

BNL--43872

DE90 008511

Neutrons: The Kinder, Gentler Probe of Condensed Matter

J. D. Axe

**Brookhaven National Laboratory
Upton, New York 11973**

Presented at the 1989 Fall Materials Research Society Meeting

**Boston, Massachusetts
November 27-December 2, 1989**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DM
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

NEUTRONS: THE KINDER, GENTLER PROBE OF CONDENSED MATTER

JOHN D. AXE

Brookhaven National Laboratory, Upton NY 11973

ABSTRACT

Neutrons play an increasingly important role in the characterization of advanced modern materials. They provide information that complements rather than competes with that provided by other scattering probes. Although neutrons require heroic efforts to produce, the techniques for using them are not particularly difficult, and with the advent of sufficient user friendly facilities, are becoming a routine tool in the arsenal of expanding numbers of materials scientists.

INTRODUCTION

Perhaps our growing understanding of elementary particles will someday allow us to design probes of condensed matter in much the same way as we manipulate the properties of molecules or genes today. But even with such unlimited possibilities it is hard to imagine improving much upon the particle that James Chadwick discovered in 1932.

Unlike beams of electromagnetic radiation, electrons or other charged particles which are used as probes and which interact primarily through the long-range Coulomb fields, neutrons interact primarily by way of nuclear forces. Although these forces are strong they are sufficiently short-ranged to allow neutrons to penetrate deeply (several centimeters) into most materials, whereas electrons or x-rays of comparable wavelength are confined to the surface. As a consequence neutrons easily probe materials in the bulk, even perhaps in a complex high pressure or low temperature environment. (Neutron scattering measurements have studied the spontaneous nuclear magnetization in silver at temperatures as low as $2 \times 10^{-9} \text{K}$ [1].) The nuclear forces vary from isotope to isotope (even for the same element) in an erratic way, a fact that has been used to advantage in structural investigations of materials containing light atoms, and has been rendered more powerful by ingenious isotopic labeling schemes in the study of polymers, molecular assemblies such as micelles, and biological systems.

Thermal neutrons, which are readily produced in the core of a reactor or through moderation of spallation neutrons in a pulsed proton accelerator have a wavelength distribution peaked around 1.6Å, and are well suited for studying variations in atomic structure on a microscopic scale. Yet, thermal neutrons, which by definition have no more energy than a room temperature air molecule, cannot disrupt even the most delicate of materials under study. This is a direct consequence of the relatively heavy mass of the neutron. (By contrast, x-rays or electrons with wavelengths around 1Å have energies around 12 keV and 3.3 eV, respectively.) An even more fundamental consequence of neutron mass is that thermal neutrons have energies comparable to the thermally induced fluctuations in solids (about 1/40 eV), making them uniquely well suited to the study of the thermally important dynamics of materials by inelastic scattering. In addition, the magnetic moment of the neutron provides it with a unique

capability of examining the magnetic properties of materials, crystal field levels, and particularly the dynamics of such systems.

INSTRUMENTATION AND SOURCES

Perhaps less well known than these special properties of neutrons is the quiet progress that has been made in the energy range available for neutron studies, which has expanded greatly due to new developments in sources and instrumentation in the last one and a half decades. Figure 1 shows the energy-momentum region available to the modern practitioner of neutron scattering. With current techniques one can study excitation energies varying over some seven orders of magnitude, and excitation wavelengths varying over six orders of magnitude.

Studies that involve large energy or momentum transfer naturally require epithermal neutrons. Pulsed spallation neutron sources have greatly expanded our capabilities in this area. To see why this is so, note that the very short pulses (sub-microsecond duration) of 500-1000 Mev protons supplied by the accelerator produce equally short bursts of fast neutrons. The energy of these neutrons must be slowed by collisions in a surrounding moderator. These moderators must achieve a compromise between slowing power and burst width of the slowed neutrons, which varies between 1 to 50 microsecond duration. As a result, the spectral characteristics of neutrons from pulsed sources differ from those of reactor neutrons, in that there is a much larger component of higher-energy neutrons (energies above 100 meV). The exploitation of this new energy regime is one of the great opportunities presented by spallation sources.

