CONDENSED MATTER RESEARCH WITH PARTICLE BEAMS

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Particle beams have opened up new horizons for condensed matter scientists. Electron/positron synchrotrons produce high brightness electromagnetic beams over a wide spectrum from the far infra-red to the hard X-ray region, facilitating new science in e.g. protein crystallography, powder diffraction, X-ray spectroscopy and liquid structure studies. The pulsed spallation neutrons produced using proton accelerators allow structural and spectroscopic studies of higher resolution and energy transfer than is possible using neutrons from fission reactors, opening up new areas of e.g. crystallography, molecular spectroscopy, magnetism and surface chemistry. Examples of this new science are discussed, with emphasis on the Synchrotron Radiation Source at Daresbury, and the ISIS pulsed neutron and muon source at the Rutherford Appleton Laboratory.

Introduction

Condensed matter science has built up an impressive array of experimental techniques. These are able to give high quality information not only on atomic, molecular, electronic and magnetic **structures** of crystalline, amorphous and liquid assemblies, but also on their **dynamics**. Structural information can be obtained over a wide range from sub-Ångstrom to micron and above, while excitations may cover decades from μeV to eV and above. Particularly important are techniques using electromagnetic radiation (e.g. X-ray scattering, UV, IR and Raman spectroscopy) and elementary particles such as electrons and neutrons.

As the field is clearly well furnished with experimental techniques largely (though not entirely) available at the home laboratory, it would seem perhaps not a promising area for particle beams to compete in. Over the past 5-15 years, however, experimental probes produced by particle beam machines have not only extended the power of the existing techniques, but have most dramatically opened up new areas in experimental condensed matter science.

Of particular importance has been the exploitation of (a) bright, tunable beams of electromagnetic radiation produced by electron/positron synchrotron storage rings, and (b) pulsed spallation neutron sources based on proton accelerators. The former began to be used in the early 1970s in parasitic mode, followed by dedicated sources such as the SRS at Daresbury. The latter are a more recent arrival on the condensed matter scene, the first such machine (IPNS at Argonne) coming on stream in 1981, while the most powerful - ISIS at the Rutherford Appleton Laboratory - has recently celebrated the fifth anniversary of its first neutrons. With particular reference to SRS and ISIS, characteristics of the electromagnetic radiation and neutron beams of particular interest to the condensed matter scientist (who may be a chemist, biologist, materials scientist or engineer, as well as a physicist) will be underlined, and examples given to illustrate the new science being done.

The Basic Scattering Experiment

In a general scattering experiment, an incident (e.g. X-ray or neutron) probe of wavelength λ will transfer **energy** $\Delta\epsilon$ and **momentum, Q** to or from the sample. In general, the probe will be scattered through an angle 2θ, the scalar value of the momentum transfer being given by $Q = 4\pi\sin\theta/\lambda$. In **elastic** measurements, $\Delta\epsilon=0$, and measurement of scattered intensity as a function of momentum transfer Q gives information on **structure**. In the particular case of a crystalline sample, a series of sharp peaks at discrete Q values is obtained. These peaks are essentially fourier components of the structure, which can therefore in principle be reconstructed by inversion. An **inelastic** experiment in which $\Delta\epsilon=0$ will probe the (e.g. thermal, magnetic) **excitations** in the (liquid, glass or crystalline) sample. Ideally, the scattered intensity $I(Q,\Delta\epsilon)$ is required as a function of both energy and momentum transfer.

In general terms, the "power" of an experimental probe might be characterised in terms of the above quantities. First, the **statistics** with which $I(Q,\Delta\epsilon)$ can be measured is clearly important: without adequate statistics, the features being measured will be poorly defined and the more subtle effects missed. Secondly, the **range** of Q and/or $\Delta\epsilon$ over which a measurement can be made will determine the kind of information that can be obtained. Finally, the **resolution** that can be achieved in Q and $\Delta\epsilon$ may also be crucially important. As a general statement, we can assert that, e.g. X-ray and neutron beams produced from particle beams can reduce - often dramatically - the limitations of existing techniques in accessing one or more of these measured quantities.

