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The Complementarity of X-Rays and Neutrons

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THE COMPLEMENTARITY OF X-RAYS AND NEUTRONS

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Nature is subtle and grudgingly reveals her secrets. In such an uneven contest scientists need to exploit every possible advantage. Just as high energy and nuclear physicists use hadrons, leptons and photons as scattering probes, so the modern condensed matter scientist relies upon NMR, ESR, μSR, infrared, optical and UV spectroscopy as well as classical transport and thermal measurements, to understand material properties. For structural studies electron and x-ray diffraction are commonly used. Traditionally neutrons, because of the expense and the potential for greater environmental impact associated with their production, are reserved for studies where their unique properties mandate their use. The emergence throughout the world of major user facilities for both synchrotron x-rays and neutrons has recently underlined the degree to which x-ray and neutron scattering studies complement one another.

Let us quickly review some of the advantages of neutrons. Neutrons are more penetrating, more precise (to the extent that they scatter from the nucleus rather than the extended electron cloud), more uniform in scattering power, more "magnetic" and more massive (and thus less energetic) than x-rays of comparable wavelength. Indeed, if expense and ease of access were not a factor, neutrons would very often be the probe of choice.

MAGNETIC SCATTERING

Let us begin our survey with magnetic scattering, a subject that has in the past been the exclusive province of neutrons. Recently, with the advent of polarized, high brightness x-ray sources, considerable progress has been made in magnetic x-ray scattering. For example, the natural intrinsic x-ray momentum resolution has been used to reveal subtle commensurate lock-in transformations in rare earth antiferromagnets that had previously gone undetected with neutrons.[1] But the ratio of scattering amplitudes favors neutrons by a factor of order $\mu_n m_e c^2/\hbar\omega \approx 10^3$ (μ_n is the nuclear gyromagnetic ratio, $m_e c^2$ the rest energy of the electron and $\hbar\omega$ the energy of the x-ray photon). This fact guarantees the superiority of neutrons for most magnetic structure measurements as well as all inelastic scattering studies. Consider, for example, **Fig. 1**, which shows the growth of antiferromagnetic (AF) superlattice reflections in a polycrystalline sample of the magnetic superconductor $TbMo_6S_8$. Now imagine reducing the magnetic peak intensities relative to the structural ones by 10^6. At some point the peaks become lost in the intrinsic diffuse background, which for x-rays is due to Compton and inelastic phonon scattering. (However, in favorable cases, this problem can be mitigated by the use of the x-ray polarization selection rules.)

On the other hand an exciting new discovery is the resonant enhancement of magnetic scattering that occurs near certain x-ray absorption edges.[2] **Fig. 2** shows such an example of AF superlattice for the uranium M-edges ($3d_{5/2} \rightarrow 5f_{7/2}$) in UAs, where the

cross section reaches 10^{-2} of the charge scattering. Other convenient resonances occur at L-edges of rare earths. But the analogous L-edges for 3-d transition elements are at 0.7 keV, an x-ray wave vector useful for study of ferromagnets, but too short for studying AF structure. Among the many interesting prospects for resonant enhanced magnetic x-ray scattering is the study of surface and interfacial magnetism.

Recently, anomalous x-ray scattering has been used to determine the valence of copper ions in high T_c superconductors.[3] **Fig. 3** shows the x-ray form factor derived for Cu atoms at two different crystallographic sites in $YBa_2Cu_3O_6$. It can be seen that the Cu(2) site form-factor agrees well with that expected for Cu^{2+} whereas Cu(1) agrees with Cu^{1+}. This result confirms the magnetic structure determined with neutrons which shows the magnetic moment to be on divalent Cu(2) sites,[3] but is in principle more powerful, since it can determine the spatial distribution of different valences (e.g. Bi^{+3} and Bi^{+5}), even if no magnetism is involved.