A more fundamental difference between reactor and pulsed neutron sources is that all experiments at pulsed sources involve time-of-flight techniques to analyze the scattering events. Since the neutron bursts are spaced 20 to 100 milliseconds apart, the duty cycle is low. Furthermore, the peak intensity of the neutron bursts from existing spallation sources do not greatly exceed the steady state value from the highest flux research reactors. Fortunately, for many types of experiments the time structure of the bursts can be used in a very efficient way to more than overcome the disparity. A comparison of a typical diffraction experiment with steady state and pulsed neutron sources is outlined in Figure 2. On the left, a monochromator crystal selects a narrow band of neutron energies from the thermal distribution of a reactor. This monochromatic beam falls on a sample, which scatters the beam from one diffracting plane into the detector. The detector signal is constant in time. On the right, the pulsed source allows a wide spectrum of neutron energies to fall on the sample in sharp pulses. Neutrons of many energies are then simultaneously scattered by different diffracting planes and their times of arrival are analyzed to determine the nature of the scattering. Thus the time-of-flight method uses a much larger interval of the energy spectrum than does the steady state method (center panel of Figure 2).

Table I shows a comparison of the major U.S. research reactor facilities in the U.S. Also shown is the major European neutron scattering center at Institute Laue-Langevin in Grenoble, France. Note that the characteristics of the ILL source are very similar to those of the HFBR and HFIR, but that there are many more instruments. This is the result of the extensive use of neutron guides, which totally reflect long wavelength neutrons, leading them to guide halls physically removed from the crowded central reactor floor. In such a low background environment there is ample room for additional instruments. Table II shows a similar comparison of the U.S. pulsed neutron

scattering facilities with the major new U.K. facility, SNS, at Rutherford-Appleton Laboratory. The peak thermal flux depends upon neutron energy and details of the moderator design, but the stated numbers for a "standard" room temperature moderator are included for comparison with reactor sources. Average spallation neutron fluxes are down from the peak fluxes by a duty factor of about 10^3 . Roger Pynn surveys neutron instrumentation at reactor and pulsed sources in the following contribution to this Symposium.

The European experience has proven beyond doubt the desirability and cost effectiveness of neutron guide halls. A new guide hall is in advanced construction at the NIST reactor, and plans exist for a similar extension of the capabilities of the HFBR. But the most ambitious and exciting U.S. plans are for an Advanced Neutron Source, which is presently in conceptual design. If funded, this facility will surpass the flux performance of existing reactors, make extensive use of hot and cold sources, and be the major focus of U.S. neutron scattering activities for the next century. A description of plans for ANS is given by John Hayter in this Symposium.

Table I. Research Reactors for Thermal Neutron Scattering.

	Thermal Power MW	Av. Thermal Flux (10^{14} n/cm ² sec)	No. of Instruments	Comments
High Flux Isotope Reactor Oak Ridge, TN	100	15	9	Transplutonium Production
High Flux Beam Reactor Brookhaven, NY	60	12	14	Cold Source
NIST Research Reactor Gaithersburg, MD	20	2	11	Cold Source, Guide Hall
Missouri Univ. Reactor Columbia, MO	10	1	7	Irradiation Facilities
Institute Laue-Langevin Grenoble, France	60	12	~40	Cold & Hot Sources, Guide Hall
Advanced Neutron Source Oak Ridge, TN	350	80-90	~40	Cold & Hot Sources Guide Hall

Table II. Spallation Sources for Thermal Neutron Scattering.