Synchrotron Radiation

When high energy electrons (or positrons) are confined to a circular orbit by strong magnetic fields in a storage ring, very **bright**, highly collimated photon beams are produced over a wide continuous spectral range. Although this "white" beam is used in certain experiments, normally a narrow - but still intense - waveband of **monochromatic** radiation is extracted. The energy of this monochromatic beam can be varied, this turnability giving a flexibility which is not available from a laboratory X-ray source, and can be particularly powerful when working close to absorption edges. The very high energy X-rays available in the most advanced sources are particularly promising for high resolution structural studies.

Two examples illustrate the power of synchrotron radiation in the X-ray region. First, major contributions have been made to protein crystallography, using both monochromatic X-rays (where tuning close to an absorption edge of a heavy atom can solve the crystallographic phase problem) and white radiation for very rapid data collection. For example, the structure of the foot and mouth disease virus was solved recently at Daresbury[1], in a study which would not have been possible without synchrotron radiation. This is the first animal virus structure to be determined in Europe. The details of the structure throw light on the

mechanism by which the virus may prevent recognition by antibodies.

Secondly, the high brilliance makes millisecond time-resolved studies possible. For example, very low angle diffraction studies on muscle **under contraction** have been developed at both the SRS at Daresbury and DESY[1,2], in order to try to understand the structural changes that occur as chemical energy is transformed to produce force. Several developments have recently come together at Daresbury to produce impressive diffraction patterns in 10 ms time slices during the contraction processes as well as in the resting and contracted states. When interpreted fully, this work should throw new light on the muscle contraction mechanism, and enable the standard models to be tested and if necessary revised. Many other non-biological examples exist of new areas which synchrotron radiation has opened up in X-ray spectroscopy, and in structural studies of crystalline and non-crystalline systems and surfaces.

Pulsed Spallation Neutrons at ISIS

Although neutron studies of condensed matter have developed using reactor sources in which **continuous** beams of high energy neutrons are produced through fission, perceived limits to the growth of reactor sources have led to the use of particle accelerators to accelerate high energy protons onto a heavy metal target to produce neutrons by spallation. Such sources have been constructed over the last few years in the UK, USA, Japan and Switzerland. The most powerful of these is ISIS, a **pulsed** spallation neutron source situated at the Rutherford Appleton Laboratory of the UK Science and Engineering Research Council.

ISIS is not, however, just another way of producing neutrons. The neutrons produced have characteristics which allow us to do condensed matter science that would be difficult, inefficient, or impossible on a reactor source. Central to these characteristics is the **pulsed** nature of the source from which the following specific advantages follow.

a) Experiments that require a **wide dynamic range** in $\Delta\epsilon$ or Q are favoured.

b) The **incident white (polychromatic) beam** allows us to collect a complete diffraction pattern at a single fixed scattering angle, the variation in Q ($=4\pi\sin\theta/\lambda$) being given by λ, not θ, variation. For example, fixed 90° scattering geometry is used with tight collimation to exclude background scattering from e.g. pressure cells, taking powder crystallography data close to 180° maximises the geometrical resolution, and measuring liquid scattering at low angles minimises troublesome inelasticity corrections.

c) Pulsed sources have inherently **very low backgrounds**. The source is essentially switched off when the data is being collected.

d) The use of **time-of-flight** detection using a white beam gives pulsed sources a major advantage of **high resolution**. This can be increased essentially arbitrarily by increasing the flight path.

e) Finally, the primary necessity of retaining the pulse structure through the moderation process, which brings the neutron energies into a useful range, results in an incident neutron spectrum which contains a significant high energy component. These **epithermal neutrons** make pulsed sources unique in their ability to probe high energy excitations through measuring large energy transfers $\Delta\epsilon$ (e.g. in magnetism), and very high momentum transfers Q. This high Q capability facilitates structural studies with very high resolution indeed.