SURFACE STUDIES

Neither x-rays or neutrons have yet had the impact of LEED in the study of surface structure. But electron diffraction has its own disadvantages and is impractical in the study of high-vapor-pressure solids. In spite of a lack of surface specificity, early neutron scattering studies were important in establishing the structure of mono-layer and few-layer films of such model systems as rare gases and simple hydrocarbons on graphite.[4] These studies were carried out on exfoliated graphite, which possesses a very large surface/volume ratio. It is now clear that the greater spatial resolution and surface sensitivity afforded by bright, well-collimated synchrotron x-rays offer advantages that neutrons cannot match for the study of surface structure. On the other hand, inelastic neutron studies are now beginning to yield valuable information concerning the dynamics of sub-monolayer films. For example, **Fig. 4** shows the successive rotational and translational melting transformations of ethane on graphite derived from high resolution incoherent inelastic scattering measurements.[5] This field of inelastic surface studies will profit greatly by increases in flux contemplated in the Advanced Neutron Source, a 10^{16} n/cm^2-sec reactor now under design at Oak Ridge National Laboratory.

STRUCTURAL BIOLOGY

Neutrons complement x-rays in two distinctly different ways in structural biology, both depending on the unique and contrasting neutron scattering power of light-and heavy-hydrogen isotopes. At high resolution, neutrons are used in conjunction with x-ray electron density maps (on which hydrogen atoms are not visible) to complete the structure determination. **Fig. 5** shows, for example, the structure of surface-bound water molecules on the respiratory protein myoglobin.[6] This water of hydration, which is manifest only in low order Bragg peaks, is typically ignored in refinement processes.

Although the contributions of crystallography to structural biology are profound, it must be remembered that biology is not mineralogy. Cells are not constructed like rocks, and appropriate non-crystallographic techniques are essential in studying the correlations

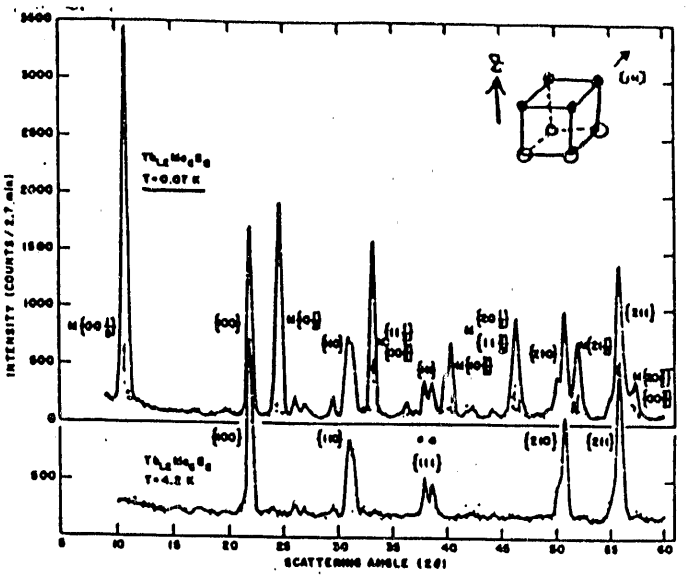

Fig. 1. Neutron powder diffraction patterns for the magnetic superconductor $TbMo_6S_8$, showing the growth of antiferromagnetic bragg reflections. After W. Thomlinson, *et al.*, Phys. Rev. 23, 1981, p. 4455.

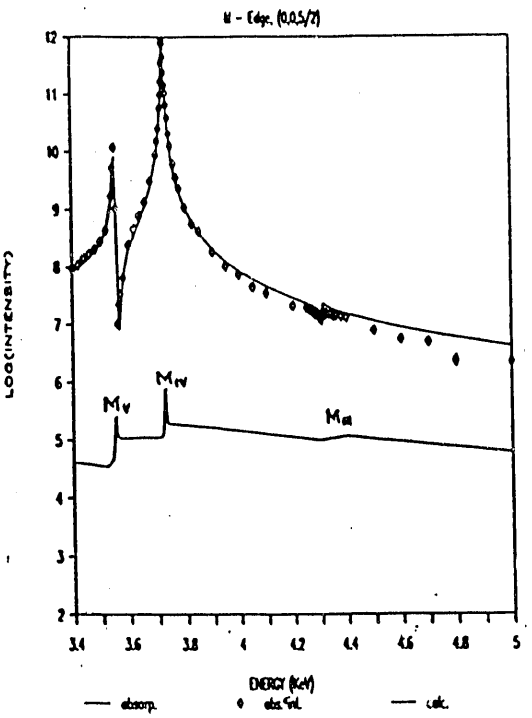

Fig. 2. Resonant enhancement of magnetic x-ray scattering near the $3d5/2 \rightarrow 5f7/2$ transitions in UAs (Ref. 2).

