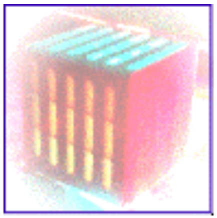


A Workshop on

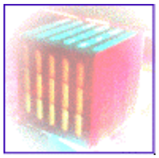
NOVEL MATERIALS FOR EXTREME ENVIRONMENTS

New Experimental Opportunities in Neutron Scattering

A Vision for a Neutron Instrument for Materials Research
under Extreme Environments

September 11-12, 1998
Intense Pulsed Neutron Source, Argonne National Laboratory

Co-sponsored by Argonne and Oak Ridge National Laboratories



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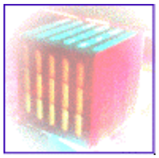


Executive Summary

Knowledge of structural and dynamic response of atomic nuclei and electrons in substances under extreme environments is essential to the development of new materials for novel applications for the 21st century. Neutron scattering is a powerful tool capable of probing the microscopic properties of condensed matter subjected to a variety of experimental conditions. By virtue of the simple nature of neutron-matter interaction, neutron-scattering data can afford direct, quantitative comparisons with rigorous theoretical calculations or computer simulations. Beginning in 2005, high fluxes of cold-to-epithermal neutrons will be available to the materials research community at an unprecedented level to be generated by the Spallation Neutron Source (SNS). However, the design of neutron instruments optimized for studying materials behavior under extreme environments has not yet begun. This workshop convened a team of experts from universities, industry, and government laboratories to examine the scientific basis, materials issues, sample environments, and data visualization/interpretation schemes for neutron scattering in the next century. The team has considered the scientific cases and experimental configurations for studying a number of key materials, which resulted in the specification of some conceptual parameters for a dedicated instrument at SNS for the characterization of material behavior under extreme environments.

The requirement for functional high-strength materials at high temperatures has led to intense studies of nitride- and carbide-based ceramics, e.g., Si_3N_4, SiC, and related alloys or composites. Additional incentives include their lower density, lower thermal expansion, and better corrosion and oxidation resistance as compared to the metallic analogs. However, the current strength and reliability of nitride and carbide ceramics are not sufficient to replace the metallic counterparts in applications such as heat engine components. The strength of ceramics depends on the nature of atomic bonding such as covalency versus ionicity as well as the microstructure such as flaws and stresses within the materials. In the case of high-temperature studies, furnaces operating up to ~2000°C are widely used at neutron-scattering facilities. However, they are predominantly used in a vacuum environment for diffraction experiments. Consequently, high-temperature properties, particularly atomic dynamics of ceramics under ambient or oxidizing atmospheres, cannot be properly characterized. *In-situ* investigations of chemical reactions, corrosive behavior or densification processes further demand accurate control and monitoring of molecular streams or application of pressure in conjunction with very high temperature. Many sub-fields of materials science, such as gas separation by high-performance ceramic membranes, air-purification catalytic devices, fracture-toughened structural materials, and high-efficiency power sources, will be benefited greatly by the capability of neutron diffraction and spectroscopic measurements under these conditions.

Experimental investigations of the molten state of inorganic materials impose technical difficulties not only because of extremely high temperatures but also because of lack of suitable containers. Recent advances in containerless techniques by levitation and floating-zone melting provide an attractive alternative to sample containment. These techniques, which have proven useful in synchrotron x-ray studies of molten oxides and glasses, require further development in order to be useful for neutron experiments. If successful, new studies of many molten materials of technological importance (e.g., fuel-cell electrolytes) and fundamental relevance (e.g., silicate melts in the mantle of the Earth) will become possible.

Materials under high pressures exhibit distinct properties, many of which cannot be probed accurately due to technical difficulties in preparing the proper sample environment. Crystalline and magnetic phases have been studied at moderate pressures (< 3 GPa) by neutron diffraction. Recent development in high-pressure vessels has demonstrated the feasibility of neutron experiments at 10 GPa or more. This opens the possibilities of studying pressure-induced electronic transitions in oxides, superconductors, and Kondo systems. At present, thermodynamic data of most key minerals under high pressures are lacking. Neutron spectroscopy is the only well-established method for measuring the Grüneisen parameters of individual phonon modes. Information of this kind is of vital importance to earth sciences.

The provision of a high magnetic-field environment is a challenging task because of the enormous energy involved. The combined utilization of pulsed-field magnets on a pulsed-source neutron instrument has brought forth the realization of effective data collection over the time fields with the presence of very high magnetic fields, as recently demonstrated by Japanese researchers. By virtue of magnetic neutron scattering, a rich variety of magnetic-field induced phenomena, such as electronic and nuclear magnetization, cyclotron resonance, de Hass-van Alphen effect, and superconductivity transitions can be carried out.

While neutron scattering has a long and successful history in studying fundamental properties of condensed matter, neutron scientists should not lose sight of the needs for microscopic characterization of practical, complex materials, such as nano-to-micro and heterostructure of mixed crystalline and glassy solids, composites, microelectromechanic devices, etc. Novel materials featuring tailored functions are immensely important to the well-being of modern, technology-driven societies. Data interpretation of neutron measurements of these materials is complex, but can be facilitated through collaborations with multi-scale computer simulations and theoretical modeling. For example, the emission of ballistic phonons in fracture dynamics and the electro- or magnetostrictive effects in materials due to creep, wear or fatigue can in principle be studied by neutron scattering.

Conceptually, the neutron instrument for materials research under extreme environments for the 21st century should comprise three modules:

1) An incident beamline which features multiple neutron-energy selectors (e.g., choppers) for background suppression, frame-overlap elimination, and band-width adjustment. Intensity enhancing and phase-space manipulating devices such as guides, collimators, beam focusers are to be selected, interchanged, and automated according to experimental requirements.
2) A sample environment which allows flexible installation and exchanges of various kinds of ancillary equipment (goniometers, furnaces, cryostats, pressure cells, magnets, chemical reactors, etc.), and provides additional ports for probing, monitoring, and controlling the sample conditions.
3) A scattering chamber which consists of an evacuated flight-path and a wallpaper-like coverage of high Q-resolution position-sensitive detector pixels from the smallest angles to back-scattering geometry.