Some Examples

High Resolution Powder Diffraction

The world-beating resolution of the high resolution powder diffractometer HRPD has allowed ISIS scientists to extend dramatically the power of powder diffraction. Situated on a long 96m beam line, uniquely high d-spacing resolution is achieved that is essentially constant over the wide d-range made available by the use of a white beam. As an illustration of the quality of data obtainable, Figure 1 shows the scattering from p-xylene. Such neutron powder patterns are unachievable on reactor sources, and are unmatched on other pulsed sources. Data of this quality means that, using HRPD, **we can obtain single crystal quality data using powder techniques.**

A recent example is the refinement of the **anisotropic** temperature factors of benzene[3], a procedure which previously required single crystals. Results were essentially identical with those of a benchmark single crystal experiment by Jeffrey et al[4], although the single crystal data took about fifty times longer to collect! The powder results were able to demonstrate the inadequacy of two models of the molecular vibrations. Further examples of single-crystal quality powder work are the determination of crystal structures ***ab initio*** from powders, (e.g. $FeAsO_4$[5], α-malonic acid[3]), and the study of hydrogenous samples (e.g. squaric acid[6]), which are generally a problem for neutrons because of the high background from incoherent scattering from the proton. Of particular note is the solution of the structure of the hydrogen-ordered form of "ordinary" hexagonal ice[7].

The very high resolution of HRPD also allows subtle structural changes to be detected that can be crucially important. In early work on high temperature superconductors, data on $La_{1.85}Ba_{0.15}CuO_4$ indicated subtle structural anomalies around the superconducting phase transition; Figure 2 shows a splitting of the (040) and (400) Bragg reflections at 120K[8] that had been missed by others. In addition to structure determination applications, peak shape analysis provides new information on both defect structures and their behaviour as external conditions change. Examples from the superconductors include the investigation of structural imperfections such as bulk micro-twinning and oxygen stoichiometry gradients by detailed analysis of the diffraction peak shape. Such work has important materials science implications.

High Intensity Powder Diffraction

The POLARIS powder diffractometer is optimised for **high intensity** with **good resolution**. It is particularly suited to **rapid measurements** (and hence to studying in real time phase changes and solid state reactions) or to small samples. A large 90° detector bank is used for work on systems under pressure, including a detailed structural exploration of high pressure ice

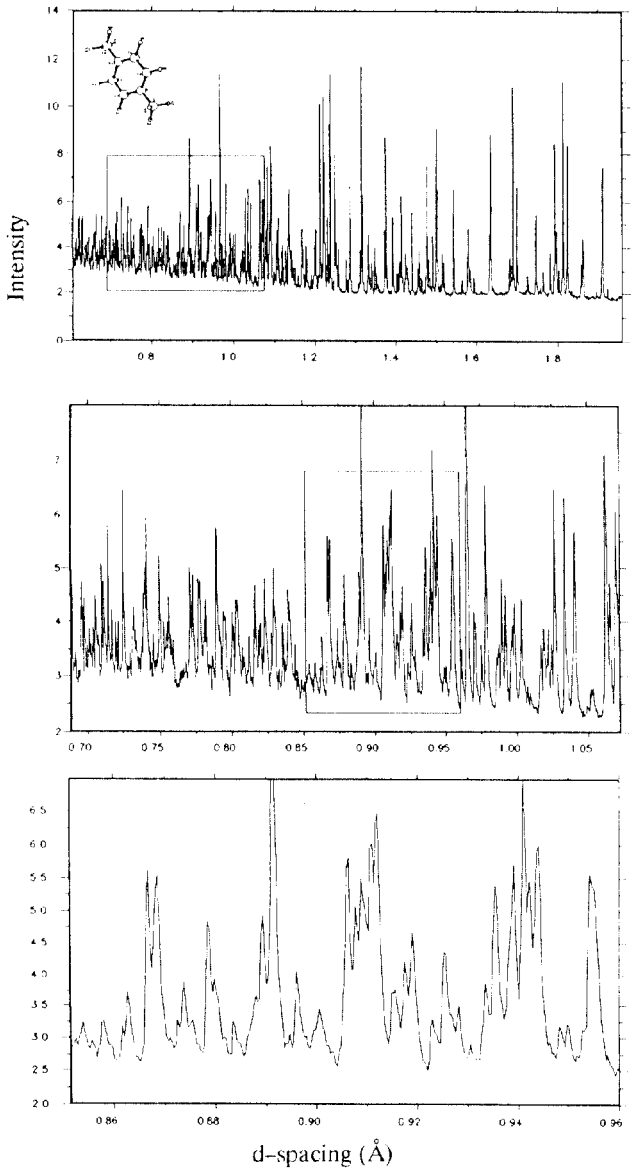

Figure 1 Data collected on HRPD from p-xylene. The corner plots show successive zooms on the data.