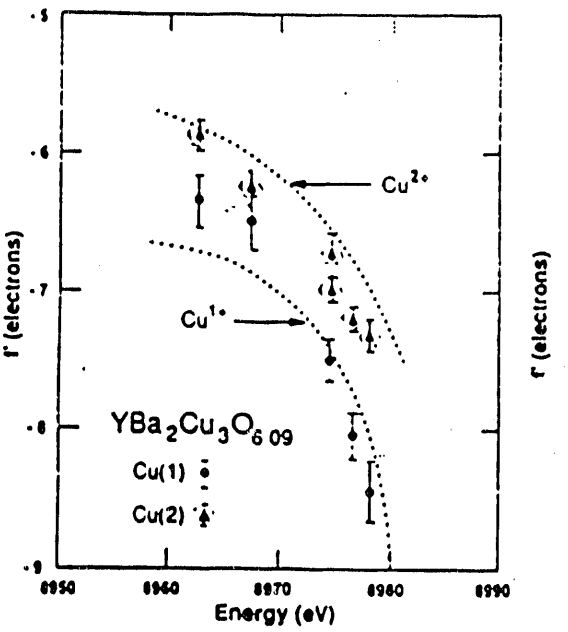

Fig. 3. X-ray scattering amplitude vs. x-ray energy for mono-and di-valent Cu-sites in a high-temperature superconductor near the K-absorption edge. (Ref. 3).

between structure and functionality in real, biological systems. The large scale conformation (tertiary structure) of proteins, nucleic acids and lipids determined in an artificial crystalline environment by a combination of x-ray and neutron crystallography, often changes significantly in a biologically relevant setting. Here is where small angle neutron scattering (SANS) experiments come to the fore. SANS uses the different scattering power of H and D to selectively reveal aspects of complex biological assemblies which are invisible to x-rays. Entities such as ribosomes, with a level of complexity above that of proteins (and, in fact, the site of protein synthesis within the cell) can be mapped out by triangulation techniques on successively deuterated pairs of the constituent proteins.[7] Similar techniques can be applied to viruses, lipid membranes, etc.

NEUTRON REFLECTOMETRY

Glancing angle neutron reflectometry is another promising and rapidly growing field. Just as in classical optics, a beam of neutrons encountering a flat, less-optically-dense medium will be totally reflected below a critical angle, typically on the order of a degree. For larger angles of incidence the specular reflection falls away in a manner which provides information on the density profile of the interface. **Fig. 6**, for example, shows the specular reflectivity of a block copolymer film on a flat substrate in which phase separation of the constituent polymer blocks into separate lamella has begun.[9] The inset to Fig. 5 shows the contrast variation which is related by Fourier transformation to the measured reflectivity. X-ray specular reflectivity measurements on such samples would detect no contrast between deuterated and hydrogenerated polymer blocks, but are nonetheless of considerable utility since they provide an accurate measure of the overall film thickness, which is an important constraint in fitting the neutron data.

INELASTIC SCATTERING

Because photons are massless and have a purely relativistic dispersion relation in contrast to the classical massive neutron, they probe very different energy-momentum regions in inelastic scattering, as **Fig. 7** illustrates. Over the past 15 years considerable skill and expense have gone into the design of specialized neutron scattering instruments, which now cover a dynamical range of about 8 orders of magnitude in energy transfer. Practically speaking, the study of thermal energy excitations on microscopic wavelength scales belongs exclusively to neutrons. In my opinion, this is true despite the demonstration of 10 meV-resolution capability for x-rays described elsewhere in these Workshop Proceedings.[8] It is my view that the future of inelastic synchrotron x-ray scattering is very promising, but lies not in competition with neutrons, but rather in the study of higher energy interband electronic excitation and collective effects such as plasmons and other charge density waves. Because these effects are one--rather than Z--electron per atom effects, the scattering intensities are weak, but the resolution requirements can be correspondingly relaxed. An estimate of the instrumental characteristics appropriate for the study of charge- and spin-excitations in itinerant electron systems by x-rays and neutrons respectively are shown in Table I.