This versatile instrument will function primarily as a spectrometer but can also be configured as a diffractometer so that studies of structural and dynamic properties can be made while maintaining the same sample environment. Since a huge amount of data will be generated for each setting, the design of the data acquisition system has to incorporate state-of the-art technology for real-time, multiple displays and visualization.

Background

A workshop on "Advanced Materials for Extreme Environments: New Experimental Opportunities in Neutron Scattering" was held at Argonne National Laboratory on September 11 and 12, 1998. This meeting, jointly organized by Argonne and Oak Ridge National Laboratories, was a prelude to the Spallation Neutron Source (SNS) Instrumentation Workshop to be held November 11-12, 1998 at Knoxville, Tennessee. The SNS is the next-generation neutron facility to be built at Oak Ridge, Tennessee. The US Congress has appropriated $130M for the SNS construction beginning in FY99. The project will take seven years to complete with a total budget of $1.33B. In order to solicit input from the scientific community to prioritize the research programs and to optimize the design of neutron-scattering instruments, a total of seven small topical workshops have been organized prior to the November meeting in Knoxville. This workshop was the first one, focusing on novel materials and special environments. Some 40 participants from universities, industry, NASA, Air Force, NSF and DOE laboratories attended the two-day meeting which featured 25 invited talks and plenty of stimulating discussions. The agenda, the members of the Organizing Committee and a list of participants are given in the Appendix.

The workshop covered four elements: science involving advanced materials, neutron instrumentation, data visualization and interpretation, and remote experimentation. The emphasis was on the characterization of materials (ceramics, liquids and molten salts, composites, metals and alloys, nuclear-waste storage media, catalysts, and sensors) under special environments (high temperature, high pressure, high electromagnetic field, oxidizing and corrosive conditions). The speakers were asked to introduce the state-of-the-art in their research areas and state the issues, problems, and needs for future investigations. Since SNS is expected to provide unprecedented capabilities, futuristic or novel ideas in neutron experimentation and data interpretation were encouraged throughout the presentations and discussions among the participants.

Incremental improvements of neutron instrumentation have been made over the years for studying materials under extreme environments. This report recapitulates some major achievements attained thus far and presents a number of challenging scientific problems for future SNS experiments.

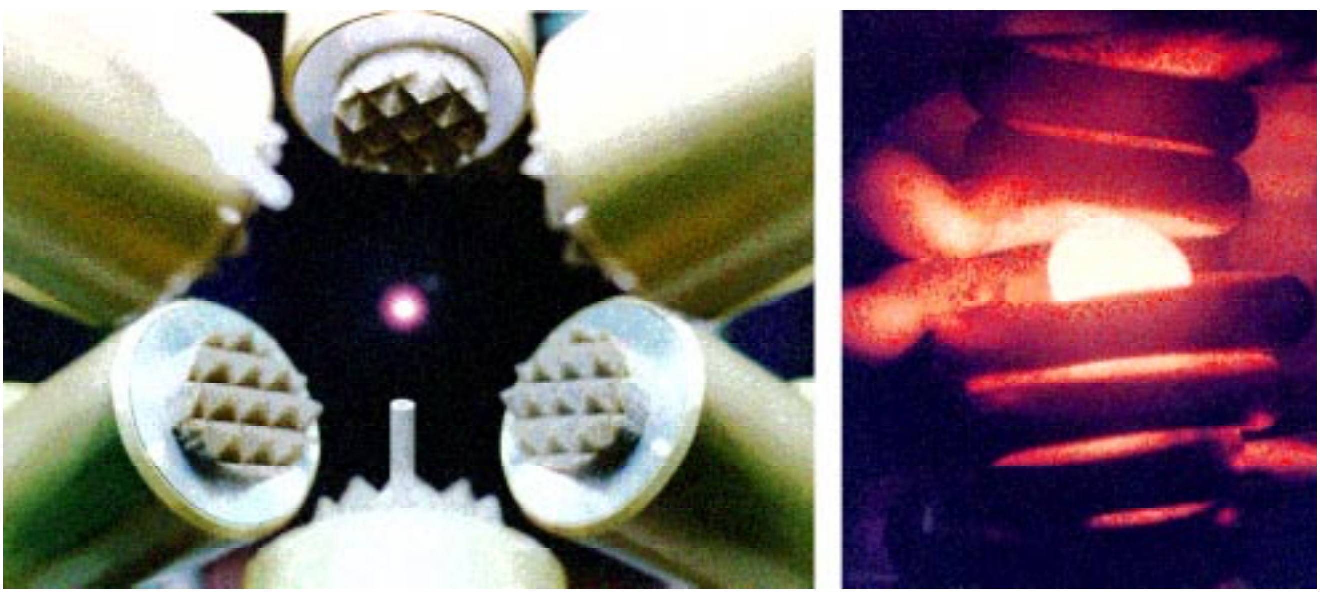
Materials Issues under Extreme Environments

High Temperatures

The requirement for high strength at high temperatures has led to intense studies of nitride- and carbide-based ceramics as well as transition-metal-based alloys. In the case of intermetallic systems, the instabilities of the bcc lattice of the so-called “anomalous” metals (e.g., Zr, Ti, La) toward the ω-phase at temperatures near melting, and the generalized Kohn anomalies manifested in softening of phonon branches at certain wavevectors were well-characterized by inelastic neutron-scattering measurements at high temperatures. The experimental results of a variety of metallic systems were explained satisfactorily by first-principle, self-consistent electronic band calculations. The trend of recent experiments appears to target more complex alloy systems such as the high-temperature Ni- or Ti-based superalloys.