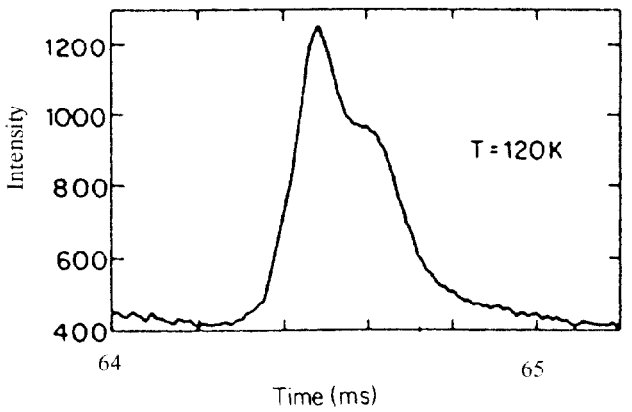

Figure 2 The orthorhombic splitting between the (040) and (400) Bragg reflections from $La_{1.85}Ba_{0.15}CuO_4$ at 120K.

phases.

A recent example is a study of the structural changes occurring on discharge of alkaline batteries[3]. Significant structural changes are seen to occur during discharge, including the expansion of the lattice associated with the intercalation of protons, and of the formation of ordered Mn–O–H phases close to the point of battery failure; these essentially hinder proton diffusion through the MnO_2 lattice.

POLARIS is also used increasingly in the non-destructive study of residual stress in engineering components, information which is important in predicting their failure characteristics and lifetimes. Time-of-flight neutron diffraction is an ideal tool for determining non-destructively the strain in a volume as small as 1 mm^3 at any point within a component.

Single Crystal Diffraction

Single crystal diffraction studies also can exploit the advantages of pulsed source neutrons. In particular, a wide coverage of Q is available, while the very high Q (0.3$Å^{-1}$) allows structural refinements to very high resolution indeed, as well as studies of anharmonicity, thermal disorder, and extinction.

The use of an extensive position-sensitive detector gives ISIS an instrument SXD which is particularly well suited to surveying the regions **between** Bragg peaks where information on disorder is available. It is thus a particularly suitable instrument for studying phase changes that occur with the appearance of superlattice peaks, twinned systems (e.g. high temperature superconductors), diffuse scattering, and static disorder. An example of diffuse scattering studies is found in recent work on yttria-doped zirconia[3], in which oxygen vacancies do not distribute themselves randomly in the structure. In the section shown in Figure 3, reflections such as (114) or (116), which are prohibited by the symmetry of the cubic zirconia structure, are seen. These arise from oxygen vacancy ordering which distorts the underlying cubic structure. There is also considerable diffuse scattering away from the Bragg positions which arises from vacancy clusters.

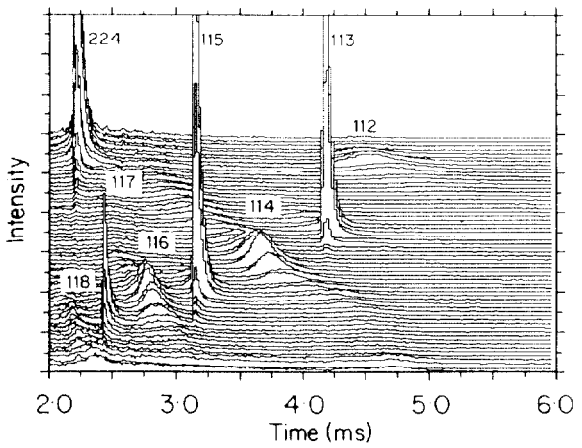

Figure 3 Bragg and diffuse scattering in the (hhl) plane of yttria-stabilised zirconia.

Reflectometry

Neutron reflectometry is a technique which has been pioneered at ISIS. By measuring the reflected intensity as a function of scattering vector Q, the structures of surfaces, simple and complex interfaces, and adsorption of molecules at interfaces can be studied.

