits for more experimental evidence.

- In what way does the transition from a mesoscopic regular quantum system proceed to a chaotic quantum system?
- How does a mesoscopic strongly interacting quantum system reach its equilibrium? This question can be studied by various pre-equilibrium reactions with fast neutrons.
- Was there an inflationary period in the early phase of the big bang? It is believed that the electroweak phase transition has led to an almost instantaneous blow up of the early universe from a very small to a very large scale. In order to differentiate by observation between the inflationary and the standard big bang models, one needs to know the precise temperature dependence of a number of neutron induced reactions, which are essential for primordial element abundances. Some of these experiments are extremely difficult, but should be addressed with ESS as precisely as possible.
- How are the heavier elements produced in stellar processes? Here are many open questions, in particular: how were some "stellar bottle necks" circumvented? Or, what were the time scales, temperatures, and particle fluxes involved in this process? Also, a neat separation between isotopes produced in the big bang and isotopes bred in the stellar environment is needed to decide the question of inflationary versus conventional big bang genesis.

There are many more interesting questions in this general field. For instance, interestingly, neutron-proton electromagnetic Bremsstrahlung is expected to be much larger than proton-proton Bremsstrahlung. Fast neutron-deuterium reactions are expected to shed more light onto the intricate three body quantal problem. Finally, Doppler broadening and recoil free absorptions at neutron resonances could be exploited both in solid state and applied physics.

A third use of this fast neutron beam would be in **applied physics**. Here we propose three **flagship** applications.

3.3 Element-sensitive neutron tomography

Recently, in Garching it was shown that even with a rather weak thermal neutron beam one can produce three-dimensional neutron tomographies with high spatial resolution (200 µm). When one uses this method with an epithermal neutron beam with energies of up to, for instance, 400 eV, then one can turn this method into truly isotope, i.e. element sensitive tomography. By wiggling the neutron energy over a neutron resonance one can image the three-dimensional distribution of almost any element beyond element number $Z = 23$. This method could be used not only for the destructionless investigation of small engines and devices, but also for in situ investigations of chemical processes, for instance in an electrical battery.

3.4 Temperature-sensitive neutron tomography

As is well-known, most neutron resonances have a width of several tenth of eV, or less. Again, by wiggling over the specific neutron resonance, one can obtain a three-dimensional tomography of a temperature distribution, separately for each element. The temperature distribution of technically important alloy components like molybdenum, tungsten, tin, tantalum or niobium, can be obtained in this way.

3.5 Element-sensitive neutron autoradiography

Neutron autoradiography is a well established method to image the internal structure or thin sheets of matter, for instance of artistic paintings of silicon chips. Also this method could be made element-sensitive, by using position-sensitive electron detectors for image formation, in temporal coincidence with element specific γ- rays detected in a non-position sensitive large γdetector.

Further imaging methods can be developed by using state-of-the-art 4π detection systems, as they are in widespread use in medical research and diagnostics.

There are many more topics in applied physics and engineering that can be addressed with nuclear physics methods. In the ESF report, we have grouped them into the four general fields:

- Structure analysis
- Element analysis
- Structure modification
- Element transmutation

Some of these topics will be addressed in other sections of this survey. Here, we only want to express our general feeling that this field of industrial applications of neutron-nuclear methods is largely underexplored.

In view of the large amount of work possible with an epithermal neutron beam, one should discuss the question whether one such guide will be sufficient.

4. High-resolution thermal beam for neutron-interferometry

Neutron interferometry is a powerful tool for precision measurements of scattering lengths and for studies in quantum mechanics and measurement theory. The topics addressed in the field of neutron optics have been listed in the recent ESF report. They were grouped into the following subfields:

- Wave optics
- Spin optics
- Topology
- Gravitation
- Quantum optics
- Time optics versus space optics
- Devices

Many new, interesting, and often useful ideas exist for further progress in neutron optics and neutron scattering techniques. Therefore, a special work place for neutron interferometry, with built-in vibration suppression, will be indispensable at ESS.

5. Beam positions for yet undiscovered neutron uses

It should be wise to leave, close to the source, beam ports with the highest possible cold and/ or thermal neutron flux free for future uses. This beam is not necessarily meant to serve the many topics listed in the domain of particle, nuclear and applied physics and engineering, but rather to keep the possibility open to realise any unconventional idea that may come up during the next decade.

In the same spirit, it should be good to foresee a through-going neutron beam hole, which gives an almost background-free sight onto a high density neutron cloud.

6. Other particle sources

Besides neutrons with an energy range of 16 orders of magnitude, a spallation source provides also high-intensity sources of gammas, electrons, positrons, four kinds of neutrinos (separated in time), two kinds of muons (polarized), three kinds of pions, and of fission products covering a large part of the table of isotopes. The list of possible applications of such particle beams cannot be covered here. Therefore, we have picked out just one field of research, namely muon particle physics at intermediate energies.

6.1 Topics in muon particle physics

The muon is a point like heavy leptonic particle. Here we present two main topics in muon particle physics: precise tests of the standard model, and the accurate determination of fundamental constants. These high precision experiments all require good counting statistics. Therefore, new sources with high muon fluxes are indispensable for further progress.

In muon particle physics, measurements are done both on the properties of the **free muon**, like:

- mass
- magnetic moment
- magnetic anomaly (g-2)
- lifetime
- muon decay spectra and correlations
- muon Bremsstrahlung
- rare and exotic decay modes

and on properties of **muonic systems** and reactions, like:

- muonium (μ^+e^-)
- muonic atoms
- capture of negative muons in nuclei
- muon neutrinos
- muon induced fusion and fission

As is well known, precision measurements on the **free muon** provide for very accurate tests of quantum electrodynamics and of the weak interaction. For instance, there exist interesting proposals to measure g-2 with muons confined in a Penning trap. Further, from the precision measurement of the muon lifetime, the Fermi coupling constant of the weak interaction is deduced. Also of high current interest is the search for right-handed contributions to the left-handed muon decay amplitudes.

The experiments on **muonic system** provide for precise tests of bound state quantum electrodynamics. Note that in studies of the hydrogenlike muonium atom (μ^+e^-), more than one order of magnitude higher accuracy can be reached than in natural hydrogen (p^+e^-), simply because the muon, unlike the proton, has no internal structure. For spectroscopy on muonium and muonic atoms, pulsed muon beams are better suited than continuous muon beams, especially when coincidences with pulsed laser or microwave radiation are required.

Among the muonic atoms, muonic hydrogen ($p^+\mu^-$) is of particular interest. Precision measurements of its ground state hyperfine splitting and its Lamb shift are expected to yield improved information on the proton's electric and magnetic form factors. Such measurements are important for the understanding of the strong interaction at low energy, and as empirical input for corrections necessary in hydrogen spectroscopy.

In muonic atoms, electroweak interference effects are much larger than in electronic atoms, because of the short range character of the weak interaction and the reduced size of the muonic atoms. Of particular interest is the case of $(^4\text{He}\ \mu^-)^+$ where electroweak effects could be observed in the spontaneous 2S-1S single photon decay. Also, the 2S lifetime is of interest to searches for an electric dipole moment of the muon. Muonic ^{3}He, if polarized, could be used to search for T-invariance violations in nuclear muon-capture. In the past, such experiments could not be performed due to the lack of suitable muon sources.

A promising new technique is the production of slow muon beams from frozen noble gases. These beams have an energy distribution as narrow as a few 10 eV. They will allow applications in surface studies in condensed matter research, as well as the efficient production of fundamental muonic atomic systems.

In summary, there is a rich program in particle, nuclear, and applied nuclear physics waiting for ESS.

Scientific case for a muon facility at the ESS

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Prologue

This report will provide the scientific motivation and future perspectives for the use of muons (μSR) in condensed matter science, materials research and physical chemistry in Europe with particular reference to the ESS project.

The diversity of phenomena now studied by μSR is a reflection of the diversity of the μSR user community. This community has seen a remarkable growth over the last two decades. In Europe its growth has been made possible by the construction of the meson factory at the Paul Scherrer Institute (formerly SIN) in Switzerland and has been nurtured further by EU financial support for new high intensity pulsed muon facilities at the UK's spallation neutron source, ISIS. The growth of theμ SR -community and the number of active experiments at these two currently existing muon sources in Europe, as documented in the enclosed graph, testifies to the increasingly important role that μSR spectroscopy has assumed in the above mentioned fields. A continuation of the growth can be expected as the use of the μSR -technique spreads to European countries so far only little engaged in μSR-research. Estimates show that, e.g. in Spain the number of groups using muons is likely to increase from 2 at present to 20 in the future, provided that sufficient beam times and support can be made available.

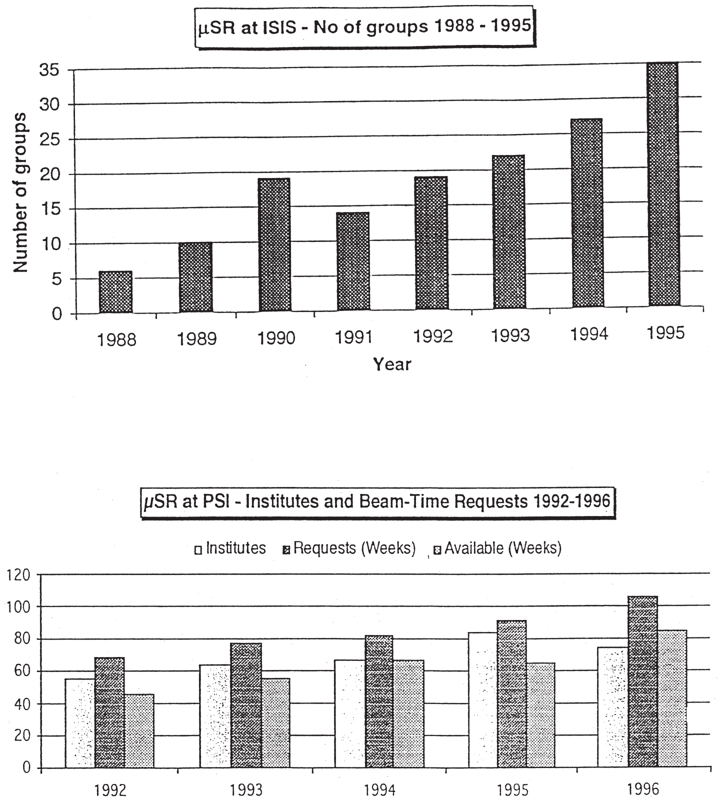
The juxtaposition of muon and neutron facilities at ISIS has enabled the complementarity of μSR and neutron scattering to be explored and exploited in greater depth than ever before, whilst also exposing a wider scientific community to the enormous potential of muon beam techniques. The ISIS model, of adjacent muon and neutron scattering facilities, is one that the European Spallation Source should seek to emulate. In this way the continuing cross fertilization of the muon and neutron communities will be ensured, and the impact of muon and neutron techniques enhanced. The further development of μSR spectroscopy using not only positive but also negative muons and the exploitation of its vast potential depends crucially on the long term availability of powerful muon sources. The European Neutron Spallation Source, besides its main purpose to provide neutron beams of unprecedented intensity and quality, could also serve as a muon source with superior characteristics as compared to present day facilities, being able to satisfy the needs of a growing community for increasingly more powerful and sophisticated facilities.

The possible availability of a high intensity and pulsed muon source is not only relevant for muon applications but would also allow a new generation of fundamental studies of muon physics, impossible at present (see theme 9). Therefore this report includes also a section (see appendix I) on future perspectives of an ESS muon source in basic muon physics.

Sections II-VII below document the diversity of phenomena studied successfully by μSR -spectroscopy. The presented exemplary examples are furthermore chosen to highlight some of the achievements, in particular the very much recognized results on high T_c superconductors and heavy fermion systems (see sect. 4.2), quantum diffusion of light interstitials (see sect. 5.1.1) and reaction kinetics and structure of free radicals not only in liquids but also in the gas phase (see sects. 5 and 6).

Concerning the future role of μSR at the ESS we think that the *use of ultra slow muons can be identified as a key area of research.*

Finally in the appendix some ideas are presented on how different muon sources of different kinds could be accommodated within the ESS accelerator scheme. It is deemed important that the requirements for powerful μSR facilities are taken into account in the ESS planning from an early stage on.



Development of μSR activities at ISIS and PSI in recent years.

Much of the motivation to building an advanced source like the ESS rests on the faith that tomorrow's scientists will have better ideas than today's experts can imagine, but they can do their job only if we are wise enough today to provide them with the appropriate tools.

1. Introduction

In this document we shall demonstrate that μSR -spectroscopy is an indispensable technique in condensed matter science: it ranks in importance alongside NMR, ESR, Photoemission, Raman spectroscopy, neutron scattering, X-ray scattering etc. and will undoubtedly remain so in the future. μSR has tremendous potential as a tool with which current scientific and technological problems can be approached. It is also an evolving technique which will be readily adapted as new problems unfold. Both these aspects of the μSR technique will be discussed in the following sections, but first we shall consider some generalities of μSR itself.

1.1 Muon states in matter

Implanted in matter muons are present either in a diamagnetic state (quasi free μ^+) or in a paramagnetic state where the μ^+ is coupled to an unpaired electron (i.e. in muonium (μ^+e^-), or in muonated chemical radicals). In the first case, the muon may serve as a more or less passive spectator (for instance in the study of magnetic phenomena), in the second case it is the electron which could act as an extremely sensitive probe passing on what it experiences to the μ^+ by way of its hyperfine coupling (e.g. muonium in semiconductors). A different avenue of research is opened up by the fact that muonium or muonated species take part in chemical reactions and molecular transformations which can be followed by appropriate means. In fact, muonium or muonated radicals may serve as substitutes for atomic hydrogen or the corresponding radicals, respectively. But also the "free" μ^+, e.g. in metals, is of interest by itself since again it may serve as a substitute for protons and other light impurity atoms.

1.2 Samples

The μSR technique is universally applicable: muons can be implanted in any material at any temperature (implantation of μ^+ does not heat up the sample). This is in marked contrast to techniques such as NMR, Mössbauer spectroscopy and γ PAC for which specific target nuclei are required. Moreover the implantation of muons does not lead to lasting radiation damage or activation of the sample.