	Av. Fast Neutron Production (10^{15} n/s)	Pulse Frequency (HZ)	Peak Flux (10^{14} n/cm ² sec)	No. of Instruments	Comments
LANSCE, Los Alamos, NM	6	12	14	9	Cold Source Guide Hall
IPNS Argonne, IL	4	30	9	9	Enriched U-target Cold Source
SNS, Rutherford U.K.	16	50	14	14	Deple.ed U-target Cold Source

POWDER DIFFRACTION

The use of neutron powder diffraction for both basic and applied research has increased dramatically in recent years. At facilities which provide dedicated powder

diffraction capabilities to users, the requests for instrument time consistently exceed availability. This increased interest in powder diffraction is largely the result of improved data analyses that collectively are known as profile refinement methods [2]. These techniques attempt to redress the main inherent difficulty of powder methods, namely that in even moderately simple crystal structures different Bragg reflections become increasingly crowded together as the scattering angle, 2θ , increases. It is impractical to circumvent this by arbitrarily increasing the resolution of the instrument in order to cleanly separate the peaks. However, having characterized the resolution of the instrument, it is possible with modern computers to calculate the intensity profiles of partially overlapping patterns by least-square refinements of the individual peak positions and intensities. At the current high flux sources, a resolution of $\Delta d/d=3 \times 10^{-4}$ can be achieved [3].

The method offers the natural advantages of constant scattering factor (no form factor), high penetration power and freedom from texture and preferred orientation which are often associated with small x-ray samples. The additional beauty of the technique is that it can be more or less routinely and reliably applied to the refinement of crystal structures with of the order of 50 positional parameters. This includes many materials in such technologically important areas as superconductivity, catalysis, magnetism, and fast-ion conductivity. Zeolites, for example, have considerable commercial importance as ion-exchangers, molecular sieves and heterogeneous catalysts for hydrocarbons reactions. Figure 3 shows the result of a recent determination of the localization of benzene in sodium Y zeolite, in which a powder refinement was first obtained for the base zeolite, and the position of the absorbed benzene deduced by difference Fourier techniques [4].

NEUTRONS, MAGNETISM AND SUPERCONDUCTIVITY

Neutron diffraction has played an important role in the structural characterization of the new copper oxide high temperature superconductors. The discovery of $\text{YBa}_2\text{Cu}_3\text{O}_7$, for example, was quickly followed by several x-ray determinations of the cation positions. However, because of twinning problems and the relatively weak oxygen scattering, x-rays were unable to establish the oxygen stoichiometry and location with much certainty. This knowledge, which is vital to a proper understanding of these materials because oxygen vacancies provide the necessary electronic doping, came only as a result of neutron powder diffraction studies [5].

An atom with a magnetic moment has, in addition to a nuclear scattering amplitude, a magnetic scattering amplitude,

$$p = \gamma r_0 S f = 0.54 S f \times 10^{-12} \text{cm}$$

where γ is the nuclear gyromagnetic ratio, r_0 the classical radius of the electron, S the spin quantum number of the atom and f the form factor of the magnetic electrons. In general, the magnitude of p is comparable with nuclear scattering lengths. The phase of the magnetic amplitude depends upon the relative orientations of the moments of the electrons and neutrons, and causes polarization of the scattered neutron beam, an effect which can be additionally employed to distinguish nuclear and magnetic scattering.

Consequently, magnetic neutron scattering provides a unique tool for the study of the spatial magnetic order (ferro- and anti-ferromagnetic, spin glass, etc.). Once again, high temperature superconductors provide important, topical examples. Antiferromagnetism has been detected by powder neutron diffraction in the insulating prototypes of most CuO-based superconductors, in spite of the small (0.5 Bohr magneton) moment [6]. Figure 4 shows an example of the magnetic phase diagram of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ deduced by neutron scattering studies [7]. As examples of quasi-two dimensional spin 1/2 antiferromagnets, these systems have considerable intrinsic interest. However, even more interesting from the standpoint of superconductivity is the observation that although the magnetic long-range order disappears quickly with metallic doping, careful magnetic diffuse scattering measurements show that substantial magnetic short-range order persists even into the superconducting phase. Such behavior is contradictory to that of conventional superconductors, and is thought by many to provide an essential clue to the mechanism of high temperature superconductivity, which is still not understood. Neutron scattering techniques have also made important contributions to the study of magnetic penetration effects, including magnetic flux lattices.

