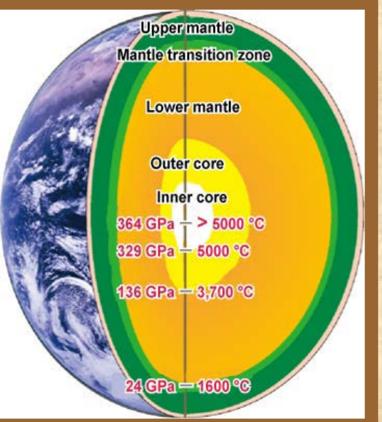
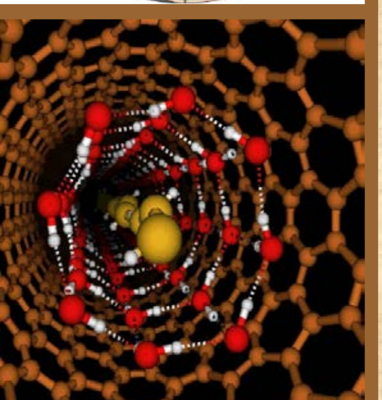
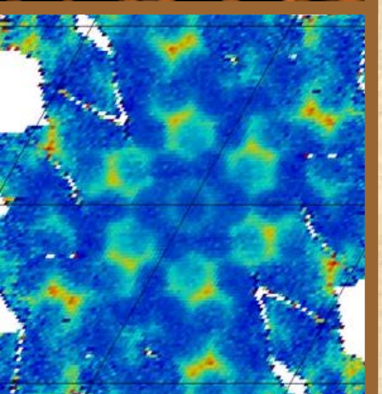






Frontiers in Materials Discovery, Characterization and Application

Workshop held in Schaumburg, IL Aug 2nd-3rd, 2014

Organized by
George Crabtree: University of Chicago and Argonne National Laboratory

John Parise: Stony Brook University and Joint Photon Sciences Institute

Chemical and Engineering Materials Division
Neutron Scattering Directorate
Oak Ridge National Laboratory

Workshop report on Frontiers in Materials Discovery, Characterization and Application

Schaumburg, IL, Aug 2nd-3rd, 2014.

Organizers: George Crabtree (University of Chicago and Argonne National Laboratory) and John Parise (Stony Brook University and Joint Photon Sciences Institute)

Sponsored by:

Oak Ridge National Laboratory

Table of Contents

I. Executive Summary

Materials are at the heart of technologies which will define the future economy and provide solutions to the compelling challenges facing society from energy security to future transport and infrastructure. Predictive modeling of materials holds the promise of accelerating the development of new solutions however as a prerequisite this requires an understanding of materials' structure and dynamics from the atomic scale to real world components and systems. In addition understanding and modeling synthesis and processing is vital to achieving transformative impact.

This report presents the outcome of the workshop "Frontiers in Materials Discovery, Characterization and Application" held at Schaumburg IL, August 2nd-3rd, 2014. The workshop explored the needs of the materials science community, future directions, and the most significant problems that could be addressed in the next decade by neutron diffraction, imaging and spectroscopy.

The workshop brought together twenty five research leaders from academia, industry, and national laboratories covering Chemistry, Materials Science, Geoscience and Engineering Materials. The agenda covered extended viewpoints on the needs of industry, impact of modeling, materials by design, infrastructure stewardship, materials under extreme conditions, frontiers in neutron spectroscopy, and high throughput experiment and optimization. All participants were also given the opportunity to offer short focused presentations for general discussion. On the second day of the workshop three topical sessions were convened on chemical spectroscopy, materials science/engineering and structural chemistry and reported back to the full group.

The key messages are that the unique physical properties of neutrons make high intensity beams indispensable to materials discovery, characterization, and application where they complement the capabilities of electrons and photons. Among these their nondestructive nature, ability to penetrate real components and materials under working condition, sensitivity to hydrogen and light elements, ability to observe modes and dynamics over virtually all length and time scales, and the ability to highlight components in complex interacting systems using isotope substitution make them unique.

In addition major impact and transformative capabilities can come about with the combination of high performance computing, software, new sample environments, and the promise of much higher intensities from new instrumentation and future sources, in particular the proposed Second Target Station, at the Spallation Neutron Source. Such advances facilitate high throughput neutron measurements, application to small samples and open up *in operando* studies, 3D spatial mapping of physical composition and state in materials including dynamics, and access to new areas of application e.g.in pharmacology. Such advances include the novel opportunity to undertake concurrent spectroscopy and diffraction measurements seeing function and structure together and to make time resolved studies of materials in action.

The principal outcomes and recommendations of the workshop are as follows. More detailed findings are listed at the end of this report:

Principal findings

Chemical Spectroscopy: Advances in sources, better optics and optimized instrument design will result in a complete transformation of neutron vibrational spectroscopy giving access to novel science.

