Proceedings of International Collaboration on Advanced Neutron Sources (ICANS-VII), 1983 September 13-16
Atomic Energy of Canada Limited, Report AECL-8488

CONDENSED MATTER PHYSICS WITH NEUTRONS

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The basic principles of the usage of slow neutrons as a probe for the study of condensed matter are presented and discussed. Various categories of experiment are defined and illustrated to show the limitations of existing neutron sources. The possibilities opened up by the introduction of advanced accelerator based sources are examined and the importance of simultaneously decreasing relative background counting rates is emphasised.

INTRODUCTION

The use of slow neutrons as a probe for the study of the properties of condensed matter has grown continuously since the first research reactors become available. Physics, in the title of this paper, must now be taken to include chemistry, biology and metallurgy in both pure and applied forms. Over a thousand papers based on the results of neutron scattering experiments are published each year. Recent reviews[1,2] have emphasised the breadth and depth of information being produced from all types of source while the proceedings of ICANS-VI[3] gives a good illustration of the quality of data obtained to date using accelerator-based sources. Today even the UK is prepared to spend the equivalent of more than US$ 20M each year on the provision of neutron sources, experimental equipment and manpower for pure condensed matter research with neutrons. At AERE Harwell, as well as our pure research programme of neutron based experiments, we have an applied neutron programme which yields a significant income from research and development programmes. Some of them come from within the UKAEA, others from other government departments and private industry. I have found myself investigating copper clustering in pressure vessel steels, metallurgy of maraging steels, the structure of nuclear waste storage glass and low energy methods for the production of ceramics and glasses.

If we take the facility at the Institut Laue-Langevin as a model for an advanced neutron source, then about 500 experiments can be expected to be performed each year which will result in about 400 research papers in the open literature. Some papers will have greater scientific significance than others. These statistics will depend on the scheduling policy adopted and it could be decided to aim for a lower throughput of key experiments.

Why is the slow neutron such a useful probe into the condensed state when available flux has been so much lower than for electromagnetic radiation sources? Put at its simplest, the reasons are fourfold.

- Slow neutron wavelengths (0.1 - 10 Å) are of the order of interatomic spacings and energies (.001 - 10 eV) covers the range of excitations up to binding energies.
- The interaction with the nucleus is via scattering lengths $b(A, I_A \pm \frac{1}{2})$ which varies unsystematically with both variables. A is the atomic weight of the isotope and I_A the nuclear spin.
- An interaction between the magnetic moment of the neutron and that of the ion produces a magnetic scattering length.
- The mean free path in an average sample is a few centimetres.

These properties combine to make the particle ideal for studying both structures (atomic and magnetic) and dynamics using bulk samples. The almost random variation of b ensures that structural information usually complements that from X-ray studies and provides the opportunity to vary the isotopic content and give extra information. When observing excitations, finite momentum is always transferred to the scattering system allowing, for example, dispersion to be uniquely investigated.

THE MEASURED-CROSS SECTIONS

The experimentalist places his sample in a beam of either white or monochromatic neutrons and measures the scattering from his sample with or without final energy and scattering angle analysis. Table 1 shows the relationship between the quantity measured and the information obtained. E and E^1 are the neutron energies before and after scattering, respectively, and 2Θ is the scattering angle. A complete measurement of the double differential cross-section over a wide range of energy transfer and scattering angle or incident energy contains all the information to describe the structure and dynamics of the system (extracting the information may well need more than one experiment). According to Van Hove[4]

$$\frac{\partial^2\sigma}{\partial\Omega\partial E^1} = \frac{\sigma}{4\pi}\left(\frac{E^1}{E}\right)^{\frac{1}{2}} S(\underline{Q},\omega) \qquad (1)$$

$$\text{where } S(\underline{Q},\omega) = \frac{1}{2\pi}\iint \exp i(\underline{Q}.\underline{r} - \omega t)G(\underline{r},t)d\underline{r}dt \qquad (2)$$

The wave vector transfer $\underline{Q}$ has magnitude

$$|Q| = \left[\frac{2m_n}{\hbar^2}(E + E^1 - 2\sqrt{E}\sqrt{E^1}\cos 2\Theta)\right]^{\frac{1}{2}}$$

and the energy transfer ω is given by

$$\hbar\omega = E - E^1$$

The double differential cross-section is thus related to a double Fourier transform of $G(\underline{r},t)$ a space-time correlation function. With present neutron sources the complete function is rarely measured completely enough in both variables (Q and ω) for structural information to be obtained. This is found from $G(r,\alpha)$ (elastic scattering, $\omega = 0$) or $G(r,0)$ (total scattering, S(Q) via a single differential experiment without final energy analysis. This means that corrections have to be made for the effects of inelasticity in the experiment. Limited structural information can be obtained from an even simpler measurement; that of the total scattering cross-section as observed in a transmission experiment which integrates over both final energies and scattering angles.