METALLURGY AND CERAMICS

The traditional, but no less essential, uses for neutrons in these fields are concerned with structure, stoichiometry and order on the atomic scale, and the changes in these properties that occur at phase transformations. Many of these questions are answered by standard elastic diffraction techniques, although the understanding of disorder and the mechanism of phase changes often center on elastic or inelastic diffuse scattering measurements. Increasingly, however, materials scientists are finding that the great penetration depth and non-destructive nature of neutrons are also making them indispensable in characterizing real materials on a more macroscopic scale using small-angle scattering techniques.

Grain boundary cavitation, whereby small voids develop and accumulate at grain boundaries of materials subjected to deformation at elevated temperature, is an important and poorly understood damage mechanism in real high temperature materials. The type of information needed to understand this phenomenon includes the number densities of the voids and their size distributions as functions of time, temperature and deformation parameters. A large number of voids should be sampled, even though the void volume fraction is low. Void volume fractions of less than 10^{-6} can be measured. A wide range of void sizes (a few nanometers to nearly a micrometer) can be detected and analyzed, making possible comparisons with various theories of cavitation nucleation and growth. Of course, similar techniques are also routinely used to study a variety of other precipitation phenomena.

Another use of neutron scattering in the study of real materials is the measurement of bulk residual stress. Other methods commonly employed (e.g., strain gauge measurements of trepanned samples, ultrasonics) are either destructive or are strongly affected by texture in the sample. Yet the ability to reliably measure the distribution of internal stress fields in fabrications and weldments, as well as in composite materials such as cermets, is vital to the safe and effective design of parts using such materials. The principle of the neutron scattering technique is identical to that using x-rays, in which the local internal lattice stress in a material is determined from the measured elastic lattice strain it produces. The magnitude of the strain is

deduced from the lattice plane spacing using Bragg law, and the direction of the strain is that of the scattering vector. The strains are small, typically $\Delta d/d=10^{-3}$ to 10^{-4} , so that extremely good instrumental resolution is required. The volume of the sampled material is defined by the overlap of the paths of the incident and diffracted beams, which are in turn determined by neutron absorbing apertures. The best spatial resolution occurs when the beam is diffracted at right angles. Figure 5 shows some sample data, taken after the release of the applied stress, on a mild steel bar subjected to plastic strain [8]. The bending causes strains which exceed the elastic limit in the outer (tensile) and inner (compressive) regions of the bar. But on release of the applied bending moment, the elastic strains in the previously plastically deformed extreme outer and inner regions of the bar reverse and, at equilibrium, oppose the strains in the central regions of the bar.

POLYMERS, MACROMOLECULES AND BIOLOGY

This is the realm of large, noncrystalline molecular assemblies, and it is often impractical to attempt detailed structure determination at the atomic level. Fortunately, lower resolution small angle scattering studies are both useful and feasible. (It is customary to describe the measured scattering in terms of a function $S(Q)$, which is the Fourier transform of the real-space correlation function, $G(r)$. Thus small momentum-transfer, Q , implies large, coarse-grained real-space resolution. In terms of the scattering kinematics $Q=(4\pi/\lambda)/\sin(\theta/2)$, where θ is the scattering angle. Consequently, small Q is achieved by some appropriate combination of small scattering angle and long de Broglie wavelength, λ , for the probe.) The choice of neutrons rather than x-rays for this purpose has largely to do with the unique neutron scattering properties of the isotopes of hydrogen.

Table III compares the scattering lengths of most of the atoms of any significance in macromolecular assemblies. The scattering lengths for x-rays are proportional to atomic number, making the heavy elements far more conspicuous than hydrogen. In the case of neutrons, not only are all scattering lengths of the same magnitude, but the H scattering length is negative. This signifies that in a certain sense H acts like a negative hole with respect to other atoms, including D. Since most of the atoms of a typical macromolecule are hydrogen, very large changes in the scattering properties can be effected by selective deuteration techniques.