Materials Science and Engineering: The demands for neutron capabilities in Materials Science and Engineering is very high and being driven by emerging challenges in infrastructure stewardship, advanced propulsion systems, advanced materials processing, nuclear fuels and radiation tolerant materials, energy storage and energy conversion integrated systems, materials by design/ICME, and materials under extreme environments.

Structural Chemistry: The field of structural chemistry makes seminal contributions to nearly every area of science. The revolutionary impact of materials by design and ability to explore systems under manifold environments and processes makes this field rich in compelling science problems for the future. The complementary properties of neutrons and xrays make them invaluable to these investigations.

Recommendations

Chemical Spectroscopy

- High Performance Computing should be vigorously pursued in conjunction with Neutron Chemical Spectroscopy.
- Create software tools that open access to new communities and disseminate understanding of the technique.
- Develop instrumentation capable of true *in situ* studies of chemical reactions, materials in action, and catalytic process
- Multimodal instrumentation that combines diffraction, tomography, and inelastic methods along with other techniques for complex systems.
- 3D spectroscopic, diffraction mapping, and *in operando* capabilities are needed.
- Libraries and databases are needed to provide reference spectra and models for future science.

Materials Science and Engineering

- Live data analysis that feeds directly back to data acquisition: adoption of “expert” systems to optimize experimental setup and data analysis
- Develop entirely new modes of user access: Requires routine “rapid access” review and processing and a new paradigm to measure impact.
- Ability to easily handle unique samples (both in and out): large/heavy samples, “hot” (radioactive) samples, proprietary samples (rare but occasionally needed)
- An institutional approach to building collaborations between industry and laboratory staff is needed and would provide great benefits.
- Need for more outreach - frequent workshops, seminars, etc., to grow the community. There are many projects that would benefit from using neutrons that are not reached at present.

- A multi-moderator target design (STS) will facilitate development of multimodal capabilities
- Development of high-resolution neutron microscopy, imaging, and tomography beamlines, including epithermal neutrons for resonance imaging/tomography is a priority.
- Demand for engineering materials on VULCAN will significantly increase with the Lujan Center closure. In order to accommodate this work, it is recommended that the VULCAN instrument be fully commissioned, adding five detector banks that were in the original instrument plan but not yet implemented.

Structural Chemistry

- Fast tracked design and construction of the instrument RAPID that was proposed in the powder workshop held at ORNL in June 2013; this is now an urgent need due to the loss of NPDF at the Lujan Center.
- A very high resolution powder instrument ($\Delta d/d \sim 10^{-4}$) at Second Target Station on a moderator providing primarily ambient-moderated neutrons.
- Multi modal instrumentation
    a. Instrument capable of measuring multiple length scales (small angle + powder diffraction and high resolution elastic + inelastic scattering on the same instrument)
    b. Adding other simultaneous measurements capabilities (x-ray, calorimetric, gravimetric, NMR, etc.) for systems that are not easy reproduce.
- Integrated and a wide variety of sample environments to do *in-situ/in operando* measurements that include but not limited to, extreme ranges of temperature and pressure, electrochemical cells and gas handling systems. It is critical that sample environments be integrated from day one into the design of these instruments.

II. Introduction

This report is a summary of a workshop on the Frontiers in Materials Discovery, Characterization and Application held at Schaumburg IL, August 2nd-3rd, 2014. It is the fourth of a series of workshops sponsored by Oak Ridge National Laboratory (ORNL) to explore future directions and needs of the scientific community. This report is intended to supply input from the scientific community to ORNL management and the Department of Energy (DOE), which will help guide the development of advanced neutron scattering technology in the United States. The workshop was convened and organized by Prof. George Crabtree, University of Chicago and Prof. John Parise, Stony Brook University. The workshop brought together twenty five researchers from academia, industry, and national laboratories, who perform research in theory, synthesis, experimental characterization and instrumentation, to discuss current topics in Chemistry, Materials Science, Geological Science and Engineering Materials. Their charge was to consider what scientific problems in Materials Science may be addressed in the next decade by neutron diffraction, imaging and spectroscopy. A list of the attendees can be found in Appendix II.

The charge to the workshop attendees was to:

1. Identify the ten major challenges relating to the first-principles mastery of the design of broad classes of chemical, geological and engineering materials;
2. Identify the missing tools/methods necessary to address these challenges using neutron scattering as a standalone technique or in combination with other techniques, and the steps required to develop the methods;
3. Construct a vision for how neutron scattering, theory, computation, synthesis, and other experimental techniques can interact synergistically to discover new materials; and
4. Elaborate the experimental advances and infrastructure needed (particularly with respect to neutron scattering) to enable more effective synergistic interaction.

The workshop consisted of a day of 8 invited 30-minute presentations with a 10-minute discussion for each presentation. All participants were given the opportunity to offer a 5-minute focused presentation and there were 9 such short presentations. On the second day of the workshop, the attendees broke into three topical sessions on chemical spectroscopy, materials science/engineering and structural chemistry. The working group reports were then summarized and discussed by all attendees in this summary workshop session. The body of this report is organized as follows:

- A summary of the presentations (both short and long) that pertain to the breakout topics are described.
- The discussions from the breakout sessions are then listed.
- The principal findings and recommendations are then given..