Table I. Inelastic Electronic Scattering

	Incident Energy	Scan Width	Energy Resolution
A. x-rays--charge fluctuations			
Compton	50 keV	10 keV	10 eV
Collective Excitations	5 keV	100 eV	1 eV
B. Neutrons--spin fluctuations			
Collective Excitations (SDW)	500 meV	100 meV	1 meV

Finally, mention should be made of the use of targets containing nuclei with long-lived excited states (Mossbauer nuclei) as resonant filters for synchrotron x-ray beams.[9] This technique is capable of generating significant quantities of spatially coherent x-rays with an energy spread, $\Delta E/E = 10^{-10}$. But it is doubtful that fluxes sufficiently intense for conventional inelastic scattering experiments can be prepared in this way, even if experiments requiring such exquisite resolution can be identified. Perhaps a more practical alternative is the investigation of hyperfine splitting of the filter-target nuclei directly by making use of the temporal beat structure that is produced in response to the sharp individual driving pulses (~10 nsec) characteristic of synchrotron radiation. A strong point of the method is that many naturally occurring stable isotopes (e.g., Fe^{57}) become candidates for Mossbauer studies, since their excitation no longer depends upon decay of radioactive precursors.

SUMMARY

This brief report is by no means a complete or balanced account of the synergism that exists between modern x-ray and neutron scattering techniques, but rather draws from examples most familiar to the author. Nonetheless, it is perhaps sufficiently suggestive of the advantages enjoyed by scientists with ready access to both techniques. The methodologies of x-ray and neutron scattering are so similar that few barriers exist (aside from the availability of the facilities themselves) to prevent scientists from using either or both techniques as appropriate to the problem under study. Coexisting, or at least conveniently located synchrotron and neutron facilities exist already at Brookhaven National Laboratory (NSLS and HFBR) in the U.S., at Saclay (LURE and Orpheé) in France and at Tsukuba (Photon Factory and KENS) in Japan. Construction under way or planned, will extend the list to Grenoble (ESRF and ILL) in France, Argonne National Laboratory (APS and IPNS) in the U.S. and in Dubna, USSR, where a 10 GeV Synchrotron is tentatively planned to supplement the existing neutron Facilities. Coincident with the growth of these facilities we will see the development of a new generation of scientists

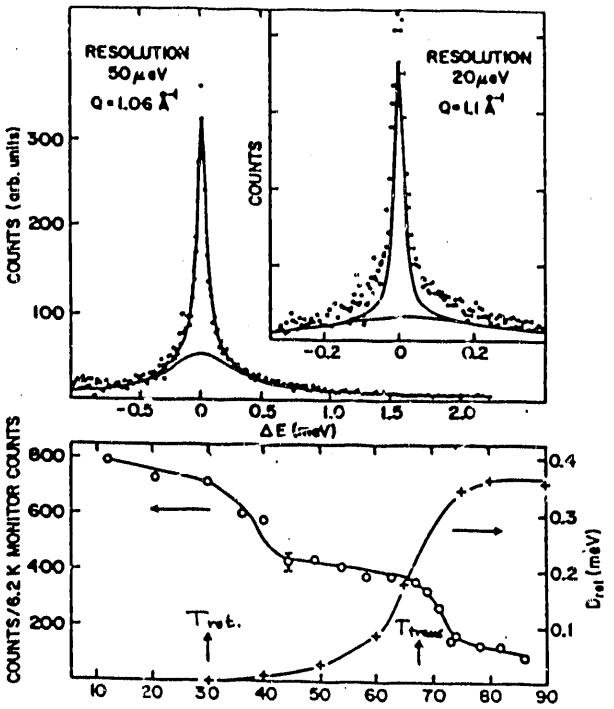

Fig. 4. Quasielastic neutron scattering study of sub-monolayer films of ethane on graphite, showing successive rotational and translational "melting" (Ref. 5).