The ramifications of selective deuteration are so numerous that only a few examples suggesting the power of the coupling of this technique with SANS will be mentioned [10]. It can be used to study the configuration of a single polymer molecule both in dilute solutions or bulk. Such studies show how the "size" (radius of gyration) and thus the conformation of a polymer molecule varies with changes in molecular weight and intermolecular interactions. Many macromolecules (e.g. block copolymers, micelles, most biological objects) are composites of different chemical species with different average neutron scattering power. Low resolution information on the spatial disposition of the components can be easily obtained by the "contrast variation" method, in which mixtures of hydrogenated and deuterated solvent are used to match the scattering density of the solvent to one of the components. The neutrons only "see" the unmatched components of the original object. Of course, in favorable cases the experiment can be repeated by matching the solvent to each of the components separately. The method is particularly powerful in differentiating, for example, the protein coat of a virus from its DNA interior.

Table III. Scattering Lengths for Neutrons and x-rays of Elements of Importance for Macromolecules.

	Neutrons ($b \times 10^{12}$ cm)	x-rays ($b \times 10^{12}$ cm)*
H	-0.374	0.28
D	+0.667	0.28
C	+0.665	1.69
N	+0.94	1.97
O	+0.58	2.25
P	+0.51	4.23
S	+0.28	4.50

*x-ray scattering lengths are given for a scattering angle of zero

NEUTRON REFLECTOMETRY

As with any other wave-like disturbance, a neutron beam on traversing an interface between two transparent materials with differing index of refraction (which is in turn determined by the scattering density) is partially reflected. The way that the reflected intensity falls off with angle of incidence is determined by the apparent sharpness of the interface. The interface may become unsharp either through true diffusion of material across the boundary or through local roughness which produces a similar average blurring of the interface. Scattering from multiple nearby interfaces interfere, and the contrast of the resulting interference pattern once again provides information on the sharpness of the interface. Since neutron scattering cross sections are typically very weak (in comparison, for example, to visible light) appreciable reflected intensity is restricted to glancing angles (5 degrees or less). Over the last few years, several specialized instruments have been constructed for studying neutron reflectometry.

Once again, neutrons offer special advantages over x-rays in the study of polymer interfaces because of the possibilities of deuteration as discussed above. Interdiffusion of entangled polymer molecules across a boundary have been studied by this method with resolution of about 10Å, better by an order of magnitude than is possible with competing techniques (IR and forward recoil spectroscopy and secondary ion mass spectrometry). These studies have helped both to confirm and refine current models of polymer diffusion. The neutron index of refraction is also sensitive to magnetic fields, and this has been used to measure the magnetic penetration depth in superconductors.

NUCLEAR TRANSMUTATION AND ACTIVATION

Although they do so with a lower probability, neutrons are absorbed as well as scattered by matter. No discussion of the role of neutrons as a probe in the material sciences would be complete without mention of processes which depend upon

absorption rather than scattering [10]. Silicon doping by transmutation furnishes one example. Every year more than 50 metric tons of silicon for the electronics industry are processed in research reactors around the world. In the processing some of the Si^{30} , which is 3% naturally abundant, is transmuted to stable P^{31} . The uniformity of distribution of the phosphorus, which vastly exceeds anything achievable by other means, translates into superior performance characteristics for devices as diverse as high power rectifiers and infrared detectors. Also, because the doping level can be very precisely controlled by adjusting the neutron flux, neutron transmutation doping is now widely used to compensate for inevitable trace boron to produce what is in effect ultrapure silicon starting material.

As the name implies, in neutron activation analysis samples placed in a neutron flux are temporarily rendered slightly radioactive by neutron capture. The nature of the radioactive decay can provide a unique signature of the elemental composition of the sample. The sensitivity varies from element to element, but exceeds one part in 10^{12} in favorable cases. As an example of the scope of this technique, a geochemical survey of a number of western states was carried out in which to the sedimentary distributions of over 30 strategically important elements were logged in this manner. Only the broad applicability and specificity of neutron activation analysis made such a large scale program feasible.

Such exquisite sensitivity has found other unique applications in many fields where the non-destructive nature of the testing is often of paramount importance. In archeology, trace element neutron activation analysis has helped to sort ancient pottery by the composition of its clay. It has been used to detect art forgeries, is routinely used in forensics to establish the identity of hair and fiber samples, and is the basis of a luggage scanning system with sufficient sensitivity to detect small but lethal quantities of plastic explosives.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Division of Materials Sciences under Contract No. DE-AC02-76-CH00016.