III. Session Reports

A. Chemical Spectroscopy

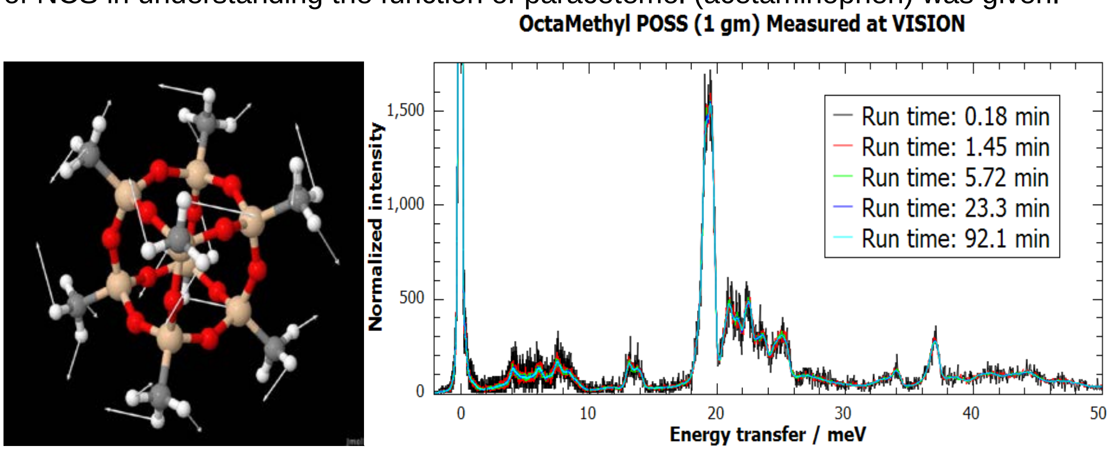
Participants: *Luke Daemon, Peter Albers, Mike Crawford, John Larese, Bruce Hudson, Alexander Kolesnikov and Thomas Proffen.*

Presentations:

"New frontiers in neutron chemical spectroscopy", Luke Daemon (LANL)

Luke Daemon presented an overview of the impact of Neutron Chemical Spectroscopy (NCS) from pioneering experiments in the 1950s until the present. The importance of NCS was shown to be derived from the inherent advantages of neutrons over photons in their penetrability, hydrogen sensitivity, wide dynamic range, non-destructive nature, absence of selection rules, and overall simplicity of neutron-nucleus interaction).

Despite the effectiveness and fast increasing power of the technique the NCS user community in the USA is still smaller than that in Europe, and focused efforts to disseminate an understanding of the capabilities and to train new users is needed. Early stage researchers including PhD students in this field are of particular importance, and outreach to non-traditional communities e.g., pharmacology and environmental science is needed to accelerate the adoption of the technique in these areas. As an example involving new communities, the utility of NCS in understanding the function of paracetemol (acetaminophen) was given.



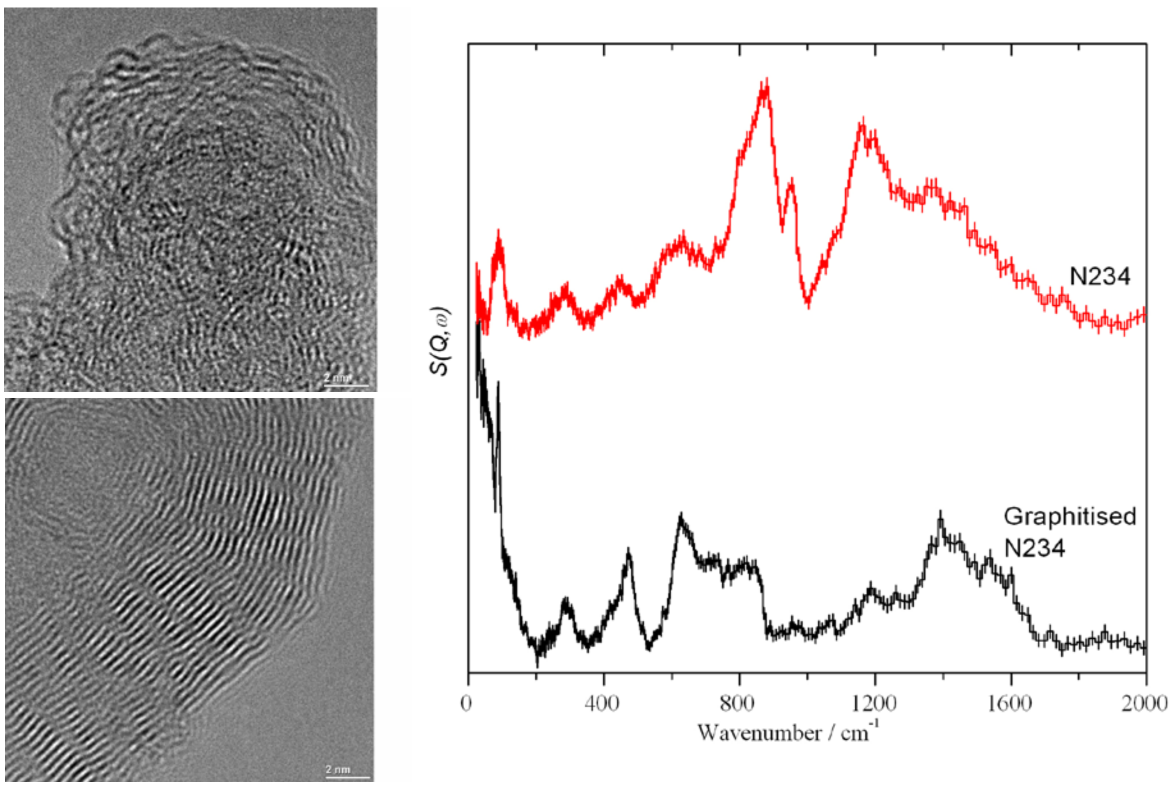
High throughput spectroscopy of Octamethyl Poss; an industrially relevant small molecule under investigation at Dupont helps understand the anharmonicity of the methyl group potential.