The wide potential applications of neutron reflectometry have allowed the ISIS reflectometer CRISP to build up in a very short time a wide scientific programme in surface chemistry, surface magnetism (using polarised neutrons) and low dimensional structures. New and unique information has been provided on the compositional and structural variations with surface depth in a range of systems.

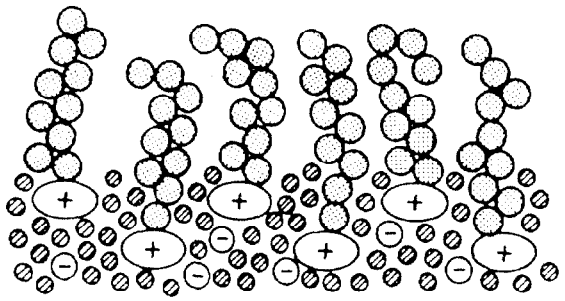

Figure 4 The structure of the surfactant decyl-trimethyl ammonium bromide adsorbed at the air-solution interface at 0.05M.

An example from surface chemistry is the development of the detailed structural model of the surface adsorption of decyltrimethylammonium bromide[9] (Figure 4). At low concentrations (less than a monolayer), a smooth surface layer is formed, the layer thickness of 16 ± 3Å indicating that the surfactant molecules are aligned with their long axes normal to the interface. At higher concentrations, the thickness increases by some 30% to 21 ± 1Å, the polar headgroups being "staggered" (see Figure 4), presumably to minimise electrostatic repulsion. The headgroup region which is 6Å thick contains the TMA headgroup, counterions, water of hydration, and about 10% of the alkyl chains. The tail group region is about 15Å thick, and contains only alkyl atoms. More recently, work has extended to other interfaces, for example adsorption at liquid-liquid, and liquid-solid interfaces.

In solid films, some emphasis has been on studying e.g. the nature of thin polymer films, interdiffusion at polymer interfaces, surface enrichment, and the ordering of block copolymers at interfaces. Low dimensional structure work has included Pt-C multilayers, GaAs/AlAs multilayers, Langmuir-Blodgett films, amorphous carbon layers, dielectric films of SiO_2 and Si_3N_4, and hydrogenation in Si/SiO_2 layers. Recent studies have also begun to probe the measurement of the non-specular or diffuse scattering from a surface, which contains information about the roughened nature of the surface.

Inelastic Scattering

The inelastic instruments on ISIS are also optimised to take advantage of the characteristics of pulsed source neutrons. High resolution is at a premium on all instruments, while wide dynamic

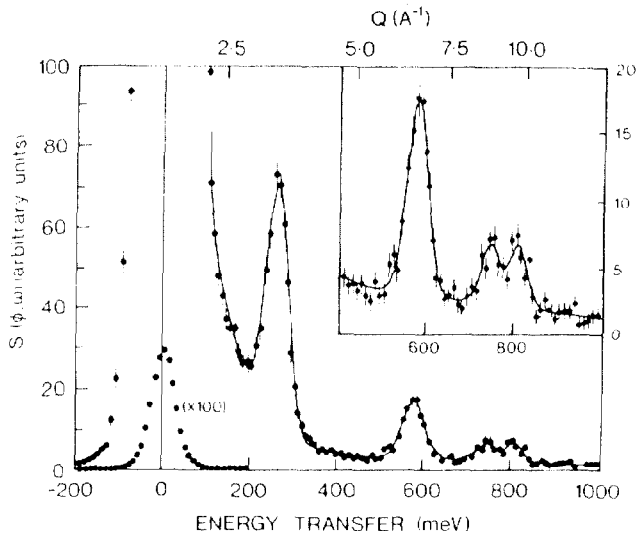

Figure 5 Neutron scattering cross section of praseodymium at 17K, showing four intermultiplet transitions.

ranges in energy transfer and/or momentum transfer are facilitated by the use of a time-sorted white beam. The power of very low backgrounds is being increasingly realised, while the epithermal component allows energy transfers to be measured that are unattainable on reactor-based instruments. Neutron molecular spectroscopy using the TFXA instrument is complementing and extending the power of the traditional Raman and infra red techniques, while the very high resolution combined with wide energy and momentum transfer ranges available on the IRIS spectrometer are leading to major advances in quasielastic and tunnelling studies.