REFERENCES

1. O.V. Lounasmaa, *Physics Today* 42, 26 (1989).
2. H.M. Rietveld, *J. Appl. Crystl.* 2, 65 (1969).
3. A.W. Hewat, *Mater. Sci. Forum* 9, 69 (1986).
4. A.N. Fitch, H. Jobic and A. Renouprez, *J. Phys. Chem.* 90, 1311 (1986).
5. There are many individual references. For a review see J.D. Jorgensen, *Jpn. J. Appl. Phys.*, 26, Suppl. 2018 (1987).
6. For a review of magnetic properties of HTSC see R.J. Birgeneau and G. Shirane in "Physical Properties of High Temperature Superconductors," D.M. Ginsberg, ed., (World Scientific Publishing, Feb. 1989).
7. J.M. Tranquada, *et al.*, *Phys. Rev. B* 38, 2477 (1988).
8. A.J. Allen, M.T. Hutchings and C.G. Windsor, *Adv. Phys.* 34, 445 (1985).
9. For reviews of neutron scattering in biology and polymer science, see P.B. Moore, *Physics Today* 38, 62 (1985), and R.S. Stein and C.C. Han, *ibid.*, 38, 74 (1985).
10. See, for example, A.D. Bromley, *Physics Today* 36, 30 (1983), for a description of other uses of neutrons in science and technology.