Another important trend for future science is the importance of multimodal studies and the need for spectrometers which can also monitor other aspects of structure and dynamics simultaneously. Examples where these capabilities are needed include in advanced functional materials, which possess complex properties such as piezoelectricity, ferroelectricity, multiferroicity, magnetocaloric features, energy storage capacity, ion or electron transport, magnetism, electrochemistry, optical properties, etc. Multimodal information would greatly enhance our knowledge of the structure and functional properties and aid and accelerate the design of new materials.

An outstandingly important goal is to observe advanced functional materials in action, i.e. catching them in the act of fulfilling their function such as *in situ* studies of electrochemical devices, evolution of materials under various applied such as light, pressure, electric/magnetic field or a pulse of gas and the capabilities for these studies are urgently required.

Finally, a key advance in NCS is the advent of new instrumentation which allows for the first time high throughput spectroscopy. To capitalize on this additional investment in handling large volume of data, large number of samples (need effective sample changers), specialized sample environments, modeling and interpreting the results and developing databases and libraries needs to be made.

Peter Albers: "*Applications of neutrons and synchrotron radiation in the chemical industry*"

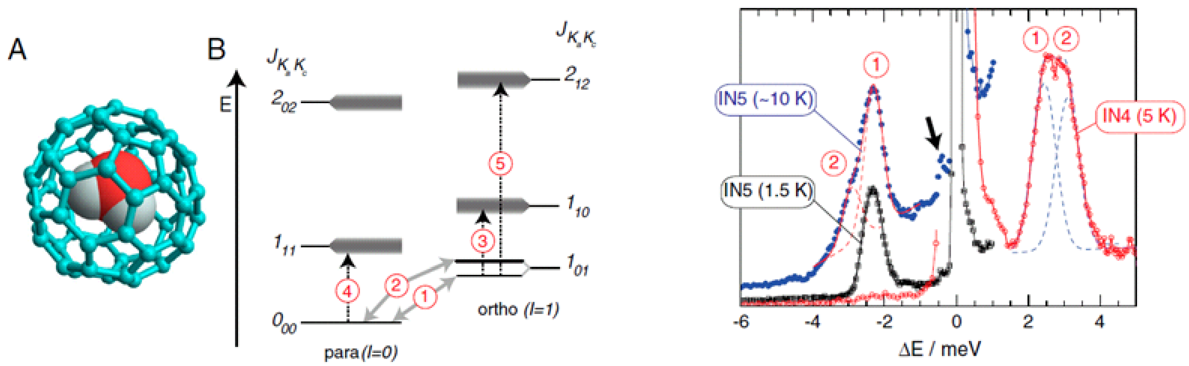


INS spectroscopy helps understand graphitisation of Carbon Black.

In his talk Peter Albers demonstrated the impact of NCS on understanding of industrially relevant problems in catalysis. Here, the high penetrating power of neutrons in matter enables studies in sealed containers allowing the investigation of catalysts under reaction conditions with realistic gas pressures. Practical applications in the chemical industry and academia were presented including Pd-catalysts from operating plants and the chemical origins of poisoning, as well as the example of hydrogen in carbon blacks (inset). Understanding the role of different molecules, their location, and adsorption directly impacts on optimizing the catalytic materials and processes and NCS is foreseen to play an import role for many years ahead.