In the case of neutron measurements of ceramic systems at high temperatures, much more work remains to be done. The reasons for the lack of experimental data are manifold. First, the temperatures required for studying ceramics are much higher, often exceeding 2000°C. Second, the high-temperature behavior of ceramics is generally sensitive to the surrounding atmosphere such as the partial pressure of oxygen, thereby demanding *in-situ* experiments under a controlled gas environment. Third, as a result of densification, alloying, transformation toughening, and/or composite reinforcement, practical ceramics inherently contain defects, noncrystalline impurity phases, anisotropies, and inhomogeneities. Consequently, the interpretation of neutron data is more complex. Despite these difficulties, neutrons as a probe possess many advantages:

- Slow neutrons interact gently with the vibrating nuclei and the unpaired electrons. The measured transition energies between the ground state and the low-lying states (normally below 250 meV) correspond to an upper temperature not far exceeding the melting point of the materials.
- Neutrons are sensitive to light elements commonly found in ceramic materials (e.g., O, C, N, Si, H) due to their favorable scattering cross sections. Furthermore, measurements can be made to be element specific in favorable cases by using isotopic substitution or by tuning the neutron energy toward nuclear resonance of selected nuclei.
- Neutrons penetrate into the bulk of matter typically of dimensions in centimeters, and they are not obstructed by the furnace (or pressure-cell) components in their flight paths.
- Atomic vibrations (phonons) are the principal excitations responsible for the thermodynamic behavior of insulating and semiconducting ceramics. Phonon dispersion curves or densities of states can be measured by neutron inelastic scattering without the restriction of selection rules.
- The method provides nondestructive evaluation of materials. Experiments can be carried out *in situ* under conditions emulating certain processing conditions.



Left: Aero-Acoustic Levitation of a molten aluminum oxide heated with a cw CO_2 laser beam to approximately 2700K, about 350K above the melting point of alumina. The picture also shows the levitation gas jet and acoustic transducers for position stabilization. Right: Electromagnetic levitation of a droplet of molten uranium in an argon atmosphere. Courtesy of Richard Weber, Containerless Research, Inc.

The direction for future experiments points toward elastic and inelastic scattering experiments at higher temperatures (above 2000°C) under controlled atmospheres on nitride-, carbide-, and oxide-based ceramics and intermetallic superalloys. Combining neutron studies with computer simulations and thermodynamic/mechanical measurements is essential to understanding of complex systems.

Molten oxides and metals are among the most corrosive materials encountered in experimental research. As a result, they often contain large concentrations of impurities which can mask subtle chemical effects and prevent measurement of their intrinsic properties. Containerless techniques by levitation or floating-zone melting eliminate contact with solid surfaces or other sources of contamination and so allow investigation of materials under well-controlled chemical conditions. The use of containerless methods also avoids heterogeneous nucleation by the container walls so that deeply undercooled liquids can be accessed and novel glassy materials can be synthesized. Recent experiments on molten aluminum oxide, $Y_3Al_5O_{12}$ and $Al_6Si_2O_{13}$ liquids and glass fibers have demonstrated that containerless techniques offer a viable means for studying the effects of partial oxygen pressure or dopant distribution in controlling the liquid/glass structure, relaxation processes near the glass transition, and the relation between cation short-range order and melt viscosity. In order to apply these techniques effectively for neutron-scattering experiments, several experimental constraints (e.g., sample size, temperature uniformity) have to be overcome.

High Pressures

Characterization of materials under high pressures is of equal importance to studies at high temperatures. In fact, complete measurements over the entire (P, T) domain are desirable. In practice, routine high-pressure neutron measurements have been performed mainly for diffraction experiments at $P < 3$ GPa. However, recent progress in the fabrication of anvil-geometry pressure cells (e.g., the Paris-Edinburgh design) and hydraulic clamp cells have enabled the measurements at (P, T) up to ~20 GPa and 1350K concurrently. For example, diffraction studies of the crystal structure of metal dioxides (MO_2, M = Ru, Zr and Hf) at temperatures over 1100K were undertaken using the Polaris instrument at ISIS. The sample volume is ~1mm^3 and measuring time per data set is ~24 h. Diffraction experiments will certainly be carried out more expeditiously or at somewhat higher pressures on an SNS instrument. However, inelastic scattering at high pressures will still be difficult if the design of high-pressure apparatus is not improved.

Scientific interests in the area of condensed matter physics at high pressures include the electronic properties of f-electrons in strongly correlated systems (from elemental lanthanide and actinide to Kondo compounds), electron-phonon (polaron) interactions in superconductors (e.g., RNi_2B_2C, R = rare earth), metal-insulator transitions (e.g., V_2O_3), and electronic topological transition (e.g., Lifshitz transition in Zn). The studies will provide important information about the parameters pertinent to theoretical models attempting to understand the complex many-body phenomena.