1.3 Muons as magnetic probes

Muons are ideal magnetic probes, since they are spin - $^1/_2$ particles and not subject to quadrupolar interactions. The magnetic moment of the muon is larger than any nuclear magnetic moment and hence the μ^+ is a very sensitive probe of extremely small magnetic fields, such as those due to nuclear or very small atomic moments.

1.4 High sensitivity of μSR

The μSR technique rests on the parity violating weak decay of the μ^+ which leads to an asymmetry of the positron decay distribution of ~ 30%. This value is much larger than that usually observed in nuclear β-decay or in the anisotropic distribution of γ-rays. Moreover muon beams possess a natural spin polarisations of close to 100% and this polarisation is fully available at the moment of implantation independent of the sample's temperature. Hence μSR is much more sensitive than, for example, γ -PAC, γ-PAD or β-PAD.

1.5 Accessible time window

The time window accessible by μSR is determined by the muon life time of 2.2 μs and by the time resolution achievable in a spectrometer (~ 1 ns when using a DC beam). Compared to NMR, muons are superior probes if one deals with very fast relaxation phenomena. The dynamical range covered by μSR extends from the neutron window down almost to the ac-susceptibility window, depending on the magnitude B of fluctuating magnetic fields (with fluctuation rate $1/\tau_c$) at the μ^+ site ($10^4 < \gamma_\mu^2 B^2 \tau_c < 10^8\,s^{-1}$, γ_μ = muon gyromagnetic ratio. For a typical B of ~ 1 kG this translates into $10^{-13} < \tau_c < 10^{-9}$ s).

1.6 Inhomogeneous features

The total spin polarization of muons at the instant of implantation is usually very well determined. The subsequent evolution of different components in the μSR signal can then unambiguously be related to absolute volume fractions, associated with different domains, structures, magnetic phases or chemical species. This permits the study of the evolution of inhomogeneous features in a given sample.

1.7 Techniques

μSR is an acronym for muon spin rotation, relaxation and resonance. Each of these techniques is uniquely optimised for a particular class of problems, thereby providing exceptional versatility.

(a) Transverse field (TF)- μSR

Standard technique for observing the Zeeman and/or hyperfine splitting of μ, muonium and muonated radicals. Good for study of static features in magnetism (e.g. vortex lattice in type II superconductors), determination of energy levels.

(b) Radio-frequency muon-spin resonance μMR
Corresponds to NMR detected by nuclear radiation. Used mostly on muonium and muonated radicals, particularly in semiconductors.

(c) Zero field μSR
No external magnetic field is applied. Important method to study weak magnetism phenomena, μ^+-diffusion, spin glasses, magnetic order etc. Enables one to observe single crystal like spectra from powder samples.

(d) Longitudinal field μSR
Study of spin lattice relaxation phenomena, critical fluctuations etc.

(e) Avoided level crossing spectroscopy
Applicable to μ^+ in metals and insulators, if nuclei are subject to quadrupolar or magnetic interactions. Most intensive use on muonium and muonic radicals if some additional hyperfine interaction (e.g. ligand hyperfine interaction) is present. Static and dynamic features can be studied (e.g. rotation of C_{60}).

1.8 Instrumentation, sample environment

Present day spectrometers are equipped with cryostats ($10\ \text{mK} \leq T \leq T\ 300\text{K}$), furnaces ($T \leq 2000$ C), magnets ($H \leq 5$ T) and pressure cells ($p < 12$ kbar). Pulsed magnets and electrical fields are being tried and considered at pulsed muon sources. Laser and other light sources have been used to study light induced effects. *In this respect the ESS with its vastly increased pulsed muon intensities can be expected to provide superior experimental conditions.* Knight shift measurements can achieve a precision of ~2 ppm, using NMR field stabilization.

1.9 Ultra slow muons

Some aspects of the μSR technique are still developing in response to the needs of the condensed matter community. The latest development is the construction of ultra slow muon ($10\ \text{eV} \leq E_{kin} < 20\ \text{keV}$) sources at KEK (Japan), PSI and ISIS, the availability of which will extend μSR - spectroscopy to the study of thin films, multilayers and eventually even surfaces.

μSR has taken more than 20 years to reach the present state of sophistication and diversity. There is no doubt that existing muon techniques will be at least as important in 20 years as they are now. It is equally certain that novel muon techniques such as those associated with ultra slow muons, will mature and assume a secure place alongside them in the condensed matter scientists' armoury of experimental tools.

2. Muon spin rotation spectroscopy in metals

2.1 Introduction

When implanting μ^+ into metals two aspects are generally involved. The first concerns the behaviour of the μ^+ and μ^+-induced features. Since the μ^+ may be considered a light isotope of the proton this aspect concerns more generally the hydrogen-in-metals problem. The μ^+ can be used as a hydrogen substitute to model the hydrogen behaviour particularly in the dilute concentration limit. Metal-hydrogen systems are the simplest alloys and amenable to theoretical treatment. With muons one studies incipient features on a microscopic scale, such as the development of magnetism, upon hydrogen loading (R. Feyerherm et al., Z. Physik B99 (1995) 3). The other aspect concerns intrinsic properties of the host material where the muon is used as a passive probe.

2.2 Past achievements

2.2.1 Modelling of "hydrogen in metals" phenomena with μ^+

a) *Study of static features and mechanisms which determine the properties of metals, metal alloys and intermetallic compounds when charged with hydrogen (or other light impurities)*
   - electronic state of μ^+ (hydrogen) impurity centre (see e.g. F.N. Gygax et al., J. Less Common Met. 101 (1984) 97).
   - lattice site of μ^+ (hydrogen) (see e.g. A. Amato et al., contribution to µSR'96 (Nikko, Japan).
   - lattice relaxation around μ^+ (hydrogen) (formation of small polaron) (H. Schilling et al., J. Phys. F: Met. Phys. 12 (1982) 875).
   - disturbing effects on neighbour atoms etc., e.g. change of crystal field splitting, change of local symmetry, modification of exchange coupling, charge transfer, change of spin density.

b) *Studies concerning dynamic features of μ^+ (hydrogen) in metals*
   - μ^+ (hydrogen) diffusion (quantum diffusion, short and long range diffusion, isotope effects - for more details see sect. 5.1.)
   - μ^+ (hydrogen) trapping and detrapping from defect sites (see also 2.2.4.)

2.2.2 Study of intrinsic electronic features of the host material

The information is either deduced from Knight shift or line width measurements.µSR-spectroscopy complements very favourably NMR and Mössbauer spectroscopy owing to its sensitivity and general applicability. But note that the μ^+ are usually located at an interstitial site and thus probe the host material from a different perspective.

- Mixed valences, valence transitions, valence fluctuations, e.g. in Ce and $Ce_{0.74}$ $Th_{0.26}$ (H. Wehr et al., Phys. Rev. B29 (1984) 638).
- Temperature dependence of the electric field gradient in the itinerant intermetallic compound MnSi which is well in agreement with predictions based on Moriya's SCR theory of spin fluctuations (R. Kadono et al., Phys. Rev. B48 (1993) 16803).
- Change of electric field gradients in ScH as a function of hydrogen concentration. This is the first such observation (F.N. Gygax et al., J. Alloys a. Compounds 231 (1995) 248).
- First demonstration of the recurrent appearance of oppositely magnetized domains due to the de Haas van Alphen mechanism in diamagnetic Be (G. Solt et al., Phys. Rev. Lett. (1996) in press)
- Van Hove singularities in the electronic density of states and the appearance of Lifshitz "anomalies" in the μ^+-Knight shift observed in Cd (W. Studer et al., Phys. Rev. B30 (1984) 2414).
- Unprecedented observation of an effect of an external magnetic field on the electric field gradients in the semimetal Bi (E. Lippelt et al., Phys. Rev. Lett. 67 (1991) 2525).

- Determination of the paramagnetic susceptibility in the superconducting state of type II superconductors via μ^+-Knight shift measurements, provides information on the symmetry of the superconducting state, effects of spin-orbit scattering and pair breaking (e.g. in UBe_{13} (R.H. Heffner et al., Phys. Rev. B39 (1989) 11345, in UPd_2Al_3 (F. Feyerherm et al., Phys. Rev. Lett. 73 (1994) 1899).
- Determination of superconducting charge carrier density from measurements of the London penetration depth in type II superconductors (see sect. 4.2).

2.2.3 Study of dynamic and static features of magnetic properties

(see separate section 4)

2.2.4 Study of lattice defects, induced by radiation, thermal or mechanical treatments, role of annealing. Study of amorphous and nanostructured materials.

Here the μ^+ is used to trace the creation, motion and disappearance of various defects, in particular monovacancies under various conditions. Work on quenched, deformed, electron and neutron irradiated Al and Fe are reported by Dorenburg et al., Z. Physik B31 (1978) 165, W.J. Kossler et al., Phys. Rev. Lett. 41 (1978) 1558, D. Herlach, in *Recent developments in Condensed Matter Physics*}, Vol. 1, edit. by J.T. Devrese (Plenum, 1981), Möslang et al., Phys. Rev. B27 (1983) 2674 and G. Solt et al., in *Effects of Radiation on Materials:* 14th International Symp. (Vol. III), ASTMSTP 1046 (1990) 180. The latter work on FeCu alloy was part of a larger study on neutron radiation induced corrosion of reactor vessel steels. So far the power of µSR to study lattice defects and their thermal behaviour and related ageing effects of alloys of technological interest has not been exploited at all to its full potential. We expect that this will be a subject of considerable interest in the future in particular in conjunction with amorphous and nanostructured materials and quasi crystals, all of which have received only little attention so far (e.g. D.R. Noakes and P. Mendels, Hyperfine Interactions 85 (1994) 299). The local probe nature of µSR, however, may be particularly suited to study certain aspects of such system.

2.3 Perspectives for the future

The problem of predicting a future role for µSR in the study of metals and alloys is as intractable as predicting the future of metals and alloys research itself. However, it is clear from the examples provided above that µSR is an exceptionally versatile technique which can provide information on a wide range of materials properties. Whether future research programmes move on to new metals and alloys, or whether there will be trend towards consolidation of our understanding of existing materials, there is no doubt that µSR spectroscopy will play a vital role.

It should also be noted that it is the field of metals and alloys research that µSR perhaps might find its first industrial role. For example, given the μ^+'s disposition to be trapped at lattice defects of various kinds, one can imagine that µSR may be a very sensitive and non-destructive technique in the quality assessment of metals and alloys of technical interest. One could even imagine large scale quality testing of e.g. steel parts with respect to corrosion and embrittlement, e.g. the development of micro cracks at a very early stage. The mentioned work on neutron irradiated FeCu-alloy is very encouraging in this respect and one may foresee here an important future area of µSR-applications, in particular at advanced muon sources.

Entirely new possibilities would arise from the availability of high intensity ultra slow muon beams (see sect. 8).

3. Research on semiconductors with μ^+

Implanted muons again mimic the behaviour of hydrogen impurities. This is of considerable current interest in view of the effect of trace concentrations on important semiconductor properties, namely their electronic and optical functions. Thus it is now understood that hydrogen can passivate electronically active dopants (in crystalline material this is usually an inadvertent and unwanted effect, although it may in the future be turned to advantage; in amorphous silicon, on the other hand, the passivation of dangling bonds by hydrogen is essential to the production of electronic grade material). There is now also an increasing awareness that isolated hydrogen centres are electrically active in their own right, acting as either donor or acceptor according to the precise lattice site adopted.

Early studies of Si, Ge, GaAs and GaP, revealed an unexpected example of metastability in that two distinct paramagnetic states of muonium were found: these have subsequently been assigned to neutral muonium sited at a tetrahedral interstice (Mu^0_T) and, remarkably, at a bond-centre (Mu^0_{BC}) . This latter site was quite unanticipated but, with the support of *ab initio* calculations stimulated by the µSR findings, is now generally accepted to be the more stable state for hydrogen, at least in silicon. This is one of the classic examples of a µSR result upsetting conventional wisdom. More recent experiments have been concerned to make a similar identification of the diamagnetic states which coexist with the paramagnetic. Where these are enhanced by thermal excitation or doping it seems likely that they represent ionic counterparts, for which theory finds the site preference to be much more pronounced. Thus the negative ion (i.e. the doubly occupied defect level) is expected to be stable only at the tetrahedral site and a signature of this Mu^-_T state has just been obtained in heavily doped n-type GaAs [Chow et al, Phys Rev B 20 (1995) 14762]; this is in fact the first clear indication from any spectroscopic method of the existence and potential role of hydride ions in semiconductor environments. The positive ion, analogous to the trapped proton, is expected to be stable only at the bond-centre in Si (Mu^+_{BC}) but may also exist at the electrostatically more favourable of the two *T* sites (T_V) in the slightly ionic compound *III-V* semiconductors. Spectroscopic signatures of all these various states will undoubtedly be obtained shortly.

A significant recent advance over the purely spectroscopic studies, important as they are for the determination of crystallographic sites and local electronic structures, is the current understanding of the transitions or conversions between these various states which may be induced thermally [Chow et al, Phys Rev B 47 (1993) 16004] and optically [Kadono et al, Phys Rev Lett 73 (1994) 2724], and the manner in which each state interacts with charge carriers. In silicon, the dynamics have now been elucidated in considerable detail, to the point where a consistent set of energy levels and barriers has been determined which is able to account for all the observations of processes such as ionization, charge and spin exchange with conduction electrons, interstitial diffusion etc., in samples with widely different levels and types of doping [Kreitzman et al, Phys Rev B 51 (1995) 13117; Lichti, Phil Trans A 350 (1995) 323].

These studies reveal a degree of complexity in the interplay between the sites and charge states of interstitial hydrogen which had not been anticipated by the semiconductor community and is attracting considerable interest; it seems likely that they will provide the clue to current problems such as the nature of the elusive hydrogen transport states, and the controversy as to whether hydrogen constitutes a " negative-U" centre in silicon (roughly stated, whether its acceptor level lies higher or lower than its donor). Aims for the immediate future are to raise the understanding of these processes in other materials, e.g. Ge and GaAs, to the same level of sophistication as has been achieved for Si and to understand why a variety of ionic states, but no neutrals, are observed in other important semiconductors, such as InP and GaSb. The first indications that interstitial muons, and by implication protons, may act as electron-hole recombination centres have, for example, recently been obtained in GaAs.