EXAMPLES

I have chosen three examples of areas where pulsed neutron experiments at accelerator based sources are attempting to solve long standing problems in respect of three very common materials - mild steel, vitreous silica and ice. It perhaps means that the new sources are performing as expected if useful contributions can be made for such well studied materials. Most of the experiments were made at the Harwell electron linac pulsed source[5] which has a low fast neutron source strength at present of 10^{14} fn/sec and thirteen instruments in routine operation or development.

Internal Stress in Steels

Internal stresses within a sample are difficult to measure but can be important. Weld failures may arise from propagation of cracks due to residual stress around a weld. Conventional measurements are made with strain gauges and a stripping technique or X-ray diffraction which only observes surface strains. Other techniques are very sensitive to texture. Neutron diffraction experiments[6] can observe stress in a bulk sample via a corresponding lattice strain. There is an extention of the lattice spacings d along the stress and a contraction perpendicular to the stress and a fractional change is observed between 10^{-3} and 10^{-4}. Experiments on welds of commercial importance are underway with the aim of optimising the welding technique. Recent measurements have revealed the variation of the strain for different lattice spacings and directions in an experiment with a rectangular bar stressed beyond its elastic limit. Work is in hand to try to reduce the data via the known elastic constants to see if a simple interpretation is possible. The widths of the observed Bragg peaks is also a function of the stress and indicates the regions where microscopic strains occur.

The shifts due to stress can also be seen in a measurement of the total cross-section as a function of wavelength (λ) since an edge is produced when $\lambda = 2d$. The edge is assumed to be rectangular and appears broadened only by the resolution function of the spectrometer and any material effects. Recent data from a transmission spectrometer on the same bent steel bar have shown that the edges can be fitted accurately and used to derive the average strain through the bar. The results so far are in good qualitative agreement with the diffraction results and show that strain measurements can be made very rapidly by this technique. With the increasing availability of area neutron detectors, it may be possible to make stress measurements simultaneously with millimetre resolution and perform stress radiography.

Structure of Vitreous Silica

This subject has been brought to the forefront again by a recent paper by Phillips[7]. Over recent years a continuous random network model of SiO_4 tetrahedra has been accepted as satisfying the experimental evidence from many techniques. Phillips believes that the failure of such models to predict the details of observed vibrational spectra means that a model based on paracrystalline regions is necessary. He supports this view by citing some electron microscopy evidence and also the failure of hand built and computer built random models to fit the measured total pair correlation function. His model comprises 50 A diameter paracrystalline regions of β-cristobalite with surfaces stabilised by a large number of Si = O bonds. Pulsed neutron experiments offer the best opportunity to study the Si - O bond length distribution and coordination. Gaskell[8] has compared our results[9] to a variety of random network models and finds the comparison to be relatively insensitive to the medium range structure or topology. However none of the models gives a good representation of the data in this region. The evidence for the existence of Si = O would come from an analysis of the first peak in the correlation function. To date there is no evidence for a distribution of bond lengths such as might be given by a mixture of Si - O and Si = O[10] The way forward however is clear in this respect. More accurate diffraction data to Q values up to 60 A^{-1} will reduce experimental widths in the correlation function and enable a more accurate analysis of the first peak.

Phillips basic objection is however to the prediction of polarised Raman spectra and the density of vibrational states as measured by neutron inelastic scattering. Raman spectroscopy is difficult to interpret uniquely so a full high resolution measurement of $S(Q,\omega)$ is needed to derive a density of states that can be closely compared to model predictions. The source at Harwell is not capable of this and progress must await experiments with progressively stronger sources.