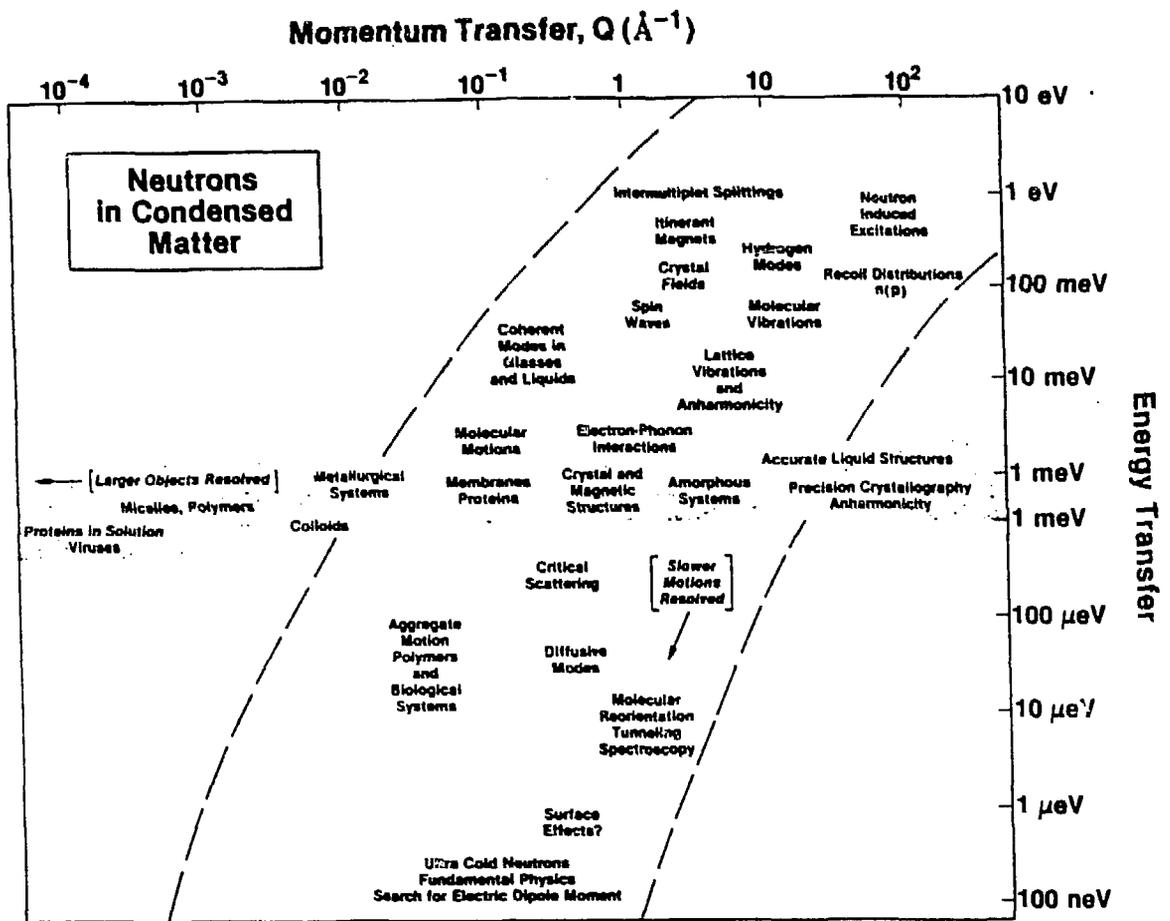


Figure 1. Schematic representation of some of the fields of science covered by neutron scattering. The fields are roughly represented by the area in which the words appear. The center-shaded-area represents elastic scattering with no energy discrimination.

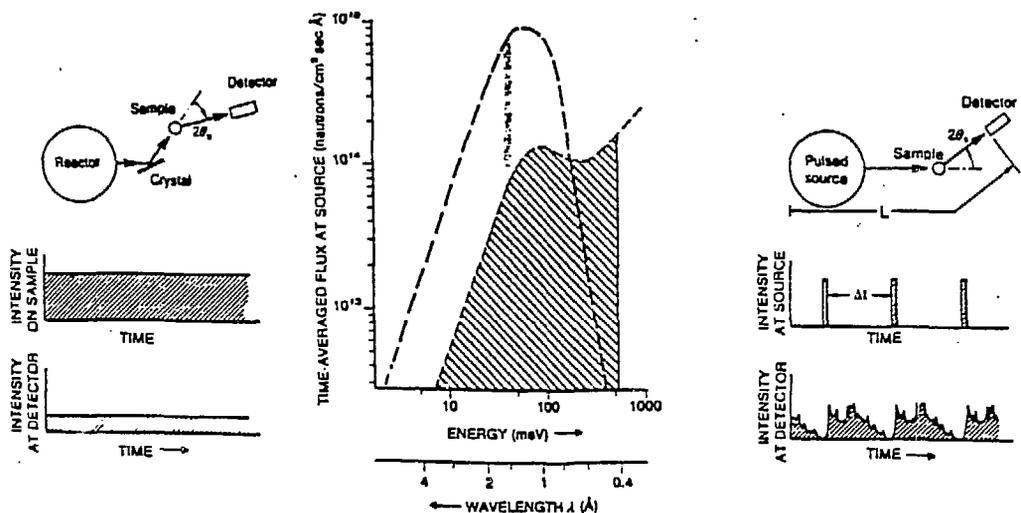


Figure 2. Comparison of diffraction experiments with steady state and pulsed neutron sources. In steady state experiment (left) steady beam of monochromatic neutrons diffract into detector. In pulsed experiment (right) pulses of white neutrons are diffracted and their energies are deduced by their arrival time at detector. Thus pulsed source makes efficient use of a smaller average neutron flux.

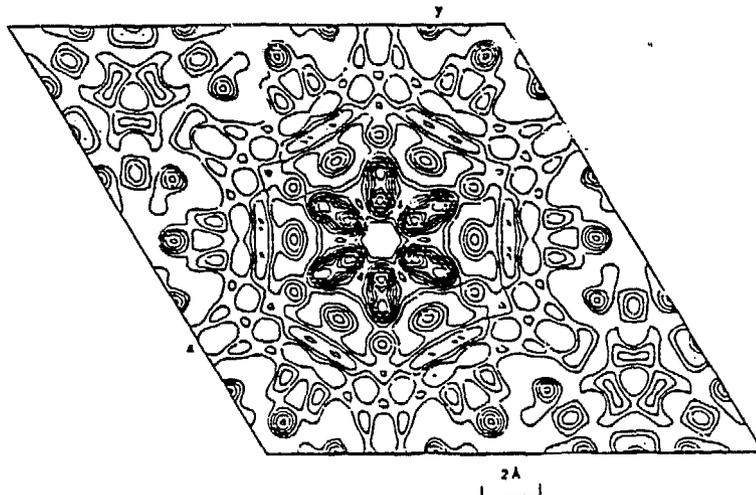


Figure 3. Fourier difference map showing the location of absorbed benzene molecule in sodium Y zeolite derived from powder profile refinement. (After Fitch, et al., Ref. 4.)