To date, μSR studies have been most successful, by virtue of the observation timescale, in characterising the isolated muonium states, located at intrinsic sites; another immediate aim will be to explore the possibilities for studying the interaction and pairing with dopants, mimicking the passivation process, and with other impurities, notably oxygen.

In this context, and in view of the primary ESS pulse structure, the power of longitudinal-field techniques which have no stringent requirements for time-resolution, is worth emphasizing. These include RF and level-crossing resonance and also the *repolarization* method, which all benefit from integral-counting data acquisition at high rates. The latter technique also works in cases where the transverse-field rotation signal is broadened beyond

detection. By implication, the discovery of anisotropic muonium centres (whose hydrogen counterparts may also be invisible to ESR) may be anticipated in other amorphous, glassy or otherwise disordered material.

Particularly exciting is the prospect of extending all such studies, which for the moment involve muons implanted into the bulk of the material, to multilayers and surfaces, when a Facility providing ultraslow muons becomes available. The sensitivity and selectivity of the μSR methods, coupled with the importance of hydrogen in connection with surface states and restructuring, makes muonium studies mandatory in this area, as soon as they become possible.

4. μSR studies of magnetic and superconducting systems

4.1 Introduction

The last decade has seen a tremendous explosion in the number and scope of muon spin rotation and relaxation studies of magnetic and superconducting systems. Indeed the μSR technique has been at the forefront of experimental investigations of the decade’s most dramatic discoveries in condensed matter science, namely high temperature superconductors, the buckminster fullerenes and organic magnets. It has provided unique and novel insights into the phenomena associated with these classes of materials. In addition μSR has continued to play a major role in contributing to our understanding of the mechanisms responsible for heavy fermion behaviour, spin fluctuations and moment localisation in transition metals, spin glass freezing and magnetic critical phenomena. With respect to spin fluctuations and critical phenomena it is worth pointing out that with μSR one measures in the limit of very small energy transfer ($\omega \cong 0$) and small momentum transfer ($\mathbf{q} \cong 0$) and hence should complement neutron scattering most ideally (see e.g. A. Yaouanc et al., Phys. Rev. B53 (1996) 350). For recent reviews see A. Schenck and F.N. Gygax in *Handbook of Magnetic Materials*, Vol. 9, chapter II, edit. by K.H.J. Buschow (Elsevier, 1995); A. Amato, Revs. Mod. Phys. 1996, in press).

4.2. Some recent successes

As a starting point for the discussion of the prospects for muon techniques in the study of magnetic and superconducting phenomena, it is useful to consider some recent and dramatic successes in muon science. The following list is illustrative, but by no means exclusive: we have selected particularly those outstanding developments which have opened the way for future muon programmes, and which constitute the starting point for "next generation" systematic muon studies of magnetic and superconducting phenomena. It should also be noted that many of the following breakthroughs have been made by European scientists working at European sources.

- The first evidence of a magnetic ground state in the high temperature superconducting cuprates (see e.g. Y.J. Uemura et al., Phys. Rev. Lett.59 (1987) 1045).
- Precise determination of flux distributions and penetration depths in high temperature and other superconductors (e.g. M. Weber et al., Phys. Rev. B48 (1993) 13022; T. Rieseman et al., Phys. Rev. B52 (1995) 10569).
- Provision of a classification scheme for superconductors based upon fundamental physical parameters of the superconducting ground state determined via μSR (Y.J. Uemura, Physica C185-189 (1991) 733; C. Bernhard et al., Phys. Rev. B52 (1995) 10488).
- The first unambiguous characterisation of flux lattice melting and dimensional cross-over in high temperature superconducting cuprates (S. Lee et al., Phys. Rev. Lett. 71 (1993) 3862).
- The first experimental observation of the theoretically predicted evolution of non-exponential spin autocorrelation functions in canonical spin glasses and frustrated magnets above the freezing temperature (I.A. Campbell et al., Phys. Rev. Lett. 72 (1994) 1291).
- Demonstration of the complementarity of μSR and inelastic neutron scattering in characterising 3d transition metal spin fluctuations at the boundary of the local moment and itinerant electron limits (R. Cywinski and B.D. Rainford, Hyp. Int. 85 (1994) 215).
- Characterisation of moment formation and magnetic order in heavy fermion compounds: e.g. unexpected evolution of short range small moment magnetic order without a clear cut cooperative phase transitions in the Fermi liquid archetypical heavy fermion compound in $CeAl_3$ (S. Barth et al., Phys. Rev. Lett. 59 (1987) 2991); e.g. ultra small moment (10^{-3} m_B) magnetic order in $CeRu_2Si_2$ (A. Amato et al., Phys. Rev. B50 (1994) 619).
- Characterisation of moment formation and magnetic order in C_{60} based compounds, e.g. in the soft ferromagnet (TDAE) C_{60} (A. Lappas et al., Science 267 (1995) 1799).
- Clarification of the type of coexistence of magnetic order and superconductivity in the heavy electron superconductors $CeCu_2Si_2$ and UPd_2Al_3 (R. Feyerherm et al, Physica B206 & 207(1995) 596; Phys. Rev. Lett. 73 (1994) 1849).
- The use of μSR in removing ambiguities in spin structures determined by powder neutron diffraction (J.I. Garcia-Munoz et al., Phys. Rev. B51 (1995) 15197).
- Determination of internal field distributions at mK temperatures in purely organic ferromagnets (*p*-NPNN and 3-QNNN) (F. Pratt et al., Synth. Met. 61 (1993) 171) and characterisation of the spin density wave in organic metals (e.g. $BEDTTTF_2\,KHg(SCN)_4$) with amplitudes as small as $3 \cdot 10^{-3}\,\mu_B$ (F. Pratt et al., Phys. Rev. Lett. 74 (1995) 3892).

Current international interest is focused upon the scientifically and technologically important Giant Magnetoresistive (GMR) effect in manganite compounds, magnetic order in nanostructured magnetic clusters and GMR and magnetic exchange in magnetic multilayers. Proposals for muon beam time to study the first two areas have already been submitted to muon facilities. The third area must wait for developments in slow polarized muon techniques. It is clear that in the near future μSR will play a vital role in elucidating all three phenomena.

4.3 The development of μSR programmes

4.3.1 Moment localisation and spin fluctuations

One of the early successes of experimental μSR was the characterisation of longitudinal spin fluctuations in the itinerant electron ferromagnet MnSi (R.S. Hayano et al., Phys. Rev. Lett. 41 (1978) 1743), in which it was shown that the temperature dependent spin relaxation closely follows the form predicted by Moriya's self consistent renormalisation (SCR) theory of spin fluctuations (e.g. T. Moriya, *"Spin Fluctuations in Itinerant Electron Magnetism"* Berlin: Springer (1985)). Despite this success, and the growing acceptance of Moriya's unified SCR theory, there have been relatively few further μSR studies of moment localisation and the onset of long range magnetic order in itinerant transition metal magnets. However, a full understanding of these phenomena is essential to modern magnetism and the provision and accessibility of high quality μSR facilities will inevitably lead to such an understanding. Moreover, the growing theoretical interest in systems in which predominantly antiferromagnetic spin fluctuations are superimposed on a topologically frustrated lattice presents a significant challenge to μSR, a technique which provides a unique time window for studying such phenomena.

4.3.2 Heavy fermion physics

Heavy fermion physics has already benefited immeasurably from the insights provided by μSR techniques. The exceedingly small magnetic moments (10^{-3} μ_B) often associated with the heavy fermion state are still largely beyond the sensitivity of neutron measurements. However, μSR can provide information not only on the configurations of such moments but also upon their dynamics. It is likely that ordered magnetic states associated with even smaller atomic moments may exist: μSR is essential to their detection and characterisation. The interplay between the magnetic and superconducting states in strongly correlated systems is complex. μSR in transverse geometry affords the possibility of measuring unambiguously the fundamental parameter of the superconducting state, the penetration depth λ. Several heavy fermion systems are characterised by a λ in excess of 1000 nm. Such a λ is beyond the range of most current μSR facilities. However the ESS should offer the possibility of determining λ's of this magnitude either by providing increased count rates with the associated gain in sensitivity over a wider time range, or through a direct profiling of the *surface of the heavy fermion superconductors* using ultra slow muon techniques.

4.3.3 Organic magnets

Organic magnets are of enormous current interest. It has long been predicted that systems based only upon *s*- and *p*-electrons cannot exhibit long range magnetic order (exception: solid O_2). However several truly organic systems have recently been found to display spontaneous magnetic order associated with extremely small moments albeit at modest temperatures. Other organics exhibit *spin density wave ordering, semi-metallic conductivity and even superconductivity* at relatively high temperatures. Such functionality is not yet technologically significant, although a deeper understanding of the underlying phenomena will undoubtedly lead to considerable materials development. μSR is already playing a significant role in the characterisation of these systems and will continue to do so.

4.3.4 The superconducting ground state

The superconducting ground state is characterised by the penetration depthλ , which in turn is related directly to the number density and effective mass of the superconducting electrons. Perhaps the greatest contribution of μSR to solid state science over the last ten years has been in the direct and unambiguous mapping of the flux distribution in a wide range of superconductors. These measurements are significant both scientifically and technologically. On the one hand they have led to a remarkable classification scheme for superconductors, in which each family of superconductors can be characterised in terms of its critical and Fermi temperatures (Y.J. Uemura, Physica C185-189 (1991) 733), and on the other they have led to profound and technologically important insights into the phenomenon on flux lattice melting in *high temperature superconductors*. The development of cold muon facilities at the ESS will allow these studies to be extended to the distribution of flux at the *surface of bulk and thin film superconductors.*

4.3.5 Spin glass systems

Spin glass systems are amongst the most widely studied magnetic systems of the last twenty years. Theoretical calculations and simulations have predicted Kohlrausch or stretched exponential relaxation of the spin autocorrelation functions over a wide range of temperatures from $4T_g$ down to T_g (T_g = spin freezing temperature). Few experimental techniques other than µSR offer an appropriate time window with which such behaviour can be quantitatively probed. Recently µSR has been used to characterise a wide range of spin glass and *superparamagnetic systems*, and the Kohlrausch relaxation is found to be mirrored closely by the muon spin relaxation itself (e.g. I.A. Campbell et al., Phys. Rev. Lett 72 (1994) 1291). It is suggested that the muon spin relaxation function may be used to directly extract details of the evolution of the distribution of single atomic spin or cluster spin relaxation spectra, in which case µSR will prove an invaluable tool in the study of systems of great technological importance such as *nanoscale magnetic clusters* and *bulk GMR alloys.*

4.3.6 Nuclear magnetism

Nuclear magnetism has not yet been investigated by µSR techniques although such techniques are ideal probes of low temperature *nuclear spin configurations and critical phenomena*. The provision of ultra low temperature sample environment facilities on the ESS muon beam lines will open up new and exciting possibilities for the study of nuclear magnetism.

5. Testing theories of fundamental dynamic phenomena by means of isotope effects

Dynamics governs fundamental phenomena such as the transport of mass and of heat, chemical reactions and many other processes, in principle, all time-dependent phenomena are mass dependent. It is therefore of central interest in today’s research.

While interactions between static atoms do not depend on nuclear mass, dynamic phenomena are mass dependent. Among all isotopic atoms, the hydrogen isotopes (T,D,H) provide a factor of 3 for the largest conventional mass ratios. This is extended to an unprecedented factor of 27 when the muonium atom ($\mathrm{Mu} \equiv \mu^+e^-$ which, based on its ionisation potential and Bohr radius, clearly should be regarded as a light hydrogen isotope) is included. Any theory of dynamic effects can thus be tested with extreme sensitivity when Mu is compared with H, D, and T, or μ^+ with p^+, d^+, and t^+.

5.1 Past achievements

5.1.1 Quantum diffusion in solids

Diffusion of light interstitial crosses over from a stochastic, thermally activated process at high temperatures to a coherent tunnelling process at lower temperatures. Thus, there is a minimum in the mobility at a certain temperature. Corresponding theoretical predictions were confirmed for positive muon diffusion in copper (C.W. Clawson et al., Phys.Rev.Letters, 51 (1983) 114, R. Kadono et al., in *Perspectives of Meson Science*, T.Y. Yamazaki, K. Nakai and K. Nagamine, eds., North Holland, Amsterdam, 1992), and for Mu diffusion in KCl (R.F. Kiefl et al., Phys.Rev.Letters 62(1989) 792). Quantum dynamics was also found to be responsible for the diffusion of Mu in solid N_2 and in heavy rare gas solids (V. Storchak et al., Phys.Rev.Letters 72 (1994) 3056; V. Storchak et al., Hyperfine Interactions 85 (1994) 117). A theoretical foundation has been given by J. Kondo (in *Perspectives of Meson Science*, T.Y. Yamazaki, K. Nakai and K. Nagamine, eds., North Holland, Amsterdam, 1992).

In solids, the light isotope is normally expected to diffuse faster than the heavier one. For diffusion of H and D in ice this holds at high temperatures, but there is a cross-over, and below 200 K D is faster than H. The effect is ascribed to a bottleneck in the transition state of the jumps between two adjacent sites, which leads to a higher zero-point energy in the vibrations perpendicular to the diffusion coordinate. In contrast, motion of Mu is dominated by tunnelling, so that diffusion of both, D and Mu, have a lower activation energy than that of H. (D.M. Bartels, P. Han and P.W. Percival, Chem.Phys. 164 (1992) 421.)

5.1.2 Diffusion in liquids

Normally, diffusion in liquids is thought to follow Stokes-Einstein behaviour which assumes that diffusion coefficients scale with the inverse radius of the species of interest, but that they are independent of their mass. This contrasts with the behaviour found in gases and in solids, and one expects that the Stokes-Einstein relation should break down when the diffusing solute is small compared with the solvent molecules. It has been verified only recently, based on the analysis of diffusion limited reactions, that the diffusion of H is faster than that of D in liquid water, and in particular, Mu is faster than H by a factor of two. (E. Roduner et al., J.Chem.Soc.Faraday Trans. 91 (1995) 1935).

5.1.3 Chemical reactions

Mu can be both, faster or slower than H by up to two orders of magnitude and more, depending on the nature of a chemical reaction (E. Roduner, Progress in Reaction Kinetics 14 (1986) 1).