The Dynamics of Ice

Although the vibrational spectra of H_2O at low temperatures has been extensively studied, it is only the advent of accelerator based sources with a relatively rich epithermal energy spectrum that has allowed neutron measurements to reach the intramolecular vibration region with any accuracy. The problem has been that the vibrational density of states extends up to nearly 0.5 eV. As well as being of interest to established the force constants applying to the ice structure for its own sake, it is hoped that a thorough understanding may lead to a better picture of the structure and dynamics of amorphous ice and water. Measurements published this year[11] have at last succeeded in obtaining a clear picture of features in the density of states to its upper limit. The width of the O-H stretching mode was found to be in close agreement with optical data. A more complete experiment has recently been performed with IPNS[12] spanning a region of $S(Q,\omega)$ which enables the assignment of features to be critically examined. One of the great advantages of neutron spectroscopy over optical spectroscopy is the absence of selection rules.

The other major advantage lies in the ability to directly measure the dispersion of excitations in chosen directions in a single crystal sample. In an experiment with the Constant-Q spectrometer at Harwell, the dispersion of the O-D stretching modes in a single crystal of heavy ice was observed[13] for the first time. Several flat branches were found in the energy range between 230 meV and 330 meV. Although this was an incomplete experiment, it did demonstrate the capability of accelerator based sources to provide the most detailed dynamical information in previously inaccessible region of energy transfer.

POSSIBILITIES WITH ADVANCED SOURCES

Almost all of the results discussed above come from experiments with a low flux accelerator-based source. It is interesting to speculate on the effect of increased source strength on the scientific applications.

a) Improved Statistical Accuracy and/or

Resolution
- leading to more detailed and accurate interpretation.

b) More Samples can be Studied
- systematics in alloy systems, temperature variation etc, can be extended. Applied experiments become more attractive.

c) Smaller Samples can be used
- isotopic substitution with rare isotopes becomes possible and the study of difficult to grow single crystals. Small samples mean easier to make multiple scattering corrections.

d) More Accurate Techniques can be employed
- more structural derivations based on $S(Q,\omega)$ measurements or elastic diffraction, more polarised neutron experiments.

e) New Experiments
- mainly deriving from the rich epithermal spectra or the pulsed nature of the source. An extended range of excitations involving small cross-sections could become possible. Diffraction with short wavelength neutrons can minimise corrections for inelasticity. Kinetic experiments on relaxation phenomena.

The count rate an experimentalist records contains two components. Firstly, the signal from the sample which is proportional to the flux incident on the sample, the number of atoms in the beam and the desired cross-section. Secondly, there is a background component which has to be measured separately and subtracted. The consequences c) d) and e) above in particular rely in many cases in improving the signal to background ratio as the flux on the sample is increased by moving to a more powerful source. This arises since the criterion for a minimum sample size or limit of energy transfer often comes from an unacceptable signal to background ratio. The requirement is that the background does not go up in proportion to the flux on the sample. Pulsed accelerator-based sources are in a favourable situation here since the fast neutron source is switched off during the experiment. The remaining problem is to deal with the fast neutrons which have interacted with the sample and shielding materials and this becomes more important as the neutron energy used in the experiment is raised. In this energy region (> 1 eV) the background in the beam itself can be important and it is no longer good enough to remove the sample to measure the background. This discussion emphasises the need for innovatary source, beam tube and instrument design as the flux is raised, so that scientific results can be gathered in new areas.

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TABLE 1

QUANTITY MEASURED	CLASS	INFORMATION DERIVED	RANGE	SCIENTIFIC FIELDS
$\sigma_s(E \to E^1, 2\theta)$; $\frac{\partial^2\sigma}{\partial\Omega\partial E^1}$ barns $st^{-1}eV^{-1}$	Inelastic	Dynamics [Structure]	10^{-6}eV → 1eV	Tunnelling; Molecular Spectroscopy; Diffusion; Surface Studies; Lattice Dynamics; Amorphous Dynamics; Spin Dynamics; Momentum Distribution
$\sigma_s(E,2\theta)$; $\left(\frac{\partial\sigma}{\partial\Omega}\right)_{eff}$ barns st^{-1}	Diffraction	Structure [Dynamics]	1000 Å → 1 Å	Biological Structures; Mixed Phase Systems; Crystallography; Magnetic Structures; Amorphous Structures; Surface Structures; Molecular Structures
σ_s (E) Barns	Total Scattering Cross-section	Structure [Dynamics]	1000 Å → 1 Å	Mixed Phase Systems; Applied Crystallography; Amorphous Structures; (Multiple Scattering Corrections)