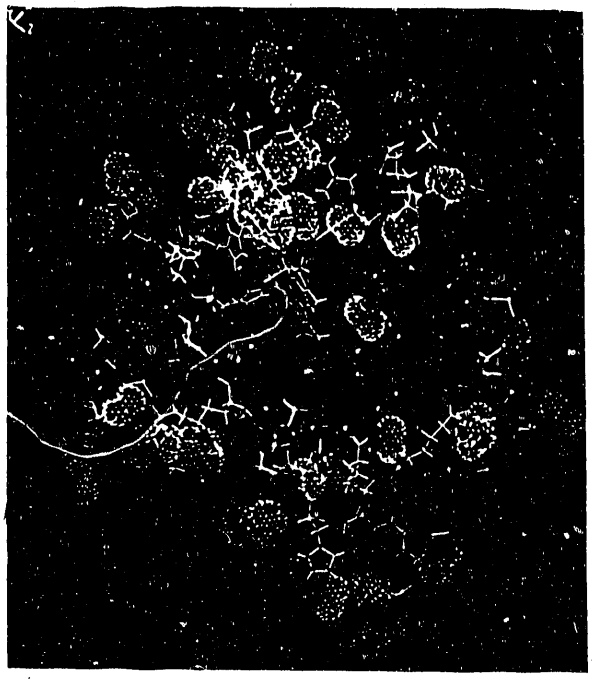

Fig. 5. Skeletal model of the respiratory protein, myoglobin, showing the position of 87 weakly bound surface water sites (space-filling dotted clusters). (Ref 6).

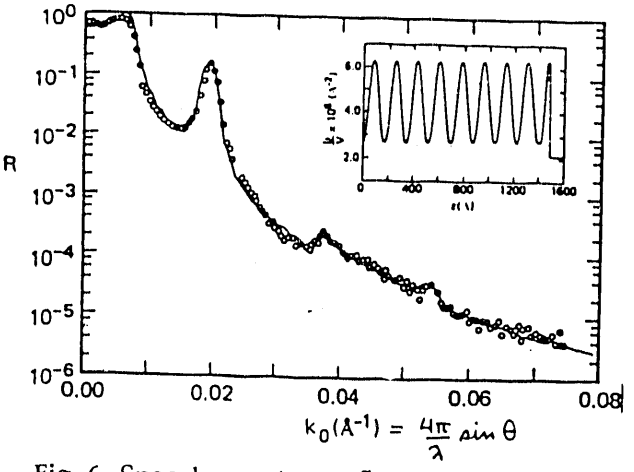

Fig. 6. Specular neutron reflectometry of a thin annealed films of diblock copolymers on a Si substrate, which induces phase separation of the two polymer constituents. The inset shows the deduced scattering density profile. After Anastasiadis, *et al.*, J. Chem Phys.,1990, 92, p. 5677.

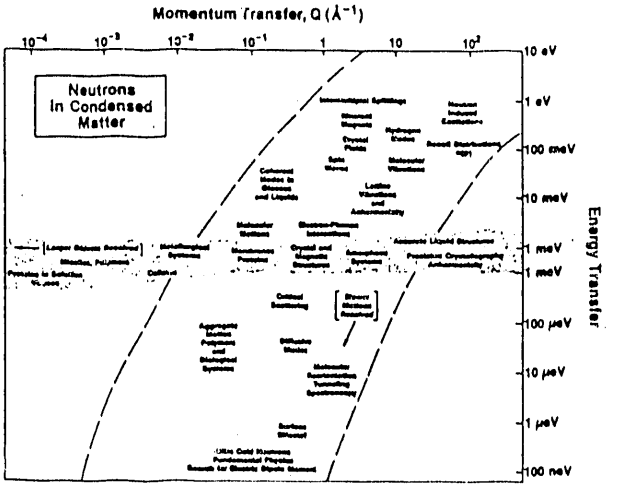

Fig. 7. Schematic representation of some of the phenomena studied by inelastic neutron scattering. Note the wide (6 to 8 order-of-magnitude) range in both energy and momentum. The central shaded area represents elastic scattering.

equally at home with both techniques and for whom x-rays and neutrons are complementary, not competing, means to an end.

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