$H + H_2 \rightarrow H_2 + H$ in all its isotopic variants is *the* prototype chemical reaction for tests of dynamic theories and of the accuracy of potential energy surfaces. Again, Mu has provided the most sensitive test (I.D. Reid et al., J.Chem.Phys. 86 (1987) 5578).

Reactions over narrow and not too high barriers are dominated by tunnelling. Because of this, Mu was found to be faster than H by a factor > 75000 in a transfer reaction. This is believed to be a world record for a kinetic isotope effect at room temperature (E. Roduner and K. Münger, Hyperfine Interactions 17-19 (1984) 793).

Solvent friction is important when the motion of a charge, atom, or group is fast compared with the reorientation time of solvent molecules. Although known in principle since the pioneering work by Kramers in the early forties, these effects have gained new interest only recently because of the development of experimental techniques which can monitor fast processes. It was found that the nonequilibrium solvation effects effectively quench the tunnelling enhancement of Mu addition to benzene in aqueous solution (E. Roduner and D.M.Bartels, Ber.Bunsenges.Phys.Chem. 96(1992) 1037; B.C. Garrett and G.K. Schenter, in *Structure, Energetics, and Reactivity in Aqueous Solution*, ed. C.J. Cramer and D.G. Truhlar, ACS

Symposium Series 568, Amer.Chem.Soc., Washington D.C., 1994). In this area, µSR experiments provide a valuable alternative to subpicosecond laser experiments.

5.2 Current and future developments

The availability of ever faster computers makes more and more complex problems numerically tractable. Accurate potential energy surfaces are being calculated on which dynamic processes are solved. This progress in theoretical methods challenges experimentalists. Hydrogen isotopes are ideal simple probes of complex environments, and Mu, because of its low mass relative to H, is particularly sensitive.

The interest of reaction kineticists is moving beyond $H+H_2$ and its isotopic variants. $H+O_2$, H+NO, H+CO are today's challenges of *ab initio* people, and $H+C_2H_2$, $H+C_2H_4$ are on the horizon. Central to these reactions is collisional energy relaxation. Experimental rate constants as a function of temperature and pressure for Mu, H and D will be important in calibrating the theoretical methods.

As regards diffusion in solids it is the coupling of the moving probe to the phonon spectrum of the lattice which determines diffusion. Its dependence on impurities and defects in the periodic lattice is still difficult to treat. Even more complex is diffusion in liquids, but molecular dynamics simulations are becoming more reliable. This will soon call for further and more accurate experimental data.

6. Muons as spin labels in physical chemistry

By addition of Mu to unsaturated organic molecules, muons are substituted in organic free radicals as highly polarised spin labels. µSR techniques are used to spectroscopically characterise the radicals, and the muon spin label monitors the dynamics.

6.1 Past achievements

6.1.1 Radical structures

Nuclear hyperfine coupling constants in free radicals are very sensitive to the radical structure. Thus, the radicals are identified by means of the hyperfine couplings. Unlike conventional magnetic resonance techniques, ALC-µSR immediately provides also the sign of a nuclear coupling relative to that of the muon. Moreover, it is remarkable that a significant number of radicals have been observed by µSR but not yet by ESR, and despite much effort the ^{13}C couplings of for example the unsubstituted cyclohexadienyl radical have not been observed by ESR whereas they have been by µSR (R.F. Kiefl et al., Chem.Phys.143 (1988) 613).

6.1.2 Structure of diamagnetic compounds

The muon lifetime does not permit resolving chemical shift differences or nuclear couplings of Mu-substituted diamagnetic molecules. However, in solids, quadrupole coupling constants which are also sensitive to structures have been observed (S.F.J. Cox et al., Chem.Phys.Letters 160 (1989) 85).

6.1.3 Kinetics of radical reactions

The muon is bound two bonds or more away from the unpaired electron and thus from the reactive centre. Thus, as long as the bond to Mu is not affected in a chemical reaction, kinetic isotope effects are usually negligible. Because of the extreme sensitivity of the technique there are at most a few radicals in the sample at any given time. Reaction kinetics is thus of ideal first or pseudo-first order, which is a very significant advantage over most conventional techniques. Absolute rate constants for fast reactions which are otherwise not easily accessible can be measured with high accuracy. This has been demonstrated for radical clock reactions in the liquid phase (P. Burkhard et al., J.Phys.Chem. 88 (1984) 773) and more recently also for gas phase reactions of relevance in combustion processes and in the degradation of organic pollutants in the atmosphere (H. Dilger et al., J.Phys.Chem.(1996) in press).

6.1.4 Molecular reorientation dynamics in solids

The muon hyperfine interaction is anisotropic. Reorientational motion which is fast on the critical time scale as given by the inverse hyperfine anisotropy (typically of the order of 30 ns) averages the anisotropy partly or completely. This has very characteristic effects on the line shapes of avoided-level-crossing µSR spectra, depending on the type of the averaging dynamics. It was found, for example, that with increasing temperature of polycrystalline fullerenes the resonance of MuC_{60} disappeared by broadening whereas the corresponding line of MuC_{70} narrowed and lost amplitude before they disappeared as a very sharp tick, indicating fundamentally different dynamic behaviour (E. Roduner et al., Chem.Phys. 192 (1995) 231).

6.1.5 Diffusion of surface-adsorbed radicals

Because of the high sensitivity of the µSR technique, surface-adsorbed radicals can be observed at extremely low concentrations, which makes them accessible also under conditions of high surface mobility. This contrasts with conventional methods where the radicals terminate by recombination or disproportionation as soon as they become mobile, and the signal is lost. Surface mobility is essential for catalytic activity, and it is therefore important to be able to observe the radicals under conditions where they are mobile. By ALC-µSR this is possible also for high-surface-area materials of relevance in heterogeneous catalysis. These are usually amorphous or polycrystalline powders, and they are non-transparent for many other techniques. Diffusion of cyclohexadienyl radicals adsorbed on the surface of silica and of Pd-loaded silica has been investigated (M. Schwager et al., Chem.Phys. 189 (1994) 697).

6.1.6 Dynamics of pore-confined media

Nano-structured materials are considered to have a tremendous future for various technological applications, and research is therefore very active in this area. One of the topics of current interest are cooperative effects of guest molecules in zeolites. Here, µSR has only just started to take advantage of its potential. Dynamic effects and an unusual solid-liquid-like phase transition in a benzene-loaded faujasite have been reported (M. Shelley et al. in: *Zeolites and Related Microporous Materials: State of the Art 1994*, ed. by J. Weitkamp et al., Studies in Surface Science and Catalysis, Vol.84, p.469, Elsevier, Amsterdam 1994; E. Roduner et al., Ber.Bunsenges.Phys.Chem. 99 (1995) 1338).

6.2 Future developments

Structure, kinetics and dynamics of short-lived intermediates are subjects of central interest in today's research, and there is no doubt that this will remain so for the next decades. ALC-µSR will clearly benefit from the pulsed structure and the high intensities of the ESS. Depending on the strengths of the relevant interaction, ALC resonances develop over time periods of typically 30 ns for Δ_1 resonances and 1-100 µs for Δ_0 resonances of organic radicals. The process has to compete with the muon lifetime, and this is reflected strongly in the intensities of the resonances. The high muon flux will allow for a higher statistics at long times and will therefore permit much weaker resonances to be observed. Starting to accumulate data only, say 10 µs after a pulse, leads to significant resolution enhancement ("old muon technique"). The ESS will thus make new information accessible.

7. Interaction of ionising radiation with matter

Muons are injected in the sample of interest as energetic particles. They ionise the matter along their track, undergo charge exchange cycles at lower energies, and come to rest at the end of their track either as bare or solvated muons, as neutral muonium atoms, or as muons substituted in diamagnetic or paramagnetic molecular species. Most techniques using ionising radiation integrate the information along the entire track. In contrast, the muon, like the positron or the recoil tritium atom, is a local probe which is sensitive to the end of its thermalisation track where it may undergo hot atom reactions and encounters with other radiolytical products of its own track.

7.1 Past achievements

7.1.1 Charge exchange phenomena in gases and liquids

The slowing down of charged particles in matter is well understood theoretically at higher energies, but very little is known as the particle approaches thermal energy. This basic question has been investigated using muons in gases (D.G. Fleming et al., Phys.Rev. A26 (1982) 2527). The influence of external electric fields on muonium formation in superfluid helium demonstrated that Mu forms by recombination of m^+ with distant radiolytic electrons (E. Krasnoperov et al., Phys.Rev.Letters 69 (1992) 1560).

7.1.2 Hot atom chemistry

For organic molecular gases it was demonstrated that substitution of Mu for H occurs by hot atom reactions (D.G. Fleming et al., Can.J.Chem. 64 (1986) 57).

7.1.3 Electron mobility in cryo crystals

Recently, delayed Mu formation (by combination of the muon with a mobile electron from its ionisation track) was used to measure electron mobility in solid nitrogen (V. Storchak, J.H. Brewer and G.D. Morris, Phys.Rev.Lett. 57 (1995) 2384). While the results of this microscopic method agree with those of the conventional macroscopic drift mobility measurements for the orientationally disordered β phase, they prove the macroscopic studies to be grossly wrong for the ordered α phase, probably due to electron trapping at cracks, defects and impurities. The electron transport mechanism was suggested to be fundamentally different in the two phases of solid nitrogen, being at least 5 orders of magnitude faster in the ordered low temperature phase. This is another example of the versatility of the μSR method in studying very fundamental phenomena.

7.2 Future developments

The example of the above experiment on electron mobility in cryocrystals demonstrates how unpredictable the future of science often is. Effects which were previously considered non-transparent and difficult to interpret all the sudden become clear when a brilliant scientist takes up the subject.

8. Use of ultra slow muons

At present there are three development programmes at PSI, KEK and ISIS which focus upon the generation of ultra slow muon beams with kinetic energies down to as low as 10 eV. Such beams will permit the study of thin films, multilayers, mesoscopic systems and other 2D-objects and ultimately also surfaces. The projects at PSI and KEK are based on quite different approaches. The PSI project has already proven its feasibility and first pioneer experiments may be expected in the near future (see Morenzoni et al., Phys. Rev. Lett. 72 (1994) 2793). Once available, ultra slow muon techniques will be used to address some key problems in modern physics, such as:

- Flux line lattice of 2-D Josephson junction arrays;
- De Haas van Alphen states in nearly 2D-metallic systems;
- Vortex lattice in superconducting films and multilayers;
- Spin polarization in non magnetic layers between magnetic layers;
- Spin dynamics in nearly 2D-magnetic systems, critical slowing down;
- Spin structure in magnetically ordered systems;
- Diffusion on surfaces.

One of the interesting capabilities, not well-exploited today, is the fact that the muon beam is generally not attenuated in matter but stops at a rather well defined depth or range, which depends on the beam momentum and the stopping material. In the future, the use of energy tuneable ultra slow muons with very narrow momentum resolution $\Delta p_\mu / p_\mu$ opens very interesting possibilities with respect to depth profiling of nanophase materials, such as one-dimensionally modulated multilayers, which have an enormous technological potential and their social impact is thought to sharply rise in the next future. Indeed, the actual possibilities to assemble size-selected monolayers into new materials with unique or improved properties will likely create a revolution in our capability to engineer materials with controlled electronic, magnetic, optical, mechanical, and chemical properties for many future technological applications. A wide range of multilayered materials with nanometer or mesoscopic scale modulations will be produced in the next future, including magnetic and non magnetic metal and alloys, intermetallic compounds, ceramic and semiconductors. Development of these technologies for applications will not be possible without a parallel development of a new family of scientific tools, among which muons beams should play a fundamental role.

The investigation, then, of magnetic phenomena and spin dynamics in thin magnetic/non-magnetic heterostructures will be a domain of enormous technological importance, μSR techniques offer the possibility that selected magnetic layers could be investigated. Issues to be addressed will include the physics of spin dependent transport, magnetic polarons in highly-correlated 3d-band ferromagnetic oxides, electronic localization and moment formation by potential fluctuation in narrow-*d* bands, magnetism and transport in structures of dimensions similar to the spin diffusion length, etc.

A pulsed muon source with short enough pulses and high flux rates will certainly be superior to *dc*-sources, like the one presently under development at PSI.

The use of ultra slow muons may be identified as a key area of research at a future ESS.

9. Some basic considerations concerning a μSR – facility at the ESS

The science that will be performed at an ESS muon facility will, of course, be determined by the characteristics of the muon source and beam lines. The natural pulsed structure of ESS will afford the extremely low backgrounds that currently benefit the ISIS facility, and which enable the measurement of very small damping rates associated with very small or rapidly fluctuating fields. However a 300 ns pulse width at ESS (approximately four times that at ISIS) presents a serious limitation to measurement even in modest ($B > 0.02$ T) internal or external transverse fields. This limitation can be overcome by electronically time slicing the muon pulse. Such a process is technically feasible, and while pulse widths of 20 ns should be readily achievable, further reduction to approximately 3 ns can be foreseen if beam intensity is sacrificed. Such narrow pulse widths do still not provide the flexibility of a true *dc* muon beam. It is therefore extremely important that also a quasi *dc* muon source will be available allowing to achieve time resolutions better than 1 ns (see Appendix).

It is naturally assumed that the ESS will provide in the first place positive surface muon beams. However, to exploit the full potential of μSR spectroscopy, decay beams should be made available as well. This will not only allow experimentalists to work with special sample environments (e.g. pressure cells, containers for liquids, bulky samples etc.) but will also facilitate use of polarized negative muons. μSR has so far been very little used and there is tremendous potential for unique developments as has been demonstrated by recent work at the RIKEN-RAL facility (F. Pratt et al., 1996, priv. communication).

Finally the option for ultra slow positive muons should find a prominent place in the planning for a μSR -facility at the ESS. The availability of ultra slow negative muons would open up entirely new possibilities in that spectroscopy of Auger and radiative transitions during and immediately after the muonic cascade would provide access to solid state properties usually studied with photo emission spectroscopy etc., e.g. at synchrotron radiation sources. The development of an ultra slow negative muon source should therefore be an important and most challenging goal within the ESS project.