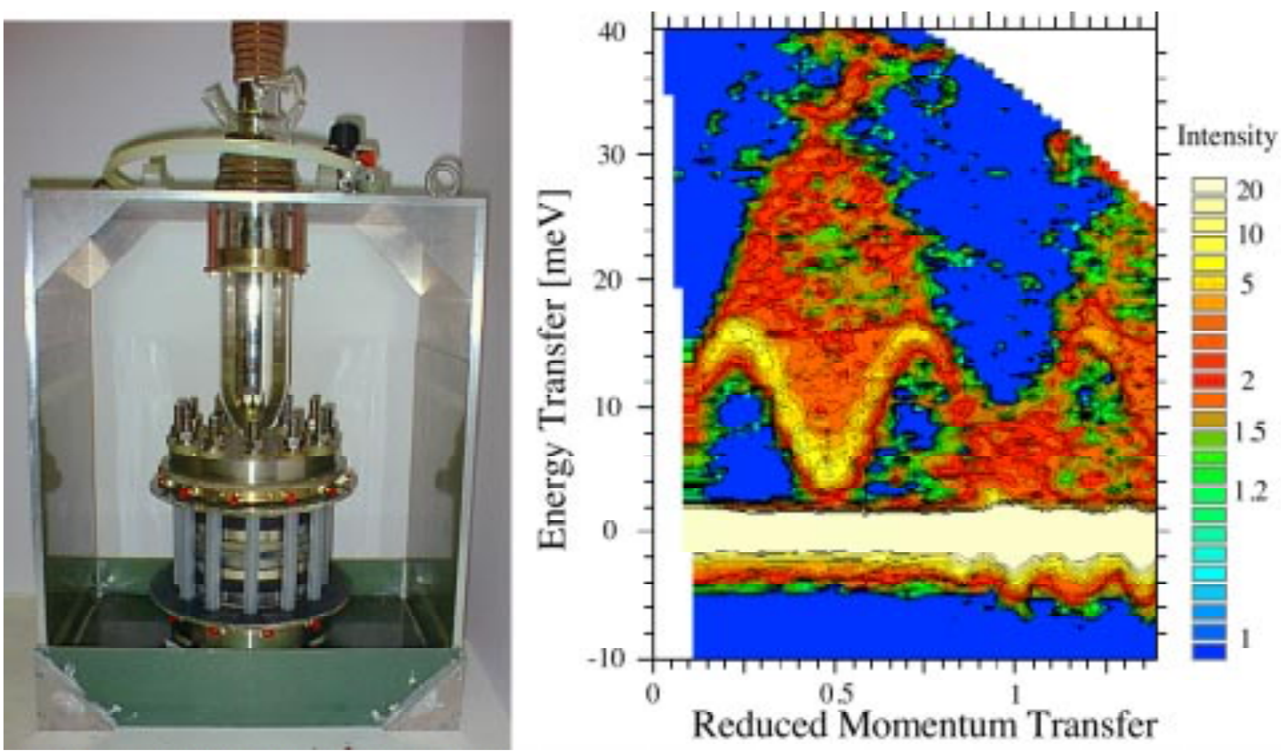
In Earth sciences any modeling of the interior of the Earth would require high-pressure data such as the Grüneisen parameters of key minerals. Obtaining the complete knowledge of the Grüneisen parameters requires the measurements of the pressure dependence of individual phonon modes. The phonon dispersion curves of quartz, corundum, forsterite, enstatite, leucite, calcite, pyrope, and zircon have been reported, but only data at ambient pressure are available. Extrapolation of these results to high pressures is highly unreliable. Estimate of the Grüneisen parameters from other macroscopic measurements hinges on underlying assumptions which are often unsubstantiated.

A complete measurement of the phonon dispersion curves of key minerals at pressures of geological relevancy will be very difficult, even for SNS instruments, due to the complex structures of many minerals and the very high pressures (of the order of 100 GPa). The first stage of inelastic experiments at SNS should aim for phonon density-of-states measurements of minerals at moderate pressures and temperatures. Such neutron results, aided by computer simulations, will provide earth scientists a first set of much needed data in modeling of geological systems.

High Electromagnetic Fields

Until recently, only neutron-scattering experiments in steady-state magnetic fields up to about 12T (generated by split-coil superconducting magnets) were possible. Pursuit of higher fields using this type of magnet is impractical due to the enormous energy involved and the problem of heat removal. However, the electronic energy induced by a magnetic field of laboratory scale is small (1T is equivalent to 0.125 meV). Therefore, there is a real need of higher magnetic fields for studying a variety of physical problems in materials such as field-induced spin/orbital magnetization, ESR, cyclotron resonance, de Hass-van Alphen effect, critical fields in superconductors, etc.

The use of a pulsed-field magnet in conjunction with a spallation source offers a feasible yet efficient alternative in achieving a substantially higher magnetic field for neutron experiments. Recently, a water-cooled, Bitter-type pulsed magnet capable of delivering a 30T field over a 1ms duration at 0.5 Hz was developed at KEK, Japan. A lifetime of over 10,000 pulse generations was reported. Inelastic experiments have been performed on the one-dimensional Heisenberg system $CuGeO_3$ to study the quantum effect on the spin excitations in (Q, E) space.



Left: A 30T pulsed-field magnet developed for neutron-scattering experiments at KEK, Japan. The picture shows the central glass dewer surrounded by the conducting-coil assembly of the magnet and the support structure. Right: The observed intensity map at 10 K and zero-field of $CuGeO_3$, a one-dimensional Heisenberg antiferromagnet below the spin-Peierls transition of 14 K. Measurements under applied magnetic fields will further clarify the quantum effects on this model spin system. Courtesy of Masatoshi Arai, KEK, Japan.

The availability of very high magnetic fields opens the way to studies of splitting of electronic bands in the vicinity of the Fermi level in Kondo-lattice systems. For example, $Ce_3Bi_4Pt_3$ exhibits an insulating ground state whereas $CeRh_2Si_2$ is a heavy-fermion metal that possesses both magnetic and superconducting ground states depending on the applied pressure and magnetic field. Very high field (up to 60T) magnetization measurements indicated drastically different behavior between these materials. The origin of such distinct magnetic response has to await future neutron-scattering studies.

The design and testing of high magnetic-field environments for neutron scattering are complicated. High magnetic field measurements usually require very low temperatures (in mKs) and good energy resolution. Thus the configuration of a pulsed magnet has to be compatible with the low-temperature apparatus. In addition, electronic noises generated during pulsation and possible safety hazards are of great concern. These and other considerations have to be incorporated in the design of the neutron instrument in the very beginning. Retrofitting high-field equipment on an existing spectrometer would be extremely costly and counterproductive.