Alexander Kolesnikov: *"Some recent results on neutron spectroscopy"*

Alexander Kolesnikov presented examples of current work highlighting the versatility of information that can be obtained in a multitude of different materials systems. This included recent results on dynamics of materials under extreme conditions: supercritical water (SCW) and hydrogen tunneling in alpha-Mn under high pressure (up to 22 kbar) obtained at SNS showing the power of neutron scattering for *in situ* studies. He also presented some work done on recently synthesized graphane, 2D transition metal carbides, called MXenes, as well as water confined in nanoporous materials.



Quantum rotation of ortho- and para-water encapsulated in a fullerene cage.

Bruce Hudson: *"Oriented, Insulated Polyacetylene: A Possible Superconducting Material"*

Bruce Hudson presented new first principle calculations related to synthesis of advanced materials. The calculations for chains of polyacetylene (pPA) include nuclear zero point motions which have a crucial effect on the electronic states forming conducting or even superconducting behavior. The calculation results showed that the zero-point level of pPA is above the Peierls' barrier and it is concluded that pPA will not exhibit bond alternation. To see this novel effect neutron spectroscopy is required because of their ability to probe the dynamics in detail.

John Larese: *"Opportunities for chemical and biochemical neutron spectroscopy"*

John Larese presented results on the study of hydration of silk proteins: they measured INS spectra from 30 mg electrospun silk, and also studied properties of the silk during its hydration in situ. Another theme was hydrogen spillover, dedicated to hydrogen storage by implementing spillover mechanism. Carbon nanomaterials, MOFs, MgO, ZnO, Pd/ZnO, Pd/Al2O3 were considered as candidates. New QENS results on Pd/ZnO were presented showing change in the H_2 behavior on Pd/ZnO from rotational to translational diffusion at T=28 K.

Break out session discussions

Chemical spectrometers at neutron sources are used to study the excitations that give rise to quasielastic (QENS) and inelastic (INS) scattering. Figure 1 shows the dynamical range of different spectrometers that are used for this purpose at the SNS.

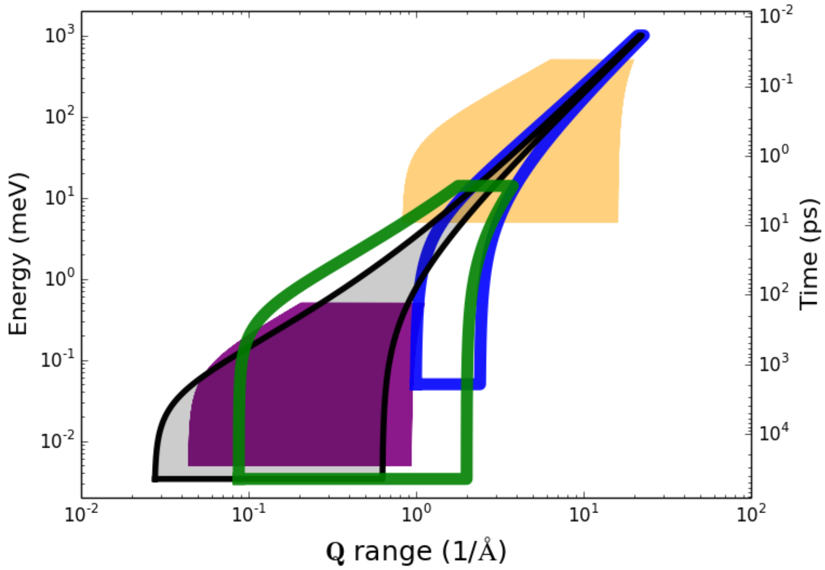


Figure 1. Dynamical range accessible for different INS spectrometers at the SNS and the corresponding time scales of the processes involved . The empty areas are the indirect geometry, BASIS (green) and VISION (blue). The black area correspond to the conceptual instrument BRAINWAVES. The solid areas are SEQUOIA (orange) with Ei=500 meV and the CNCS (purple) for Ei=5 meV.

Inelastic neutron scattering:

At pulsed neutron sources, indirect geometry instruments are used to measure the INS spectra of materials in a similar fashion as Raman or IR spectrometers. By using crystal analyzers, the resolution of these spectrometers is constant in units of $\Delta\omega/\omega$~1.5%. The trajectory in reciprocal space follows closely a parabola so that $\omega \propto \boldsymbol{Q}^2$. As a consequence of this trajectory it follows that the Debye-Waller factor increases with energy transfer, making these instruments ideal to measure vibrations and rotations of molecules below 250 meV. Examples of high resolution indirect geometry instruments are TOSCA at ISIS and VISION at SNS. Backscattering spectrometers, optimized for QENS, represent a special case of inverted geometry spectrometers with a very high energy resolution and usually a limited dynamic range (which the designers of backscattering spectrometers always strive to increase). To date, INS and QENS instrumentations were largely developed separately, but this will change with the advent of a conceptually novel spectrometer BRAINWAVES suitable for simultaneous QENS/INS studies (see Figure 1 and the Areas of Technical Development section below).