The high energy transfer spectrometer HET was designed to investigate high energy transfer processes (such as thermal and magnetic excitations). A particularly impressive example comes from magnetic studies, where HET has established the new field of intermultiplet spectroscopy of 4f and 5f electrons in metallic systems. Figure 5 shows a spectrum taken from metallic praseodymium[9,10]: in addition to observing the lowest level at 260 meV, and confirming that its form factor (i.e. its variation with Q) has significant non-dipolar terms, higher order transitions up to 810 meV were also measured. The results show there is significant screening by the conduction electrons of the Coulomb interaction between the 4f electrons. More recent measurements on metallic thulium have extended the high energy limit to nearly 2 eV, while other recent work on UPd_3 has led to the first unambiguous determination of the valency of uranium in a metallic compound.

Other fields of study opened up by HET include the probing of high energy crystal fields - e.g. in UO_2 - with unparalleled resolution to reveal subtle interactions of a few meV which raise the degeneracy of transitions at a hundred meV and more. High resolution recoil scattering from e.g. the helium liquids at high momentum transfer reveal details of initial and final state interactions which cause departures from impulse scattering. Reactor-initiated studies of itinerant magnetism in the transition metals such as cobalt have been extended by following the collective magnetic excitations to the zone boundary at 300 meV.

It was long anticipated that ISIS would be pre-eminent at high energy transfer spectroscopy. It is only with the realisation of the source with its **excellent intrinsic resolution** and **superbly low backgrounds** that the strength of HET at moderate and low energy transfers became apparent. These energy transfers are available at reactor-based sources, but if high resolution is required - as is often the case - then ISIS has the instruments of choice. A recent example is the measurement of lifetime broadening of crystal field transitions above T_c in 10% Tm-doped 1-2-3 superconductor (see Figure 6). The observed splitting is related to that observed on HRPD (Figure 2). These new results imply that the carrier pairing begins at a temperature significantly above T_c.

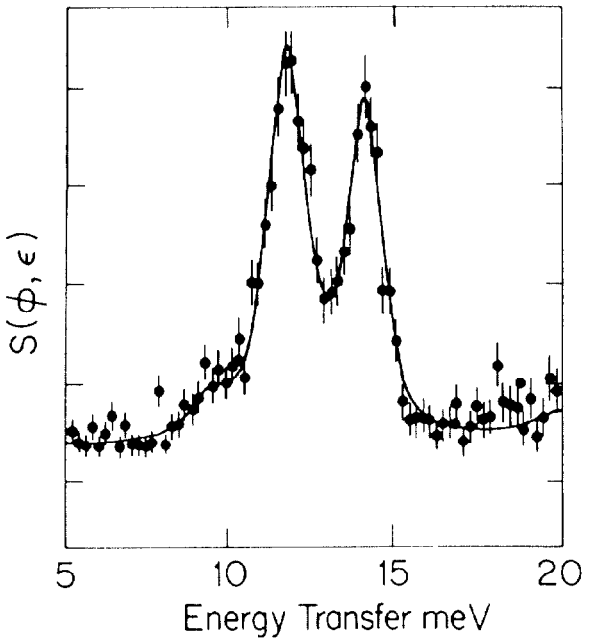

Figure 6 The crystal field transitions in the thulium-doped high temperature superconductor $YBa_2Cu_3O_{7-\delta}$, showing a splitting related to the small orthorhombic distortion.

Summary

The use of particle beams has significantly extended the experimental techniques available to condensed matter science. Many of the restrictions of energy and momentum transfer inherent in laboratory (and fission-reactor!) based techniques can be removed. Particularly important have been storage-ring sources of electromagnetic radiation and pulsed spallation sources of neutrons and muons. Not only have they extended the power of existing methods, but new scientific areas have been opened up.

Even the brightest synchrotron and pulsed spallation neutron sources are not approaching their limitations. The European Synchrotron Radiation Facility under construction will further extend the possibilities, particularly in the hard X-ray region, while the proton current of ISIS can be increased by an order of magnitude, and a lower frequency second target station optimised for cold neutron studies can be added. These enhancements would further extend the capabilities of European neutron scattering into more new exciting areas of condensed matter science.

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