The application of external electric fields on dielectric, piezoelectric or ferroelectric specimens are straightforward. Effects of electromechanical coupling can be investigated by diffraction and spectroscopic measurements. For example, the effective single-crystal electrostrictive coefficients for polycrystalline lead magnesium niobate were determined from neutron powder diffraction under applied electric fields. The measurements enabled an assessment of the combined effect of electric fields and mechanical prestress (due to processing of the ceramic samples). Inelastic experiments of phonon dispersion curves in the presence of applied electric fields can provide further information regarding the dynamic polarizability of the materials.

Chemical Reactions and Kinetics, Corrosive or Oxidizing Environments

The ability to control the chemical environment of samples examined under extreme conditions is vital to a number of very different types of studies. At one end are structural studies for which the integrity or the functionality of the sample depends on maintaining an appropriate atmosphere. Motions of oxygen ions at high temperatures in oxide ceramics (e.g., the perovskite family) have direct consequence in the ionic conductivity and phase stability of the materials. This ubiquitous nature of oxygen makes the ability to control oxygen pressure particularly important in neutron measurements for both elastic and inelastic experiments. At the other end of the environmental range is the situation found in lipid bilayers, a group of materials fundamental to biology. The phase morphology of the bilayer membranes depends on the amount of water and the hydrostatic pressure in the sample. Obviously, neutron-scattering studies of this kind of materials require a completely different set of sample environments.

Another concern is corrosion due to oxidization at high temperatures and pressures. An extreme example is liquid plutonium. It poses a radiation hazard and corrodes in both water and oxygen. In fact, it combusts spontaneously in air and alloys with most common container materials such as aluminum, copper, or nickel. High oxidization resistant ceramics at high temperatures are in heavy demand (e.g., for aerospace applications). Therefore, neutron-scattering studies of corrosion processes in materials at high temperatures are highly desirable.

Materials that are capable of facilitating chemical reactions or purifying chemical compounds are of interest scientifically and technologically. Neutron studies are of two types: identification of the reactant or product as a function of time, and investigation of the diffraction or interaction of the reactant/product with the catalytic materials. Studies of these systems are over the entire range of environmental conditions and almost all of them require a controlled chemical environment. The SNS will have a much higher neutron flux than current neutron sources, and thus allow the study of smaller amounts of materials on shorter time scales. This will lead to experiments on new systems.

For reactions and catalysis, surfaces are of particular importance. Currently, the structural variation across a flat interface can be probed by neutron reflectivity measurements. For example, recent studies of the complex arrangements of polymers at an air-water interface, and the structure of an adsorbed phenol layer on a water surface have been reported. Note that both phenol and water are volatile, thereby requiring a sample environment under a controlled atmosphere.

In many cases, it is the inelastic scattering that is of primary interest. Inclusion compounds, in which molecules are held in a framework, are well-suited for neutron spectroscopic studies. Normal alkanes included in urea form compounds that were originally developed with the idea that they could be used to separate different alkanes. Neutron studies clarified both the "translational" (longitudinal) motion and the rotational motion of the alkane chains in their urea channels.

Inclusion compounds of ice have long been known. Some, such as the clathrates of small hydrocarbon molecules (methane, ethane, etc.), are of general importance (e.g., they will clog a cold, wet gas line) and have been studied by neutron scattering. Suggestions for the presence of these clathrates on the surface of the moon Titan have been made. H_2 dissolves in ice and inelastic neutron scattering has shown that the H_2 diffuses rapidly through the structure – even at low temperatures. While there probably is no stable H_2 clathrate as the H_2 diffuses rapidly out of the ice structure, the H_2-ice system stays together long enough to allow neutron studies of the H_2 rotational bands. These studies concluded that both the translational and rotational motions, while almost free, are hindered.

Zeolites are framework materials, some natural and some synthetic, capable of including a wide variety of small molecules. The simplest, sodalite, has channels in a structure somewhat similar to ice. Other zeolites have large channels and absorb larger molecules. The absorbed molecules can be separated or reacted in the zeolite – an example is the catalytic converter in an automobile, which is made with zeolites containing Pt or other catalytic metals. Both the structure of the zeolites and the properties of the absorbents over a range of temperature and pressure have been investigated by neutron scattering. Examples are diffraction studies of absorption of cyclohexane, a molecule typical of the hydrocarbons that zeolites are used to separate, and inelastic scattering studies of the hydrogen molecules that are attached to the calcium ions in the zeolite lattice. In addition, hydrogen adsorbed on the metal centers in zeolites or on the metal particles on the surfaces of ceramics often form an important component of catalysts. These metal-support interactions, which are vital to the catalytic functions, can be studied by neutron spectroscopy. Again, a fundamental prerequisite for these investigations is a sample environment that allows the exposure of the samples to the appropriate gaseous and liquid reactants and versatile diffractometers/spectrometers that are capable of exploiting the advantages of neutron-scattering characteristics over a wide range of energies and wavevectors.