Direct geometry instruments are also usable for chemical spectroscopy (e.g., SEQUOIA, ARCS and CNCS at SNS, MAPS, MARI, LET and MERLIN at ISIS). In particular they are used to study higher energy transitions, since, by design one can select lower momentum transfer and therefore minimize the effect on the Debye-Waller factor in the case of hydrogen containing materials. The observations from INS instruments introduce a correlation between energy transfer and momentum transfer that can be rigorously modeled and interpreted.

Neutron chemical spectroscopy produces information similar to that obtained with conventional optical vibrational spectroscopy (mostly Raman and Fourier Transform Infrared spectroscopy). As in any other neutron scattering method, neutron vibrational spectroscopy is based on neutron-nucleus interactions, unlike optical spectroscopies that rely on photon-electron interactions. The former has a number of distinct advantages over the latter:

- Sensitivity to hydrogen and light elements;
- Cross-sectional changes from isotopic substitution (e.g., H/D);
- Penetrability (probe sample bulk and transmission through bulky sample environment equipment);
- No selection rules;
- The simplicity of the neutron-nucleus interaction permits the quantitative calculation of the neutron vibrational spectrum (position and intensity of the vibrational modes);
- Little to no energy deposition in the sample;
- Neutron spin;
- Neutrons exchange momentum with a sample and thus probe the Brillouin zone to produce true densities of states and meaningful line shapes;
- Access to very low energy modes related to diffusive atomic motion

These features of neutron vibrational spectroscopy enable in part the science opportunities described below. Inelastic neutron scattering requires fixing either the incident neutron energy (direct geometry instruments) or the final neutron energy (inverted geometry instruments). This is intrinsically “wasteful” as most neutrons end up being rejected. Coupled to low cross sections for inelastic scattering, this characteristic on inelastic neutron scattering was responsible for low count rates in the past few decades. The advent of high-intensity neutron sources, such as the Spallation Neutron Source at ORNL, and past experiences with crystal analyzers and filter spectrometers at weaker sources have led to the development of high performance crystal analyzers such as the ones used in VISION at SNS. Other high performance instruments, such as LAGRANGE at the ILL or a neutron vibrational spectrometer at ESS, are either in commissioning or at the proposal stage at the time of writing.

Commissioning studies on VISION have demonstrated data collection times at least 1000 times faster than TOSCA, hitherto the best instrument in its class for neutron vibrational spectroscopy. In a sample containing 44 millimoles of hydrogen, as little as four minutes was sufficient to obtain a high quality vibrational spectrum. This transformative advance in the field, in conjunction with better optics and optimized instrument design will result in a complete transformation of neutron vibrational spectroscopy giving access to novel science that are described in the following sections.

Ab-initio modeling of INS data

INS is perhaps the technique that provides the closest connection between electronic structure calculations and experimental data. The nature of the interaction between the nucleus and the neutron makes the determination of the INS spectra from first principles rigorous. So if the calculation correctly describes the physical and chemical process it should match the INS spectrum. It is fair to say that INS provides the most stringent test of the computational modeling capabilities available today.

In fact, VISION is so far the only instrument of the SNS suite that includes ab-initio computer modeling as integral part of the data analysis and interpretation. This makes VISION the ideal instrument where the partnership of High Performance computing and neutron science can flourish and make on-the-fly modeling and experiment a reality.

Molecular Hydrogen

INS is the best technique to study the rotational line of molecular hydrogen. The hydrogen molecule has a very sharp rotational feature in INS at around 14.7 meV. Neutrons, due to the very high sensitivity to hydrogen, penetrating power and in the case of VISION, very high flux at these energy ranges, are ideal to study hydrogen in the solid phase or adsorbed on surfaces and porous materials. INS can directly distinguish between molecular and atomic hydrogen.

QENS

QENS is used to probe the processes that are not vibrational, but rather diffuse or relaxational in character, and thus give rise to a signal centered at the elastic line. A QENS spectrometer must possess a very high energy resolution by default, so the most recent improvements in QENS instrumentation were concerned with the increased flux (measurement statistics) and the accessible dynamic range. The former improves the potential for extensive parametric studies, since QENS is an invariably time-consuming technique because of the reduction in the measured intensity imposed by the high energy resolution requirement. The latter is indispensable for multi-component analysis of the signal, since all but the simplest systems are characterized by multi-component relaxation dynamics, even in the presence of a single mobile entity (e.g., due to engaging simultaneously in the localized and long-range dynamics). SNS backscattering spectrometer, BASIS, provides an outstanding example of a high-resolution, QENS-dedicated spectrometer with a high-flux and a broad dynamic range. The combination of the high resolution and the broad dynamic range at the BASIS allowed for the development of a new paradigm in the analysis of the center-of-mass dynamics in liquids. In agreement with the modern theoretical understanding, the short-time motions of particles temporarily trapped inside the transient cages made by the nearest particle neighbors are followed by the cage-breaking rearrangements. This is an example of advances in instrumentation leading to breakthroughs in the data and model interpretations.