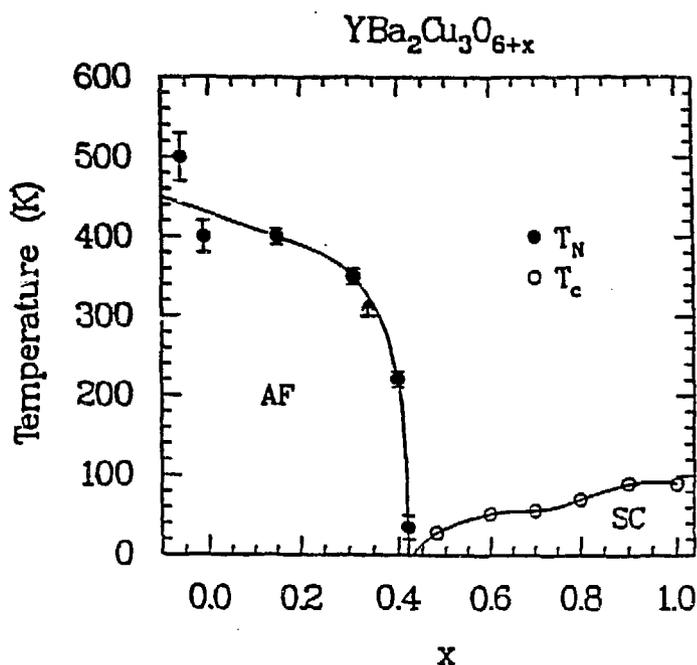


Figure 4. Phase diagram for $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ showing the antiferromagnetic phase boundary as determined by neutron diffraction on powder samples. Superconductivity onsets abruptly after the disappearance of antiferromagnetic long range order.

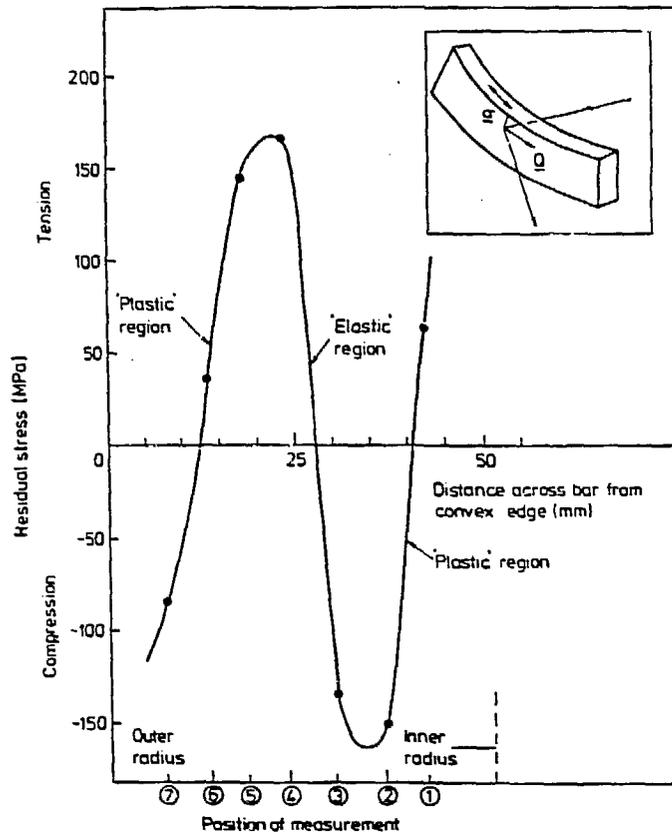


Figure 5. Variation of residual stress with position across plastically deformed steel bar after relaxation of the applied bending stress. (After Allen, et al., Ref. 9.)