Industry-Relevant Materials - Dynamical Behavior of Engineering Ceramics

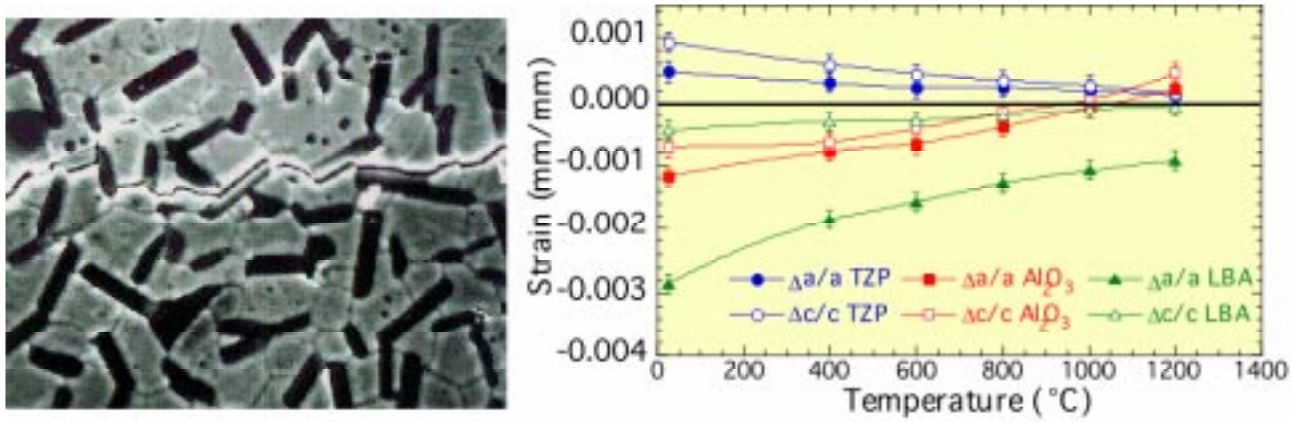
The application of neutron scattering for materials research has a long and successful history in studying fundamental properties of model systems. Such endeavors have significantly contributed to our present-day understanding of matter – from phase transformations to magnetism to polymers and other areas. While this will be a continuing mission for SNS, an emerging area of importance is related to the characterization of practical, industry-relevant materials. Industries respond keenly to two factors: the costs of materials and processing, and regulatory forces imposed by governments. The method of neutron scattering can provide valuable knowledge toward the development of cost-effective means for materials preparation and processing. Neutron facilities are funded by governments, thus these organizations are obliged to provide technical support to industries for the fulfillment of governmental policies. Future high-tech applications will undoubtedly demand materials for carrying out complex tasks under stringent or adverse conditions. A neutron instrument that is optimized for materials research under extreme environments is likely to play an important role in investigations of industrial materials.

One of the goals in materials design is to be able to introduce specific desirable properties into certain components of a complex system at an early stage during fabrication and to predict the performance of the final product. The development of high-performance ceramic membranes for an economical production of syngas from natural gas (which mostly consists of methane) is a good example. Air at pressure is introduced to one side of the membrane and pure oxygen appears at the other side. One the oxygen side, the methane is introduced and is reacted to form syngas (carbon monoxide plus hydrogen). This research requires the identification of the crystal structures of the major constituent compounds in the membrane and the understanding of the interplay of ionic and electronic conductivity in these phases with respect to the gas-separation processes at high temperatures under high or partial oxygen pressures. Neutron scattering has played a significant role in this investigation.

A major drawback of ceramics is their brittleness, which results in low fracture toughness and thus prevents their use as structural materials. However, ceramics that are synthesized by consolidating nanometer size particles are known to be more ductile, allowing larger plastic deformations. The enhanced ductility and improved mechanical properties are presumably due to the presence of a large number of atoms in inter-particle regions replacing the intergranular microstructure in conventional polycrystalline materials. The atomic organization and dynamics of an assembly of principally covalent-bonded nanoparticles and their relation with the sintering behavior and mechanical properties can be studied by neutron scattering. In the case of nanophase SiC , the structure of a crystalline core and a disordered shell of a nanoparticle, the microstructure of the powders, sintering behavior up to 1500 K and phonon dynamics have been studied by joint neutron-scattering experiments and molecular-dynamics (MD) simulations. In addition, MD simulations predicted the consolidation of the nanoparticles under high pressures and high temperatures, as well as the mechanical properties of densified n-SiC. It would be desirable to confirm these properties by neutron-scattering experiments performed under high pressure.

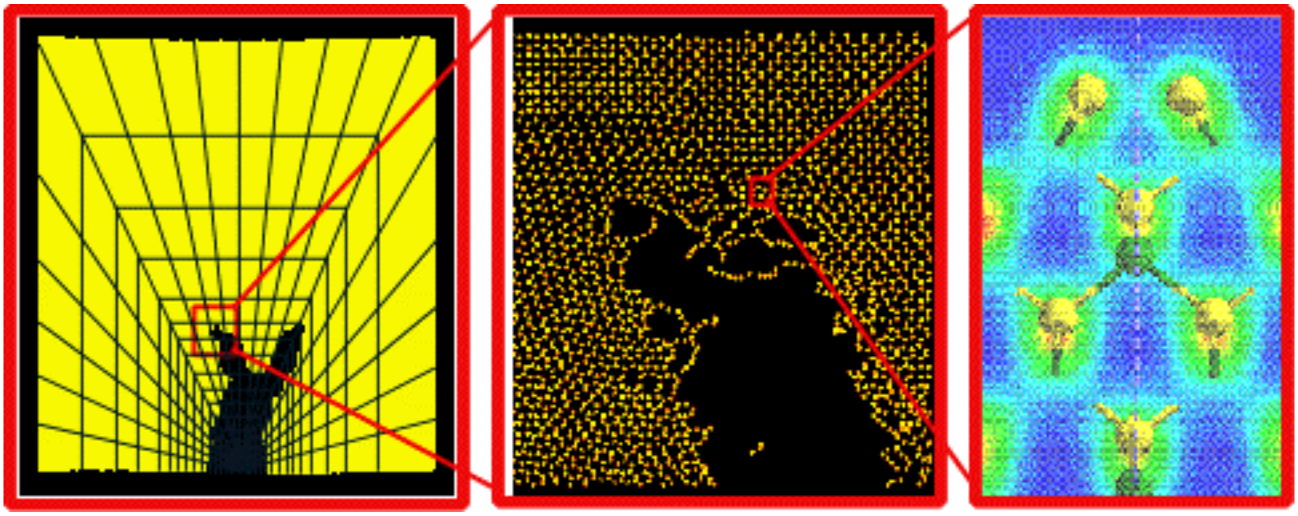
An alternative method of increasing the fracture toughness of ceramics is through tailoring the microstructure of composite materials. For example, Ce-TZP/Al_2O_3/LBA composite (Ce-TZP = 12mol% Ce-doped tetragonal zirconia, LBA = $LaAl_{11}O_{18}$) exhibits high fracture strength and fracture toughness. The elongated plate-like LBA crystalline grains and the strong, anisotropic compressive residual stresses on the LBA crystals are the keys to fracture toughening. They allow ligamentary bridging of the material and closure of crack tip along the Ce-TZP/LBA interface. The retention of compressive residual stresses on the LBA crystals up to 1200°C in air was verified by neutron diffraction. Reinforcement by coated continuous fibers within a ceramic matrix is another method for fracture toughening. It relies on a weak interface between the coating and the fiber which allows tangential crack deflection through debonding. Stable, oxidation resistant materials are preferred since the cracks permit ingress of the atmosphere. It has been shown recently that $LnPO_4$