Areas of Novel Science

1. Catalysis

Catalysis is of enormous importance to the chemical, petroleum, and pharmaceutical industries. Its impact on energy savings cannot be underestimated. The penetrability of neutrons through matter allows us to probe “real life” powder catalysts (as opposed to the clean single crystal surfaces under ultrahigh vacuum, used in conventional surface chemistry studies such as EELS or HREELS). Small flow reactors permit the observation of surface chemical reactions under static (quenched) conditions whereby a chemical reaction is conducted for a given period of time in a flow cell containing a catalyst and quenched suddenly, at which time neutron vibrational spectroscopy is used to determine the spectral fingerprint of reactions intermediates and products.

While this approach remains useful, particularly in the study of very fast catalytic processes, at higher count rates, the react/quench/measure sequence could conceivably be transformed into a true in situ experiment. Kinetic data could be obtained under real conditions while the observation of the spectral signature of (longer-lived) intermediates would provide an unprecedented level of understanding of surface chemistry and catalytic processes.

Studies of the diffusion mobility of surface species have been represented prominently on BASIS, beginning from the very first spectrometer scientific publication several years ago that concerned the complex mobility of water molecules on rutile nano-particles. Such studies may provide information on the surface transport of reactants. In contrast to INS, QENS data are always collected at a temperature of interest, while the baseline low-temperature data, representing the state with frozen diffusion processes, are used for calibrating the energy resolution of the experiment.

Other opportunities exist in clarifying the role of small concentrations of hydrogen in carbon-based catalysts, in the study of unconventional catalysts (e.g., nano-gold), and in the clarification of catalyst poisoning mechanisms especially with respect to poisoning by (weakly scattering) non-hydrogenous species. Certain progress in QENS studies of non-hydrogen-bearing species has been recently achieved (see below).

2. Chemical reaction mechanism

Most information on detailed chemical reaction mechanisms is based on kinetic data, computer simulations (determination of transition states), and the use of specialized techniques such as femtosecond laser spectroscopy or molecular beams. The data thus obtained is based on various assumptions or approximation, relies on models for interpretation, or is obtained under special physical or chemical conditions that are sometimes unacceptably far from conditions relevant to laboratory or industrial process chemistry.

High data collection rates and neutron penetrability open up for the first time the possibility of observing in detail reactions occurring on the scale of minutes to hours under realistic conditions. Thermal decomposition reactions, solid-state reactions, rearrangements, etc. are potentially amenable to this treatment. The observation of bond breaking and bond forming, functional group transformations, and intermediates would for the first time shed light on reactions mechanisms at a level of details currently unheard of. Optical spectroscopies probe only the surface of a sample and are less directly useful. The neutron vibrational data are complemented by the concurrent collection of structural data (PDF or diffraction), and remains useful even when structural data cannot be obtained. The quenching method described above remains useful to observe transient species (radicals, ions, intermediate phases).

3. Less conventional science areas

Vibrational spectroscopy, especially in its optical incarnations, is used by a wide array of scientists besides chemists. Raman and FTIR spectrometers are used routinely by materials scientists, physicists, geologists, pharmacists, environmental scientists, engineers, etc for the characterization of materials. Far fewer of them are familiar with (or inclined to use) neutron vibrational spectroscopy, even when this probe provides distinct advantages.

Reaching out to non-traditional communities (e.g., pharmacology or atmospheric science) would not only broaden and diversify the user base at a beam line such as VISION, but would also rejuvenate the field of neutron vibrational spectroscopy by bringing in new problems, new challenges, and new approaches.

For example, the detection of biomarker spectral signatures and their transformation under various aging conditions in natural samples would have a direct impact on fields as diverse as oil exploration or the study of the chemical origins of life. Pharmacology is plagued by problems associated with drug delivery, stability, and bioavailability in various biochemical environments. Atmospheric science or astrophysics is concerned about vibrational/rotational dynamics of small (highly symmetric = selection rules restrictions) on dust particles. Hydrous minerals and their dehydration pathways play a critical role in the study and prediction of deep focus earthquakes (potential generators of tsunamis). The non-destructive study of rare samples, such as meteorites, by neutron vibrational spectroscopy provides (bulk) information not obtainable in any other way.

Such and many other less conventional (for neutron scattering) science areas are actively explored in QENS studies at the SNS. It should be noted that at the present time many if not most users who perform QENS experiments on BASIS are those who either do not have neutron scattering experience at all, or, perhaps, have a limited experience with neutron diffraction and/or small-angle neutron scattering, but certainly not with neutron or other probes spectroscopy. This serves the neutron scattering community well from the standpoint of broadening its base and advancing to the untapped areas of interdisciplinary science. At the same time, this poises unique challenges due to the need for often quite elaborate data analysis of QENS data. To achieve this, frequent feedback from the instrument personnel is required, resulting in a productivity bottleneck due to the natural manpower limitations. Although the new users of BASIS gradually gain experience and proficiency in the QENS data analysis, becoming more independent, concurrent influx of novice users perpetuates the challenge.