Appendix: A Proposed Muon Facility for the ESS

A.1 Introduction

μSR is a well established and widely applicable tool to study condensed matter. It both complements and supplements neutron scattering methods. The prime motivation for building a muon source alongside the neutron facilities at the ESS is to provide a uniquely powerful muon facility which will take muon science well into the next century. ESS affords the opportunity of constructing a next generation source with both continuous and pulsed beams, thereby combining and significantly improving the best characteristics of the existing facilities at PSI and ISIS. The proposed muon facility also includes a pion/muon source dedicated to fundamental particle physics research which itself will have unique features.

A.2 The proposed muon sources at ESS

It is proposed that muon sources on the ESS will be generated from two target stations shown in figure A1. The first is Target Station A, a low power, low loss target in the stripped H^- to H^+ beam line from the linac, serving two quasi-continuous surface muon beams, before transmission of the proton beam to a possible radioactive beam facility. The features of this target are given in table 1.

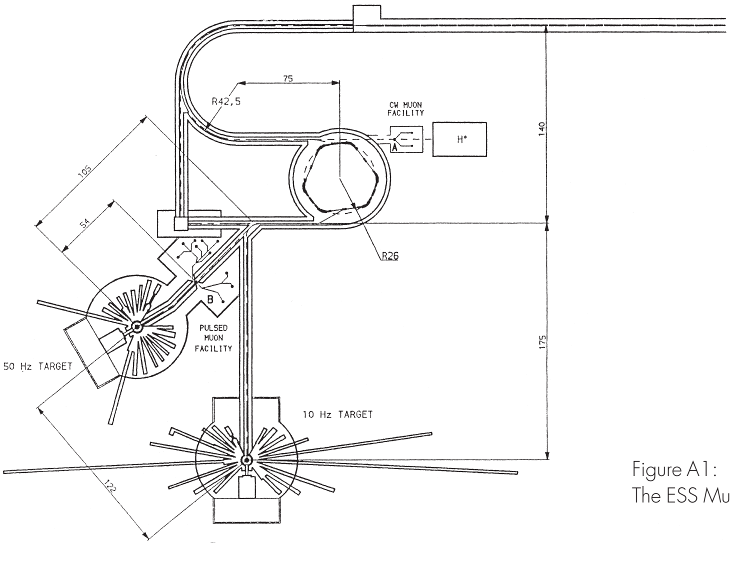


Figure A1:
The ESS Muon Facilities

Table 1: Characteristics of ESS low power Target A for quasi-continuous muon production

Thickness of target	5 - 10 mm graphite
Type of target	Water cooled at edge [1]
Incident proton current	~ 75 μA
Power generation in	0.5 - 1.0 kW
Power dissipation in target environment	4 - 8 kW
Proton loss in target	(2.5 - 5.0) % or (1.8 - 3.6) μA
Remote handling and rad hard component	Minimal
Downstream proton beam collimation	Minimal

The two surface muon beams generated on either side of the proton beam at a 90°production angle will utilise the small emittance of the stripped proton beam to produce small final muon spots at the μSR sample positions. These beams will be enclosed in an Experimental Area A dedicated to μSR studies with muons of a quasi-continuous time structure.

The second Target Station B would be a high power target station upstream of the high power 50 Hz ESS spallation target. This would be used to generate pulsed muons for two muon channels on either side of the proton beam at 90°to the direction of the protons. The features of this Target Station B are given in Table 2.

Table 2: Characteristics of ESS high power Target B for pulsed muon production

Thickness of target	2 mm graphite
Type of target	Radiation cooled rotating wheel [1]
Incident proton current	3770 μA
Power generation in target	12 kW
Power dissipation in target environment	80 kW
Proton loss in target (%, μA)	1.6 % or 60 μA
Remote handling and rad hard component	Mandatory
Downstream proton beam collimation	Mandatory

One of these channels would be a high acceptance (~ 100 msr) surface muon beam, while the other would be a πE5 type pion channel [3] with the capability of directing the pions to a superconducting decay muon channel.

A.2.1 The quasi-continuous muon source

The two surface muon facilities around Target A generate surface muon intensities of ~ $10^6 \mu^+$/sec in a quasi continuous mode with a 6% duty cycle. These would be competitive with the PSI beams, but with the advantage that the small emittance proton beam at stripping could be used to produce a smaller muon source and hence final muon spot at the μSR sample position. Crossfield electrostatic separators would be used in both beams as $\pi /2$ polarization rotators in order to expand the experimental capabilities of the sources. Remote collimation [4] would be installed to allow remote tailoring of the size of the final muon spot.

A.2.2 The ESS pulsed surface muon facility

This facility would use a rotating graphite wheel target, similar to that used successfully at PSI over a period of more than 20 years. With a typical thickness of graphite of 2 mm in the direction of the proton beam at ESS (1334 MeV, 3770 μA), a surface muon channel would collect nearly two orders of magnitude more muons/pulse than is currently available at ISIS. The comparison of ESS and ISIS muon pulses are shown in Figure A2, both sharing the double pulse structure at 50 Hz. As at ISIS, a fast electrostatic kicker can be used to separate the two pulses into three separate beam lines. This is done using a e field kicker with a central electrode to which the pulsed high voltage is applied [4]. In addition the long pulse length of the ESS muon pulse (300 ns FWHM) allows additional ‘ε‘field kickers to be used to separate muons within each pulse. In this way, it is possible to produce from a single target, a larger number of simultaneous 50 Hz single pulse surface muon beams, with a reduced time width which is variable with the timing of the kicker pulses. Figure A3 shows the proposed layout of the pulsed surface facility at ESS, giving a total number of seven experimental areas delivered with single pulses of surface muons. This number is sufficient to support a European wide µSR programme and at the same time providing some areas for special applications and development. Spin rotators would be provided in some beams where required. In such a facility, it will also be possible to deliver muons to a special area at a selected frequency by variation of the frequency of the relevantε field kicker. This would have applications where pulsed environments are applied to the sample at frequencies lower than 50 Hz.

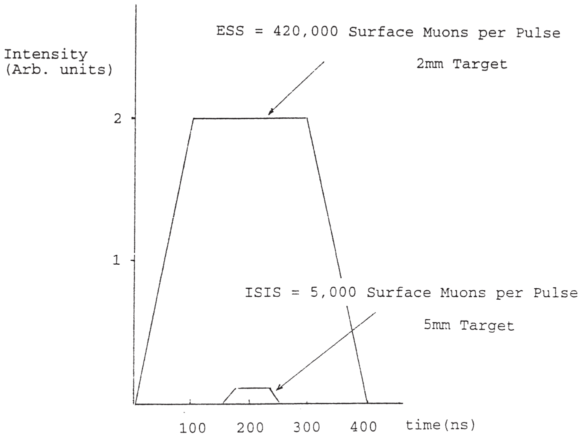


Figure A2:
Comparison between ESS and ISIS surface muon intensities and time structures

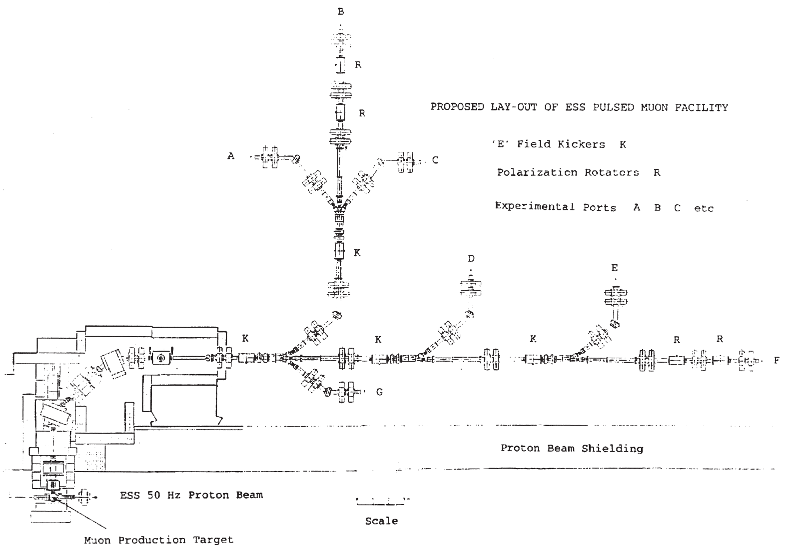


Figure A3:
Proposed layout ot the ESS Muon Facility

An electrostatic kicker development programme to produce pulse width down to (3 -10) ns FWHM is needed to allow μSR frequency responses up to 50 MHz. Another area will be used as an ultra-slow muon facility using moderation in cryogenic noble gases [5]. An ESS pulse beam of time width ~ 40 ns would be ideal for these studies and would open up a whole new field of surface studies with the μSR technique. Such a slow muon facility could be expanded to other areas as the demand from the scientific community grows.

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Other scientific opportunities with the ESS

NESS: Neutrinos at the European Spallation Source

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1. Introduction and physics motivation

The European Spallation Source ESS primarily dedicated to condensed matter research with neutrons simultaneously offers unique possibilities for the most advanced experiments in the field of intermediate energy neutrino physics. When 1.334 GeV protons are stopped in the spallation target apart from neutrons also pions will be produced at a rather high rate. From their decay and the subsequent decay of muons neutrinos of different flavour will emerge with energies up to 53 MeV. With the power of 5 MW deposited in the beam dump by the proton bursts of the ESS accelerator the resulting ν-intensities of $3.5 \cdot 10^{15}$ exceed those of the currently running ISIS facility by more than a factor of 60. With an adequate time structure this unprecedented high flux of "beam-stop" neutrinos at the ESS will open up a new era of neutrino physics with strong impacts on particle physics, astrophysics and cosmology. The physics motivation for neutrino experiments at the ESS arises from the following fundamental, yet unsolved problems:

- **neutrino mass**
  - are **neutrinos massive particles** with masses unequal zero?
  - in case they are, do they obey mass mixing giving rise to **neutrino** oscillations?
  - do neutrino masses obey a generation hierarchy as implied by the **see-saw mechanism**?
  - do massive neutrinos contribute to the **hot dark matter** in the universe?

- **neutrino identity**
  - **Majorana- or Dirac-neutrinos**: are neutrinos identical with their antiparticles?
  - do sterile, **right handed neutrinos** exist in nature?

- **neutrino structure**
  - does an inner structure of the neutrino give rise to a non-vanishing **magnetic moment** and finite charge radius?

- **conservation laws**
  - is the total or flavour **lepton number** violated in processes with neutrino emission?

- **non standard weak interactions**
  - do scalar or tensor type Lorentz structure interactions contribute in neutrino production reactions (**deviations from V-A**)?
- **new decay modes**
  - do pions or muons obey new and **exotic decay modes**
- **coherent neutrino scattering**
  - does **coherent scattering** of low energy neutrinos off nuclei exist?
  - is neutrino coherent scattering the dominant mechanism of energy transfer in supernova explosions?
- **weak interaction neutral current - charged current interference**
  - to what extent is neutrino electron scattering affected by **destructive NC/CC- interference** of W- and Z-gauge boson exchange as predicted by the Standard Model (dynamical properties of weak interactions)?

These rather extensive issues of neutrino physics can be investigated directly and accurately by precision experiments using the ESS "beam-stop" neutrino source together with the most advanced general purpose or dedicated detector systems preferably in an underground cave just underneath the target station. The signal for these neutrinos and the relevance to the above topics will be the measurement of ν-electron scattering and ν-nuclear reactions with adequate energy- time- and spatial resolution. The success of these experiments however will crucially depend on a variety of experimental conditions outlined below.

While the installation of a "beam-stop" neutrino facility at the ESS is of primary importance due to the variety of fundamental questions which can be investigated parasitic to the ongoing condensed matter research programme with neutrons, there is also a strong demand for an additional "decay in flight" neutrino beam line (DIF) providing muon neutrinos with energies in the range of 60-200 MeV from pion decay in flight. A ν-DIF installation would preferably be located upstream of the spallation target utilizing only every other or even fewer of the proton bunches with the beam directed towards the neutrino cave. Those neutrinos would primarily be used to measure:

- **ν_μ -proton elastic scattering at low momentum transfer q^2**
  - this could solve the long standing problem of the extrapolation of the NC proton axial vector form factor to $\tilde{g}_a\,(q^2 \rightarrow 0) = (g_a/g_v)(1\text{-}\Delta s/1.25)$. It would provide quantitative information to the problem of any heavy quark content of the nucleon and its spin structure independent and complementary to the great effort on the still ongoing programme of polarized charged lepton-nucleon scattering at CERN (NMC, SMC, COMPASS) and SLAC.
- **CC ν_μ -induced reactions on nuclei**
  - ν_μ energies above 100 MeV would enable CC muon production reactions on nuclei; thus a variety of exclusive neutrino-nucleus interactions can be studied both with electron- and muon-neutrinos providing nuclear structure information and/or Standard Model tests.
  - measurement of quasi-elastic ν_μ -p and ν_μ -n scattering off isoscalar target nuclei (as for instance ^{12}C) could provide additional information on the strangeness content of the nucleon.

Each of the above listed topics of neutrino physics experiments – at a beam stop source as well as at a DIF neutrino beam line – will require a detailed proposal regarding detector design and features, rate estimates and accuracy to be achieved. However there is no doubt that all these experiments are feasible and quantitative results on each topic can be attained. For particular problems of ν-e scattering, ν-oscillations, ν-nuclear interactions and ν-nucleus coherent scattering and their implications on the above topics, first Monte Carlo simulations and design studies have already been performed and as the prospect for ESS becomes more realistic, detailed proposals will be sent in.

As only one example Fig. 1 shows the sensitivity to neutrino oscillations $\nu_\mu \rightarrow \nu_e$ with a 1 kton detector (scintillator/Cerenkov or water Cerenkov) at 20 m distance from the ν-source for 1 year of measuring time (50% efficiency) at the NESS-facility. This sensitivity with $\sin^2 2\theta$ / $\Delta m^2 \leq 6 \cdot 10^{-5}$ / $4.4 \cdot 10^{-3}$ eV^2 for large Δm^2 and full mixing, respectively, exceeds all existing limits of accelerator based oscillation experiments by more than a factor of ten. In case the recent findings of the Los Alamos LSND-experiment are confirmed by the currently operating KARMEN experiment at ISIS, the NESS oscillation experiments will provide detailed information on the ν-mixing and ν-mass parameters. Similarly, ν-experiments at NESS on all the other topics mentioned above will improve our current knowledge on these fundamental questions by at least an order of magnitude.