(Ln = lanthanide) coating and Al_2O_3 fiber are the materials of choice. The crystal structure and phonon dynamics in $LuPO_4$ and Al_2O_3 have been determined by neutron scattering. However, neutron study of the fracture dynamics of $LnPO_4$ coated Al_2O_3 fibers in an alumina matrix at high temperatures has not been done.



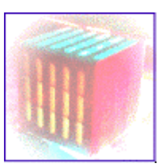
Left: A micrograph showing crack propagation in a Ce-TZP/Al_2O_3/LBA composite. The crack is deflected by tangential debonding along the interfaces between the elongated LBA grains and the Ce-TZP/Al_2O_3 matrix. Right: The residual strains in the three crystalline phases up to 1200°C in air measured by neutron diffraction. The strong, anisotropic compressive residual stresses on the LBA grains are the keys to fracture toughening. Courtesy to Shin-ichi Hirano, Nagoya University, Japan.

Along with the development of better neutron instrumentation, a close collaboration between experimental and theoretical scientists is needed for the study of complex materials. Neutron experiments are needed to validate theoretical modeling or simulation which, in turn, may predict properties of new materials and provide guidance to further experimental investigations. Sophisticated computational approaches are now available to tackle phenomena at different length scales. For example, up to a few nanometers, first principles quantum chemical and density functional methods are available to calculate electronic properties of materials including bond formation and breakage processes. In the range of 1 nm - 1 micron, the properties of materials can be very well described by the molecular-dynamics (MD) approach based on empirical interatomic potentials derived from electronic structure calculations and experiments. Recent advances in computational methodologies, parallel algorithms and architectures have made it feasible to carry out large-scale MD (~ 100 million atoms) simulations. (For example, simulation results of crack propagation in nanophase SiC and Si_3N_4 showed a much different behavior than that in their crystalline counterparts. The effects of surfaces, edges, and lattice mismatch on the stress distributions and the eventual failure at a Si(111)/Si_3N_4(0001) interface were assessed by MD simulations.) Beyond the micron scale, continuum methods such as the finite-element approach are well-suited for the study of material properties. New methods are being developed to combine electronic structure, molecular dynamics and continuum methods into a seamless materials simulation approach covering electronic-to-continuum length scales. The strain-stress relations associated with deformation (creep), emission of ballistic phonons, atomic anharmonicity associated with fracture, wear, fatigue, or damage under controlled conditions can, in principle, be studied synergistically with the multiscale simulation approach and neutron-scattering experiments.



Multiscale simulation approach combining the finite-element (left), molecular dynamics (middle), and *ab initio* electronic structure (right) methods. Courtesy of Rajiv Kalia, Louisiana State University.

A number of additional computational advances will also play a key role in neutron-scattering experiments. Data compression schemes and immersive and interactive 3D visualization tools have been designed to analyze computational and experimental results. Octree indexing based on spacefilling curves and variable-length encoding are available to reduce the data by an order-of-magnitude with a user-controlled error bound. User interface mechanisms have been developed to control the visual environment, aid in navigation, and help the user manipulate scale and representation of the visualization. Within an immersive virtual environment, the transition between mesoscopic and microscopic levels will be possible with the aid of a virtual magnifying glass as a graphical user interface metaphor. In addition, CAVE-to-CAVE link can be established to provide a shared space for doing remote experiments.



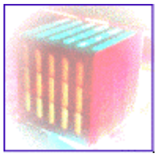
A Neutron Instrument for Materials Research under Extreme Environments

An SNS neutron instrument optimized for materials research under extreme environments must be sufficiently versatile to accommodate various demands for sample conditions, (Q, E)-range, resolutions, data visualization, etc. Competing or even opposing requirements for different types of experiments are expected. These issues will be considered and addressed by an instrument design team at a later stage. A preliminary conceptual layout of such an instrument is described below for the purpose of future discussion.