2. The ESS "beam stop" neutrino source

2.1 Neutrino production

Apart from neutron generating spallation reactions the proton interactions in the heavy metal target of the ESS also produce large numbers of pions. These pions are very quickly stopped still within the target zone, so that only a small fraction of about 0.001 will decay in flight. As most of the negative pions are captured and absorbed by nuclei, it is the decay cascade of positive pions at rest that constitutes the source of "beam-stop" neutrinos.

The two-body decay π ‘µ→ ‘+ ν_μ generates monoenergetic muon neutrinos with energy E = 29.8 MeV. The subsequent three-body decay μ‘$\rightarrow e$‘ν $_e + \nu_\mu$ produces electron neutrinos and muon antineutrinos with continuous spectra of energies extending up to 52.8 MeV (see fig. 2). Due to the purely leptonic nature of muon decay the energy spectra of both neutrino species are given by *analytic* expressions. Neutrino physics at the ESS thus does *not* depend on complicated Monte Carlo simulations of the neutrino energy distribution The pion-muon decay cascade at rest produces an equal flux of ν_e, ν_μ, and ν_μ which is isotropic and follows a 1/r^2 dependence (see fig. 4).

One of the main motivations for future neutrino experiments at the ESS will be the investigation of neutrino flavour oscillations in the appearance channels $\nu_\mu \rightarrow \nu_e$ and $\nu_\mu \rightarrow \nu_e$ with highest sensitivity. Therefore the contamination of the ESS neutrino beam with $\overline{\nu}_e$ from conventional production processes must be kept to a strict minimum. This demands any **void areas** near the spallation target to be minimized, because void areas near the target will significantly increase the number of negative pions π^- which are not absorbed. The decay of π µ→ ν_μ and the subsequent decay of µ→ $e + \nu_e + \nu_\mu$ create an intrinsic neutrino beam contamination for high precision neutrino oscillation experiments. On condition that there are no major void areas near the ESS target an intrinsic $\overline{\nu}_e$ contamination in the order of 10^{-4} can be realized. This small contamination will allow a detailed investigation of all important neutrino oscillation parameters.

2.2 ν-flux and time structure

At the ESS neutrinos are generated in a pion/muon decay cascade, the neutrino flux is therefore determined by the number of positive pions produced by a 1.334 GeV proton in the liquid mercury spallation target. In order to get a first estimate on neutrino production at the ESS, existing Monte Carlo codes for pion production at the beam-stops of proton accelerators have been linearly extrapolated from 0.8 GeV (proton energy at ISIS and LAMPF) to the ESS design value of 1.334 GeV. The accuracy of this extrapolation is limited by the knowledge on mechanisms of multiple low-energy pion production in this higher proton energy region. For the present ESS target design study a pion production yield of 0.15 π^+ per proton can be predicted, i.e. the ESS beam should generate $3.55 \cdot 10^{13}$ neutrinos per pulse or $3.55 \cdot 10^{15}$ neutrinos per second (see fig. 3).

The most important aspect for neutrino experiments at the ESS is however the time structure of the proton beam. The proton pulses have to be as compact in time as possible to guarantee a small duty cycle factor which is indispensable to suppress continuous background radiation and to achieve sufficient signal to background ratios. The time structure of ν-production at the ESS is shown in fig. 3 for the present design study, two proton bunches of 400 ns, separated in time by 200 ns. This time structure would be reasonably well matched with the different life times of π^+ (τ_{π^+} = 26 ns) and μ^+(τ_{μ^+}= 2.2 μs) – the time matching would improve with more compact bunches as for example at ISIS. The production of ν_μ is going to follow immediately the time structure of the proton beam, i.e. the ν_μ will appear in two 400 ns wide bunches 200 ns apart and their production will be completed within 1.2 μs after beam-on-target with only a few percent contamination by neutrinos originating from early muon decays (see fig. 4). The main production of the ν_e , ν_μ will then occur within the following 30 μs and the ν_e , ν_μ time distribution inherits the 2.2 μs decay time constant of the μ^+ decay. The unique time structure of these two groups of neutrinos can be exploited to identify neutrino induced reactions and to separate ν_μ induced reactions from those induced by ν_e or ν_μ through accurate time tracking of events relative to beam-on-target. This way of neutrino identification has been proven to be very successful in the KARMEN experiment at ISIS. Identification of neutrino events relative to beam-on-target requires exact beam time reference signals – in the order of a few nanoseconds – and accurate recording of the beam's time profile with a resolution of 10 to 20 nanoseconds. In case an in-beam target is in operation (for muon production), the same demands on time tracking apply for this target, because it would act as an alternative neutrino source and if less well shielded as a neutrino contamination and serious neutron background source.

3. The NESS neutrino facility

Neutrino experiments are difficult mainly due to the fact that the detection probability of strong or electromagnetic interacting background radiation is by 10 to 20 orders of magnitude higher than it is for only weak interacting neutrinos. The background event rate must not exceed the neutrino event rate, therefore a facility suitable for neutrino experiments has to be shielded heavily against the source as well as against cosmic rays, while at the same time the detector should be as close as possible to the source to take advantage of the larger solid angle.

The only way to reduce beam correlated background (mainly neutrons) is sufficient bulk shielding between the neutrino facility and the target.

The neutron flux detectable in the KARMEN detector, despite a shielding of overall 7 m of steel between the target station and the detector position, demands at least 8 to 10 m of steel for shielding at the ESS to account for the higher energy and the higher neutron flux. The very same stringent shielding requirements would have to be applied to any in-beam target station. From the experience gained with the KARMEN detector at the ISIS facility, the most suitable place for a neutrino facility would be underneath the target station. The base plate of the target station could then act as a shield and could be extended sufficiently beyond the boundaries of the target station to shadow an area around the detector cave large enough that neutrons scattered towards the detector from any direction would have to penetrate a material thickness equivalent in stopping power to the shielding in the direct path (see fig. 5). The neutrino facility cave should be lined with boracic polythene to thermalize and finally eliminate low energy neutrons that are inevitably present at a spallation source. Any building material brought into the facility should be selected with respect to a low level of natural radioactivity.

Although cosmogenic background can be analysed with highest precision during the beam pause interval between extraction cycles and can be suppressed very effectively through exploitation of the small duty cycle factor (with the present design study 10^{-5} -10^{-4}), for neutrino experiments of highest precision, an active shield of plastic scintillator in the ceiling (and if feasible in the walls) of the neutrino facility with at least 1 m of steel between the active shield and the neutrino detector is essential to eliminate neutrons originating from spallation processes caused by cosmic muon interaction with the bulk shielding against neutrons from the target station. This active shield would identify the muons and enable neutron rejection by selective timing.

The size of such a cave depends on the detector design. A large (1000 t) water Cerenkov detector surrounded by a highly efficient veto detector system with sufficient access and assembly facilities as well as space for the necessary front end analogue electronics devices would require the largest space, i.e. a volume in the order of 3500 m^3. Cryogenic detectors, scintillating fibre detectors, sodium iodide, liquid scintillator or liquid argon or helium detectors would probably require less space, but this again depends on the specific sensitivity to background reactions and the neutrino detection signatures of each individual detector system. Detailed simulations have to be carried out for each detector type to find the optimum, size and shielding requirements at such a neutrino facility.

A volume of 3500 m^3 would easily fit underneath a target station of the size of the ESS (see fig. 5). The steel base plate of course would have to be a self-supporting roof structure for the cave underneath. The distance of any detector to the target would be in the range of 20-25 m. Access to the cave could be provided by an elevator and a tunnel. With a 20-30 tons crane inside the cave any detector could be assembled in the cave from scratch or from pre-fabricated modules. Detectors of several kilotons have been assembled this way for solar neutrino experiments (SUPER-KAMIOKANDE, SNO).

The ESS will be the most intensive neutrino source for the next decades. With the high resolution detector designs available today most of the unanswered questions in the field of neutrino physics could be resolved within a few years of data acquisition.

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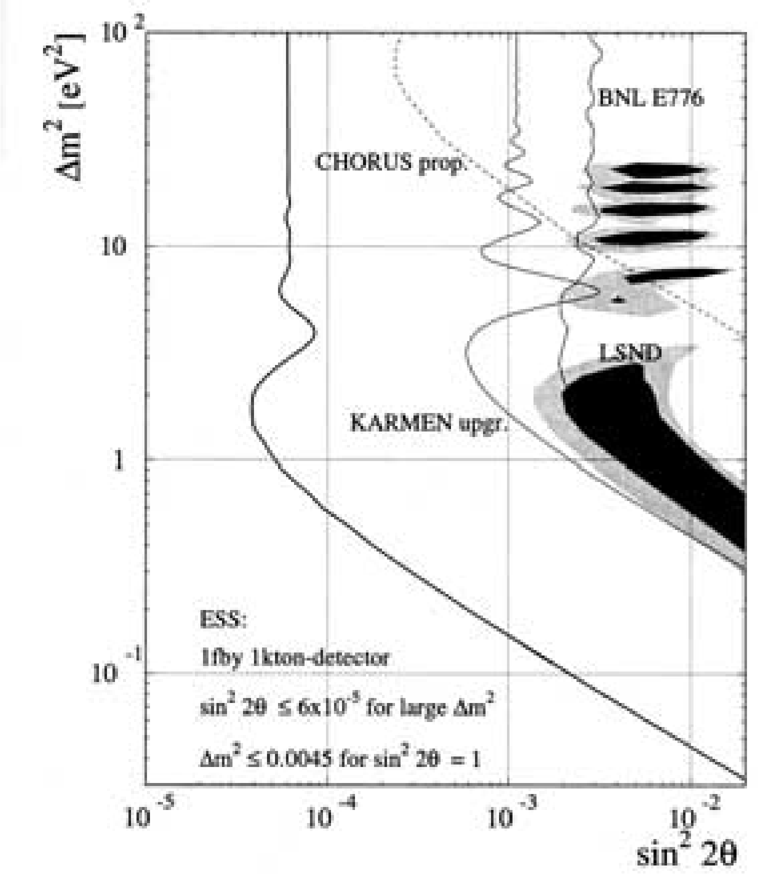

Figure 1: Monte Carlo simulation of achievable sensitivity $\nu_\mu \to \nu_e$ for type oscillation with a 1000 ton water Cerenkov detector at the ESS in comparison with published sensitivities of currently running and proposed experiments.

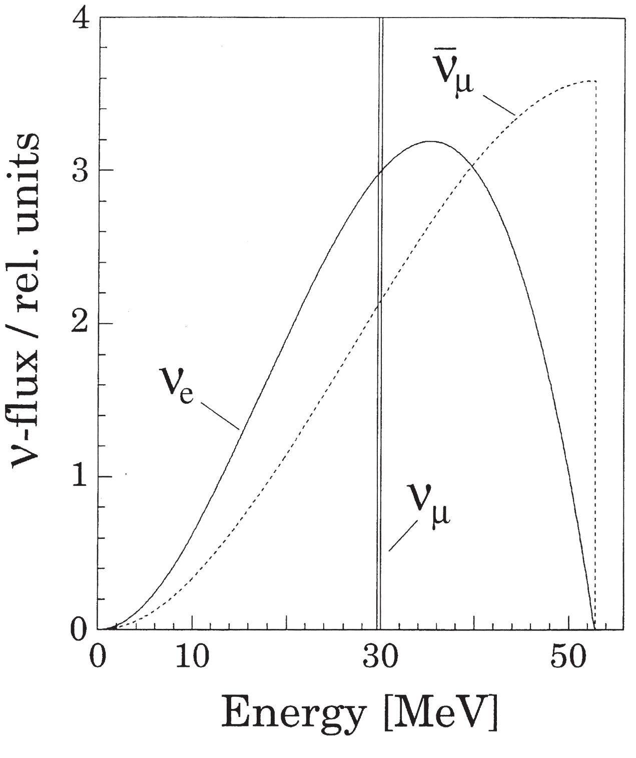

Figure 2: Energy distribution of neutrinos from a "beam stop" source.

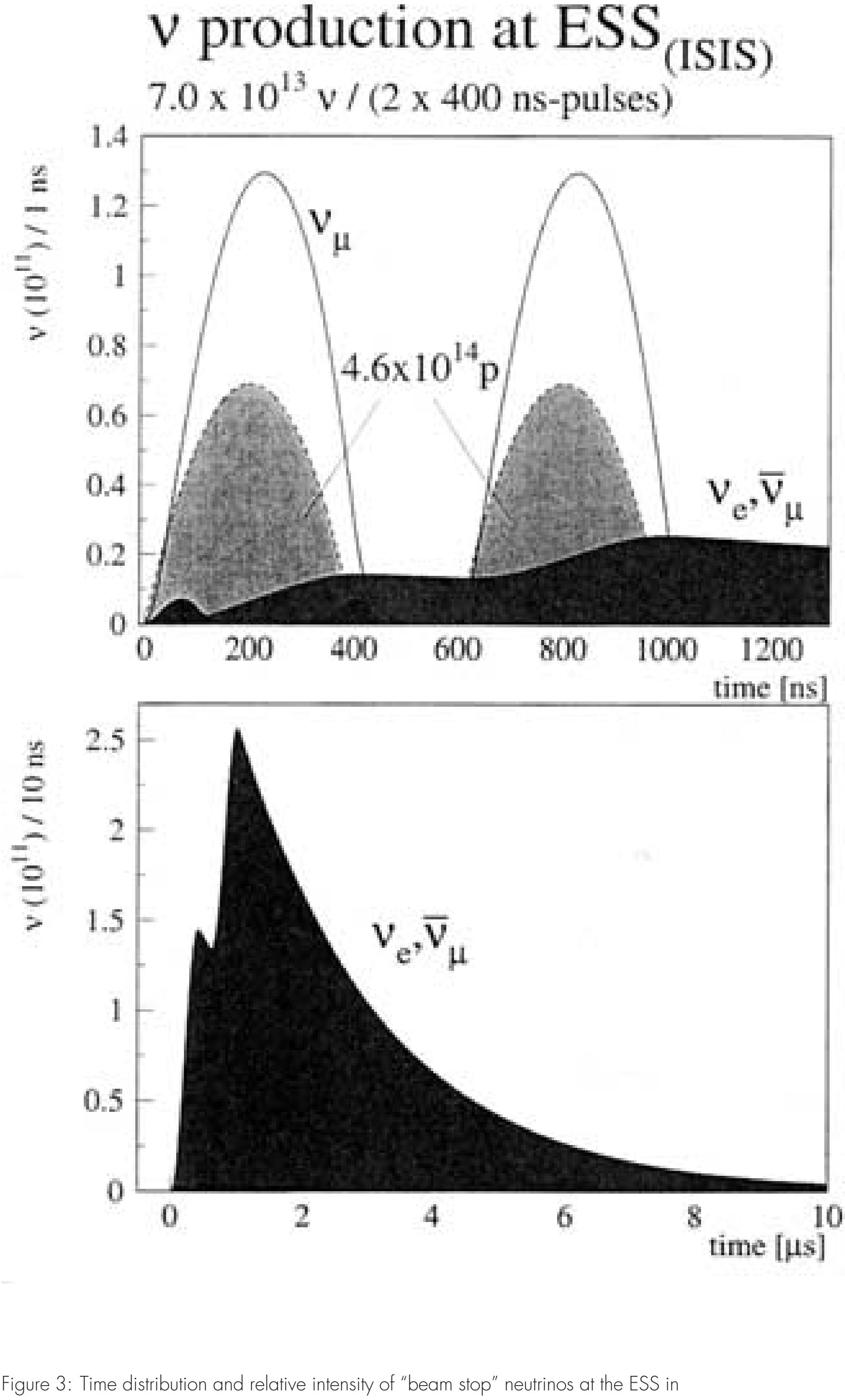

Figure 3: Time distribution and relative intensity of "beam stop" neutrinos at the ESS in comparison with ISIS (black areas).