Ancillary equipment for an extreme environment often severely limits the sample size. Therefore, the instrument will provide a high incident flux with reasonable energy resolutions (1-2% $\Delta E/E_0$). Wide-range wavevector (Q) coverage with good resolution is to be provided by continuous arrays of position-sensitive detectors from small (~1°) to high (~150°) scattering angles. In order to allow maximum flexibility for $S(\vec{Q},E)$ measurements and a clean incident beam, the design calls for a direct-geometry instrument. It will serve primarily as a spectrometer but can also be used as a diffractometer so that both dynamic and structural information can be obtained at a single setting of sample environment. This instrument consists of three modules:

- An incident beamline module: Guides will be used extensively so as to maximize intensities. Insertion devices for phase-space collimation or beam focusing on small samples will be desirable if such technology is available. Multiple neutron-energy selectors (e.g., choppers) along the incident flight path will be used for background suppression, frame-overlap elimination, and band-width adjustment. These beamline devices will be fully interchangeable and automated according to the operational mode of the instrument and sample configuration.
- A sample environment module: Maximum flexibility will be allowed for installation and interchange of various kinds of ancillary equipment (goniometers, furnaces, cryostats, pressure cells, magnets, chemical reactors, etc.). The sample chamber will be large enough to accommodate heavy equipment in an open geometry or closed environment and will provide additional ports for probing, monitoring, and controlling the sample conditions. Issues concerning materials and engineering (e.g., suitability for high electromagnetic fields), safety, logistics, etc. will be integrated into the design and operation scheme of the whole instrument.
- A scattering chamber module: An evacuated flight-path and a wallpaper-like coverage of high Q-resolution position-sensitive detector pixels from the smallest angles to back-scattering geometry will be the basic requirement. Sample geometry for special environments will require collimation of the scattered beams at certain scattering angles so as to reduce background by scattering from the entrance/exit windows of the sample environment. An adjustable set of collimation within the scattered flight-path is highly desirable.

A typical data set from this instrument will fill a histogram of $\sim 10^7$ time channels – a huge amount of data to be viewed and evaluated by the experimenters. Studies of kinetics will require many data sets thereby increasing the data-handling load. Thus the design of the data acquisition system needs to incorporate the state-of the-art technology for real-time, multiple displays and visualization.



Appendix

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Workshop Agenda

Time	Friday, Sept 11, 98 Rm A224, Building 360	
8:15 - 8:30	Bruce. S. Brown - Argonne	Welcome
	Chair: Chun Loong	
8:30 - 9:00	R. Kent Crawford - Argonne	SNS Status and Instrumentation Plans
9:00 - 9:30	John M. Carpenter - Argonne	A Brief Overview of Applications of Neutron Scattering for Material Characterization
9:30 - 10:00	Thomas A. Weber - NSF	NSF interest in the Spallation Neutron Source
10:00 - 10:30	Constantine Stassis - Iowa State U.	Neutron Scattering Studies of Materials in Extreme Environments
10:30 - 11:00	Break	
	Chair: Kent Crawford	
11:00 - 11:30	Masatoshi Arai - KEK, Japan	Material Studies in Pulsed High Magnetic Field by Neutron Scattering
11:30 - 12:00	Robert Modler - Iowa State U.	Correlated Electrons under Extreme Conditions
12:00 - 12:30	Marie-Louise Saboungi - Argonne	New and Old Issues in the Determination of Liquid Structure
12:30 - 1:00	Herbert L. Strauss - UC Berkeley	Inclusion Compounds and Zeolites
1:00 - 2:00	Lunch	
	Chair: Rajiv Kalia	
2:00 - 2:30	Rick L. Stevens - Argonne	Advanced Visualization Environments For the Next Century
2:30 - 3:00	Priya Vashishta - Louisiana State U.	Multimillion Atom Molecular Dynamics Simulations of Ceramic Materials and Interfaces on Parallel Computers
3:00 - 3:30	Roberto Car - IRRMA, Switzerland	Structure and dynamics of liquid and glasses from first-principle molecular dynamics
3:30 - 4:00	Break	
4:00 - 4:30	Ali Sayir - NASA	Directionally Solidified Single Crystal and Eutectic Ceramics for Functional and Structural Applications
4:30 - 5:00	Richard Weber - Containerless Research, Inc.	Research Opportunities in Molten Oxides and Novel Glasses
5:00 - 5:30	Ronald J. Kerans - Air Force Res. Lab.	Issues in the Design of Selected Advanced Ceramic Systems
6:30 - ----	Cocktail / Dinner Argonne Guest House Restaurant	

Time	Saturday, Sept 12, 98 Rm A224, Building 360	
	Chair: Herbert Strauss	
8:30 - 9:00	Uthamalingam Balachandran - Argonne	Ceramic Membranes for Industrial Gas Separation
9:00 - 9:30	Raymond G. Teller - BP America	In-Situ Studies of Oxygen conducting Ceramic Membranes
9:30 - 10:00	Lynn A. Boatner - Oak Ridge	The Lanthanide Orthophosphates: Chemically Durable, Radiation-Resistant, High-Temperature Ceramics
10:00 - 10:30	Andreas Glaeser - UC Berkeley	Fundamental Studies of Surfaces and Interfaces at High Temperature via Microdesigned Interfaces
10:30 - 11:00	Break	
	Chair: Jim Richardson, Jr.	
11:00 - 11:30	Steve Hull - ISIS, UK	Powder Diffraction Under Non-Ambient Conditions : Recent Developments and Future Plans at ISIS
11:30 - 12:00	Angus Lawson - Los Alamos	Successes and Failures with Powder Diffraction in Extreme Environments
12:00 - 12:30	Scott Misture - Alfred U.	Measurement of the Electrostrictive Coefficients of Ceramic Electrostrictors Using Powder Neutron Diffraction
12:30 - 1:30	Lunch	
	Chair: Constantine Stassis	
1:30 - 2:00	Rajiv K. Kalia - Louisiana State U.	Structure and Dynamic Fracture in Nanophase Silicon Nitride and Silicon Carbide: Multimillion Atom Molecular Dynamics Simulations on Massively Parallel Computers
2:00 - 2:30	Bryan C. Chakoumakos - Oak Ridge	High Temperature Crystal Structure Systematics of Oxide Perovskites
2:30 - 3:00	Elizabeth C. Dickey - U. of Kentucky	Residual Stresses in High-Temperature Ceramics
3:00 - 3:30	Waltraud M. Kriven - UI Urbana-Champaign	Design of Oxide Ceramic Composites with Transformation Weakened, Debonding Interphases
3:30	Adjournment	

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