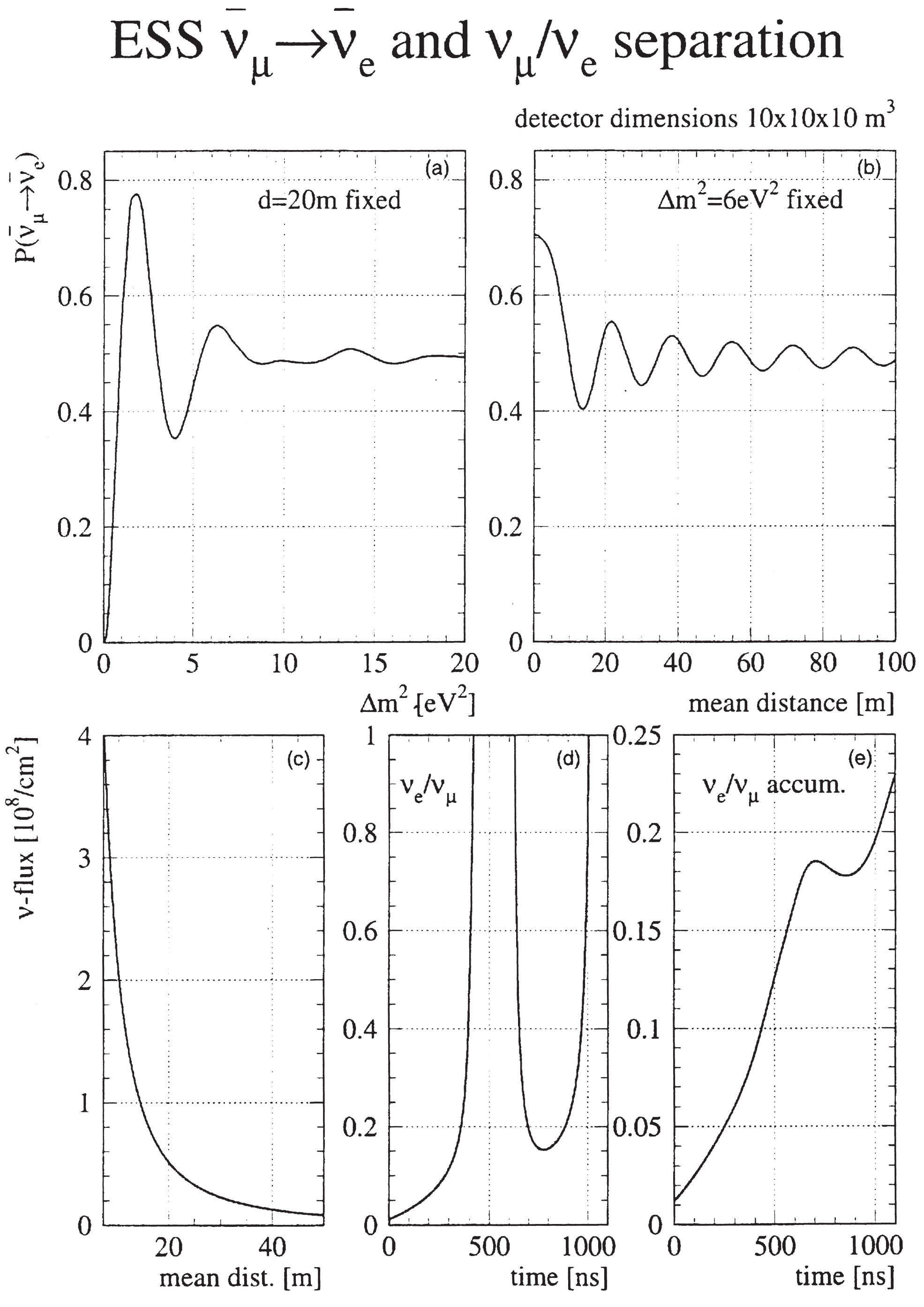

Figure 4: Oscillation probability as a function of distance and mass square difference for the $\nu_\mu \rightarrow \nu_e$ oscillation channel ((a)(b)),ν -flux over distance (c), and ν_μ / ν_e separation ((d)(e)) for the $\nu_\mu \rightarrow \nu_e$ channel at the ESS.

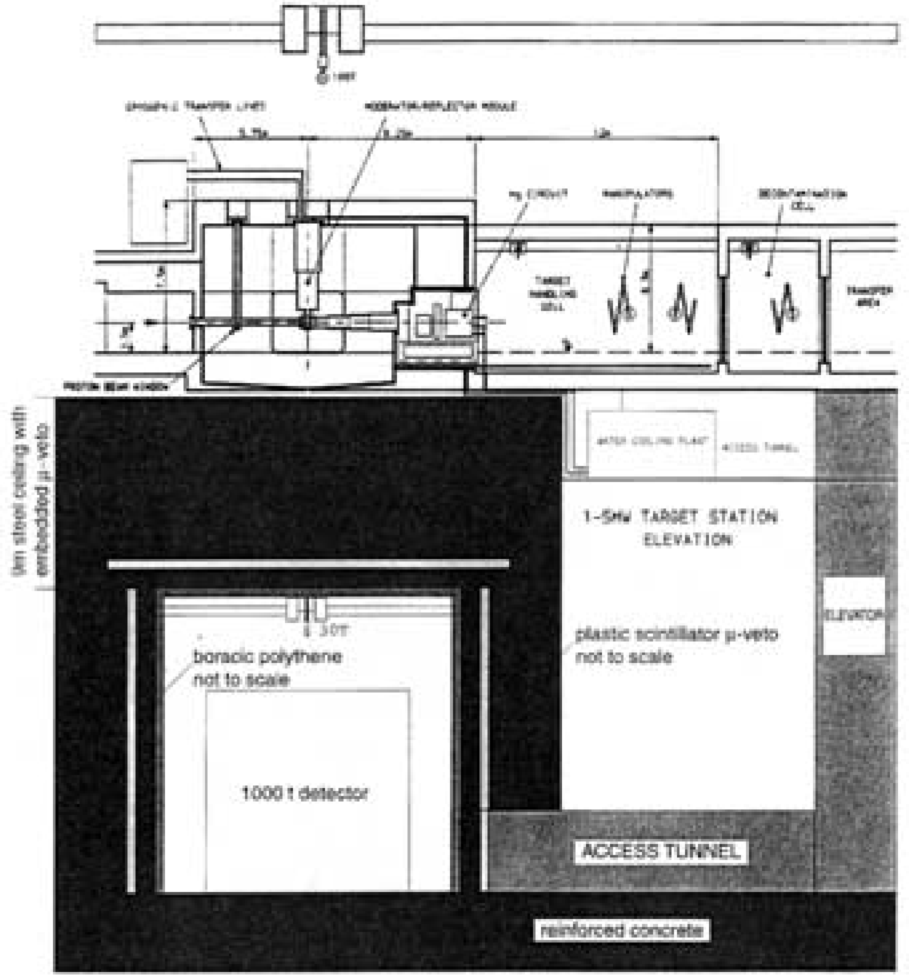

Figure 5: ESS target station elevation, design study with NESS facility.

Radioactive nuclear beams at the ESS

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1. Introduction

There is a consensus world-wide that one of the main frontiers of nuclear physics is the study of nuclear reactions induced by beams of unstable, radioactive nuclei. Such radioactive nuclear beams (RNBs) also have a wide range of potential applications in studies of condensed matter, chemistry, atomic physics, medicine and biology.

Two methods of producing RNBs have been devised. The first relies on the fragmentation of high energy, heavy ions in peripheral collisions with target nuclei. In a significant fraction of collisions of this kind a projectile-like fragment emerges from the reaction with the momentum of the beam. These fragments have an N/Z (neutron/proton) ratio characteristic of the mass of the beam particles. Hence they are unstable, radioactive species. They can be used to form a secondary beam. The principal advantages of this method of producing RNBs is that it is readily implemented at an existing high energy, heavy ion accelerator, and the method does not depend on the chemistry of the species. The main disadvantages are that the beams are weak, typically 8-10 orders-of-magnitude weaker than beams of stable nuclei, the beam is of poor quality, and they have energies well above the Coulomb barrier. They can be slowed down and injected into a storage ring but this is extremely costly.

The second method, the so-called two step method, operates on a different principle. Despite the name there are three essential steps. Firstly the radioactive, unstable species are created in an ion source/target system, which is maintained at high temperature. The second, essential step is that the radioactive atoms are released from the target rapidly and with high efficiency and then ionised. Thirdly they are extracted from the ion source and re-accelerated to the energy appropriate to the experiment in hand.

Many types of nuclear reaction can be used to produce radioactive species. The view in Europe, North America and Japan is that the ideal production method is to use a beam of ~1 GeV protons with ~100μA intensity incident on a heavy metal target. A wide range of radioactive nuclei are produced in spallation reactions on nuclei in the target: the target nucleus is literally smashed into pieces. One of the main advantages of using high energy protons is their long range, which means that the energy density in the target is low, with the result that it is easier to maintain the integrity of the target under bombardment. The choice of 100μA beam intensity for a benchmark facility is indeed based on the widely held view that a heavy metal target can withstand long term bombardment with proton beams of this intensity. The RIST project at the Rutherford Appleton Laboratory has shown that it is possible to make ion source/target systems which are efficient, reproducible and maintain their integrity over a long period with this power input. In terms of re-acceleration, many types of accelerator are possible but the favoured option is some form of linear accelerator.

2. Science case

RNBs can be used for many purposes. As with most major advances the really exciting applications cannot be predicted but already one sees a wide range of science which will be opened up.

There are weak beams of neutron-rich, light nuclei available already from fragmentation. Experiments with these beams have already overturned our ideas about as simple a question as the radius of the nucleus: the textbooks have to be rewritten. Forty years of experiments with stable beams could be summed up in two simple statements. Firstly the radius of the nucleus is given by the simple expression $R=R_0A$-, where R_0 is a constant, and A is the number of nucleons involved. Secondly the neutrons and protons occupy the same volume. Studies of reactions involving ^{11}Li, and other light nuclei with a neutron excess (^{7}Li is the heaviest stable Lithium isotope), reveal that both things are wrong. ^{11}Li is some four times larger in volume than the formula predicts and the neutrons spread out in space well beyond the protons. This is just the beginning of a veritable feast of new results and new phenomena in nuclear physics. Even the single particle levels in the Shell Model, which underlies our picture of nuclei, will change as we add an excess of neutrons or protons to stable nuclei. The result is likely to alter our view of nuclear structure drastically.

In the simplest terms, one can only understand physical systems if their properties are studied over the full range of key parameters. If we were unable to heat or cool water we would not know that it changes phase. In nuclei we have been denied hitherto the possibility of studying how its properties vary with isospin (effectively the N/Z ratio), one of the key parameters. A facility delivering intense RNBs would change all that.

A knowledge of the properties of unstable nuclei is one of the keys to nuclear astrophysics. About 1 µs after the Big Bang all quarks were locked forever into nucleons. Since then the history of the Universe has been a tale of gravity and nuclear reactions. They are the driving forces behind stellar evolution. The energy that makes the stars shine derives from nuclear reactions. In Main Sequence stars energy is generated in a series of burning stages in which progressively heavier elements are made in exothermic fusion reactions. This process runs out at Fe because such reactions become endothermic. The heavier elements are made either in a relatively gentle process of neutron capture followed by b decay, along the line of stability, involving neutrons produced in Red Giant stars, or in explosive processes such as supernovae, cataclysmic binaries and novae. The clues to the sites of heavy element nucleosynthesis are the observed isotopic and elemental abundances of the elements. In general terms stellar nucleosynthesis of the medium and heavy elements proceeds along pathways far from the stable nuclei. The observed elemental abundances are the result of a complex competition between successive reactions along the pathway and radioactive decay back towards the line of stable nuclei. How the competition ends depends on conditions at the stellar site, the temperature, density, chemical composition etc., and on nuclear properties such as reaction cross-sections, Q-values and radioactive decay rates. All of these parameters influence the timescale involved and the mixture of isotopes coming out the end. If we are to reproduce the observed elemental and isotopic abundances, the clues to the environment at the production site, it is essential to determine the properties of the nuclei lying along the paths of the network of reactions in which they are created. These nuclei are all unstable. Only the use of beams of these radioactive nuclei, incident on H or He targets, will allow us to test our ideas qualitatively. Hence RNBs are vital for nuclear astrophysics.

Another area of interest is nuclear chemistry. In particular the creation of and the chemical properties of the heaviest elements. The heaviest element created in the laboratory so far is Z=112; a few atoms created fleetingly in a Heavy ion induced reaction with a heavy, neutron rich target. Our present knowledge suggests that the long predicted stabilising effect of shell closure at Z=114 exists and that having nuclear projectiles with extra neutrons increases the production cross-section considerably.

The stability of the elements and the decay properties of the heaviest elements is of interest in itself. At the same time their chemical properties are also of vital interest because of the anticipated, large relativistic effects on the atomic electron configurations due to the high nuclear charge. The heaviest elements where chemistry has been investigated (Z£105) do not fit into the extrapolated Periodic Table, but the predicted relativistic effects were not observed. Additional experiments are clearly required on these and heavier elements. The experiments are carried out "one atom at a time" but it needs isotopes with $T_{1/2}$>0.5mn. Neutron-rich radioactive beams provide the key to such studies since this will allow access to the longer-lived, more stable isotopes near the predicted island of superheavy elements. The cross-sections for reactions with these neutron-rich projectiles are larger than for their stable brethren.

A RNB facility would also be a natural place for filling an EBIT with radioactive ions, which can be in the highest atomic charge states. This would be an ideal instrument for precision atomic physics experiments with such highly charged ions and experiments with radioactive ions aimed at examining the interplay between atomic and nuclear properties. A simple example here might be the change in nuclear decay properties with the number of bound electrons. Such playthings of the atomic physicists are also of vital interest to the accelerator technologist because a copious source of highly charged ions opens up exciting prospects for them.

Much research in materials science has derived from nuclear techniques. A first class RNB facility would be no exception. Ion beams of stable isotopes are widely applied both to modify materials and for surface processing. Ion implantation is of vital interest to industries involving semiconductor microelectronics, the manufacture of specialised tools and advanced metallurgy. Beams of radioactive ions, of the same chemical species and the same characteristics, implanted into a host sample will end up on the same types of site as the stable ions. Any modification to their radioactive decay pattern will reflect their local microscopic environment. A whole battery of techniques of this kind has been developed. They include perturbed angular correlations, the Mössbauer effect on implanted nuclei, channelling of the particles from radioactive decay, high resolution conversion electron spectroscopy, on-line nuclear orientation, positron emission and annihilation and nuclear reaction analysis on implanted radioactive ions. Such studies are largely confined to the ISOLDE facility at CERN. This facility is limited in beam intensity by the primary beam current of ~2 μA and the output beam energy of £60 keV, which restricts implantation to close to the surface. A full scale facility would provide beams fifty times more intense than those at ISOLDE and beam energies allowing implantation at much greater controlled depth in the material. Given the increasing importance of multi-layer semiconductor devices this is important. This would vastly expand this whole field of study.

One very direct application of RNBs is to provide nuclear data needed for such purposes as nuclear waste transmutation. A variety of nuclear reactions could be used to transmute long-lived and toxic fission products. For example spallation reactions induced by energetic light ions could be used. To assess the usefulness of the technique requires not only the spallation reaction cross-sections on the isotopes of interest but also the spallation product distribution in order to ensure that one is not just replacing one problem with another.

Radioactive ion beams can also be applied in medicine. For example the lungs can be imaged by detection of the gamma radiation emitted from a suitable radioactive gas which has been breathed in. If an RNB facility can deliver a copious supply of a shorter lived isotope of the same element then its use in the same application will provide better signal-to-noise and reduce the radiation dose to the patient.

A second application in medicine is related to radiotherapy of tumours using energetic heavy ions. The use of energetic heavy ions in the radiotherapy of tumours offers the advantage of localising the lethal dose at the tumour site, thus sparing the contiguous, healthy tissue. One attendant difficulty is to monitor the dose delivered to the tumour volume directly. If a weak beam of a positron emitting isotope of the same element is used first a three dimensional PET scanner can be used to locate the deposited beam exactly. The resulting RNB profile can then be used to adjust the beam energy to the exact portion of the tumour as determined by other methods such as a CT scanner.

A comment on the use of the ESS as an irradiation facility

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Since no intense 14 MeV neutron source is available at present, research and development of plasma interactive and structural materials for future fusion reactors (ITER, DEMO) must rely completely on simulation techniques using fission neutrons and light and heavy charged particles. The transfer of simulation data to fusion conditions is afflicted with severe uncertainties because none of the available simulation techniques can reproduce fusion-typical recoil spectra, displacement rates and helium and hydrogen production rates simultaneously. Numerous attempt have therefore been made during the past 20 years to employ other neutron sources in fusion materials development. However, all the earlier proposed facilities did not survive the stage of conceptual design with the exception of the deuteron-stripping source FMIT whose detailed design had been completed and important parts of the accelerator had been constructed in Hanford, USA, in 1982. Unfortunately, in 1983, the construction of FMIT had been deferred due to budgetary constraints and insufficient international support. A new effort backed by all 4 partners of the International Thermonuclear Experimental Reactor (ITER) collaboration started in 1988. Three types of sources were considered: a) driven plasma based source, (b) a d-Li stripping source and (c) a spallation source. Option (a) was soon dropped because of costs and long lead time. For a spallation device as a source of high energy neutrons the following main arguments were brought forward:

PRO

1. The recoil spectrum resulting from spallation-produced neutrons matches the fusion neutron case sufficiently well (see Fig. 1). The 'high energy tail' is similar to that for the stripping source.
2. The required helium and hydrogen production rates can be closely matched in most fusion-relevant materials.
3. The flux and fluence requirements can be fulfilled with sources in the MW power range.
4. Spallation sources can provide much larger irradiation volumes and a more homogeneous flux distribution than a stripping source.
5. Participating in an intense spallation neutron source as a 'parasitic user' would greatly reduce the investment and operating costs not only for the fusion materials community but also for the other users. This advantage is inapplicable for the stripping source which cannot offer any non-fusion application.

CONTRA

6. All planned intense spallation sources are assigned for pulsed operation (except SINQ) whereas fusion reactors with magnetic confinement are hoped to operate in a quasi-stationary mode. The ms-pulses typical for ESS lead to huge instantaneous damage rates and He/H production rates. A transfer of results obtained under these conditions to the fusion case could generate larger uncertainties than those expected from different neutron spectra.
7. Taking advantage of (5) is problematic since the installation of a voluminous irradiation facility in the fast neutron regions of a spallation source will severely degrade its performance for the original purpose.
8. At the time of the decision (1990) no definite plans for planning and constructing intense spallation sources such as ESS or ORSNS were known to the fusion community. The lead time for building a spallation-based source was thus considered much longer than for a d-Li source where valuable preparatory work had been carried out in the FMIT project.

Mainly because of the arguments (6) and (8) it was concluded to aim for a d-Li stripping source as an international fusion materials irradiation facility (IFMIF). Soon after this decision conceptual and engineering design work began and is now close to its completion [Rennich, 1995].

It should be pointed out that the decision in favour of the d-Li option was made by the fusion community working in magnetic confinement fusion (i.e. TOKAMAK or STELLARATOR type devices). In parallel to the world-wide efforts in this field there are attempts in several countries to develop controlled inertial confinement fusion. In this – mostly classified – work, solid pellets containing a mixture of deuterium and tritium are bombarded with electromagnetic radiation, light ions and heavy ions, respectively. It is hoped that the resulting implosion waves will densify a part of the fuel to such an extent that the number of fusion reactions is sufficient to reach a positive energy gain. In an inertial confinement reactor the pulse lengths, power densities and repetition frequencies are comparable to those in ESS. Its regions of high fluxes of fast neutrons would therefore be an ideal test bed for materials development for inertial confinement fusion.

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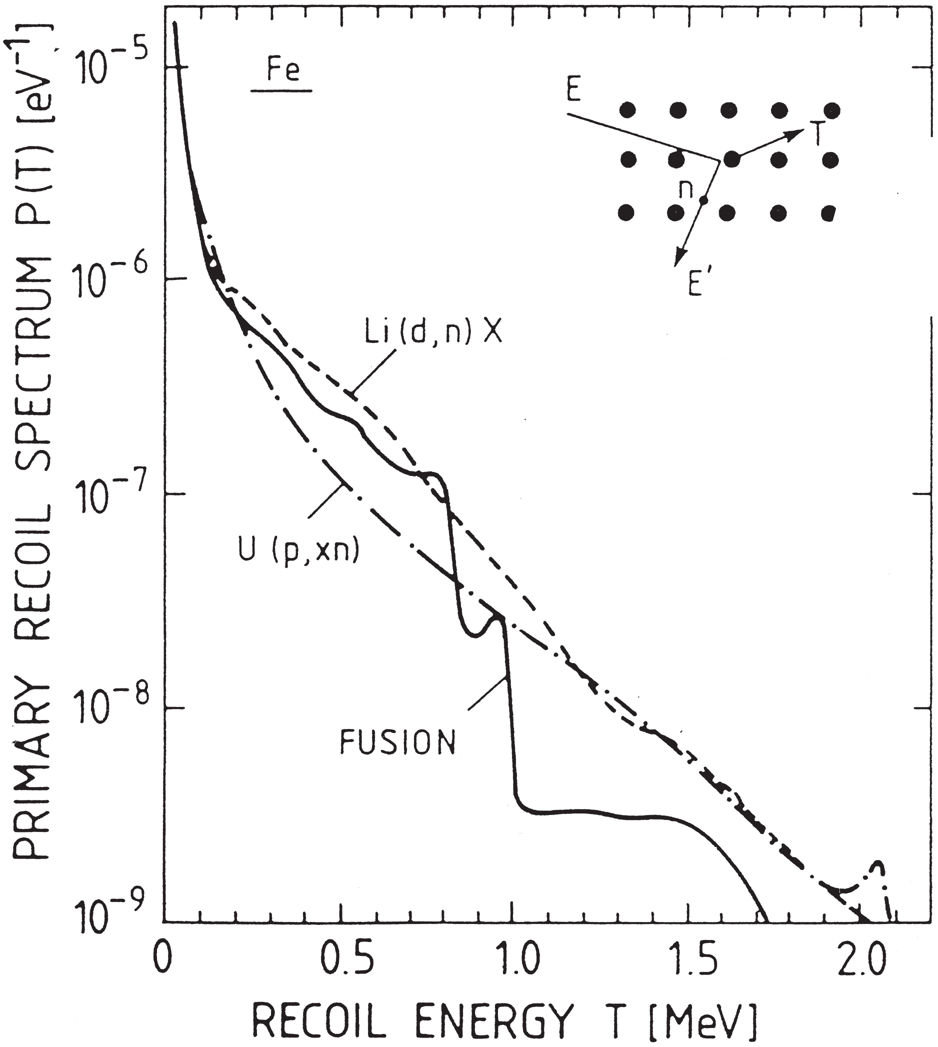

Figure 1: Primary recoil spectra P(T) for the transfer of recoil energy T to iron atoms for different high energy neutron sources [1]: spallation of uranium by 1.2 GeV protons (U(p,xn)); stripping of 35 MeV deuterons by Lithium (Li(d,n)X) and d-t fusion (first wall spectrum in DEMO reactor).

Neutron applications for ISIS/ESS – isotope production

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This report is a summary of an investigation to see whether cost effective isotope production using neutrons from ISIS/ESS was feasible.

Two isotopes only were identified as worth pursuing because of their high commercial value in medical applications. These are Tc 99m and Sr-89. The latter is marketed by Amersham as a pharmaceutical at approximately 1M$/kg under the trade name of Metastron.

Metastable technicium-99 is the basis of most gamma-camera medical imaging and is also marketed by Amersham under the trade name of Ceretec but many such companies market this isotope for imaging.

1. Neutron-based production

1.1 Tc 99m.

This isotope is a daughter product of Mo99. A conventional products route is as a fission product from thermal neutrons on uranium where 99 Mo has a cumulative fission yield of approximately 6% (i.e. 0.06 Mo99 nuclei per fission event). Alternatively it could be made by neutron capture in the stable isotope Mo89 (24.4% naturally abundant). This has a thermal capture cross section of 0.13b (against a total cross section of 5.9b). In a fission spectrum the capture cross section is 28 mb compared with a total cross section of 5.8 b. However at neutron energies between 500 eV and 10 keV a number of (n, gamma) resonances occur which could be used for producing Mo99 in a suitable epithermal/fast spectrum.

1.2 Strontium 89

This is used as a palliative (pain killer) for secondary prostate cancer, particularly in the USA. It has a very high retailing price. It can be obtained directly as a fission product with a yield of approximately 4%, but other Sr - isotopes have similar yields (Sr-90 at 5.8% and Sr-96 at 3%) so radio chemical separation could be expensive.

Direct neutron capture in Sr-88 (82.6% abundant) could yield Sr-89, with a thermal capture cross section of 5.8 mb, and a fission spectra capture cross section of 1.28 mb. However a number of resonances occur in the neutron energy range 10 keV - 100 keV.

A better candidate is Y-89 (100% abundant) using the reaction (n,p) to Sr-89. At 10 MeV the cross section is 19mb, probably increasing at higher energies (but the data is uncertain above

10 MeV). Competing reactions are (n,d) leading to Sr-88 (Stable) with a cross section of 10mb at 10 MeV, and (n, alpha) leading to Rb-86 (18 day half-life, 1MeV gamma emitter) with a 10 mb cross section at 10 MeV. This isotope could be easily separated from the Sr-89.

2. Conclusions

There is an a priori case for considering commercial isotope manufacture on ISIS/ESS for the two isotopes Tc-99m and Sr-89. The neutron yield would be straight from the target, with a specially designed partial moderator to attain the required intermediate neutron spectrum. Further detailed design calculations for the neutronics and yield are required, together with analysis of the required chemistry. Additionally there must be a desire to dedicate a significant fraction of ISIS/ESS time to the activity – what fraction would depend on the outcome of the neutronics analysis i.e. size of special moderator required, its effect on beam lines etc. Additionally, production activities would require a guaranteed twelve month production cycle for obvious commercial reasons.

Such activities would likely entail in the case of ISIS a production licence from the Medicines Control Agency, approval from HSE and HMIP and the possible involvement of the NII (because of the nature of the ISIS target). Similar licensing requirements will be in force for the ESS should it be built outside the UK. The "dosey" nature of such activities involving primary neutron sources should not be underestimated.

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