4. Complex molecular systems

Chemical spectroscopy is a versatile technique, which allows users to obtain a variety of information on chemical bonds even in complex systems. It can be used as an analytical technique to identify molecules or functional groups by their spectral fingerprint, obtain information on molecular environments or conformations (spectral shifts), get force constants or intermolecular interactions, or determine basic thermodynamic or spectroscopic in formation such as the vibrational density of states. These features of the technique complement structural information obtained by other means and sometime provide the only information available to characterize a system when structural characterization techniques are not usable or are of limited use, for example in highly disordered materials or when mixtures of phases are present. This versatility proves useful in the study of chemical systems presenting a large degree of complexity. Selective deuteration, if available, can be used to elevate the signal from the species of interest in multi-component systems if such species are hydrogenated while the others are deuterated.

a. Advanced functional materials

Functional materials possess complex properties that are either native or built-in by design. They fulfill one or more functions based on a smart response as a result of the application of a particular stimulus. All classes of materials -- metals, alloys, ceramics, polymers, glasses -- and their combinations as composite systems are involved. Properties such as piezoelectricity, magnetoresistance, electrochromic or magnetocaloric effects, optoelectronic response, etc. are often exploited in isolation or in combination. During use, these various chemical or physical effects involve local structural or dynamical changes observable *in situ* by means of elastic or inelastic neutron scattering. For example, cation transport in ionic conductors in batteries, fuel cells, or supercapacitors is associated with lattice dynamics (phonon-assisted diffusion) and the appearance of short- or medium-range distortions. Neutrons represent an ideal probe to examine these effects, which, in turn, permits users to shed light on microscopic aspects of transport mechanisms. The possibility of observing functional materials in action, even inside complex devices *in operando* thanks to the penetrability of neutrons represents a distinct advantage, which needs to be further promoted and exploited. Chemical spectroscopy, insofar as it reveals any physical or chemical phenomenon manifesting itself in chemical bond dynamics changes, is particularly well adapted for this purpose. Thermoelectricity represents another area of research in which lattice dynamics (inasmuch as it is connected directly to heat transport) is of fundamental importance. Thermal conductivity is indeed intrinsically and intimately connected to lattice anharmonicity, whose study is the exclusive province of neutron inelastic scattering. Other examples include materials for energy storage (e.g., physical or chemical hydrogen storage) and other energy applications, gas separation, or multiferroics to cite but a few. Since its inception, QENS have been used to study hydrogen storage materials. More recently, the emphasis has shifted to QENS studies of complex electrolytes, both in liquid and solid form.

b. Porous materials and intercalation compounds

Porous materials occur naturally (e.g., zeolites, clays), but are increasingly becoming important and interesting as synthetic, by-design structures in macromolecular or inorganic chemistry.

Metal-organic frameworks (MOFs), mesoporous silica or aluminosilicon structures, hybrid organic-inorganic structures, or synthetic clays have enormous potentials in applications as varied as hydrogen storage, gas separation, catalysis, environmental cleanup efforts, drug delivery, oil or gas recovery, or electrochemistry. Intercalation chemistry is currently going through a revival with the development of new cathode materials for battery applications. In both classes of materials (porous and intercalation), conventional powder diffraction is of limited interest because the materials often present low to no periodicity. Spectroscopy remains of considerable interest in clarifying various aspects (conformation, interactions) of host-guest interactions. Neutron vibrational spectroscopy has several distinct advantages in the study of these systems, not the least of which is the ability to observe the dynamics of guest molecules inside bulky or complex hosts. Inorganic hosts are often weak scatterers, which permits the easy observation of guest dynamics, particularly when the guest is a hydrogenous molecule. Studies of diffusion dynamics of molecules confined in nano-pores have long been a traditional domain of QENS, and are still represented prominently in the gamut of experiments performed on BASIS. Thanks to the high intensity and signal-to-background ratio of BASIS, we have successfully probed the diffusion dynamics of non-hydrogen-bearing molecular species in confinement (CO_2, N_2, etc.), which represents a serious advance with respect to the traditional QENS studies of hydrogen-bearing species in confinement. The same characteristics of BASIS make it suitable for probing diffusion dynamics of lithium in various (mostly battery-related) materials.

c. Nanoparticles

The importance of nanosize materials in basic science, as well as for a multitude of application need not be discussed again here. Structural studies based on diffraction, pair distribution functions, or small angle scattering abound, but lattice dynamics studies remain scarce. Large surface-to-volume ratios in nanoparticles have profound and hitherto unexplored effects on dynamics. The scattering of phonons at boundaries, finite phonon lifetime effects, phonon localization and interaction with local or extended defects (including surfaces), or resonant bulk or surface modes are only a few of the effects that have been observed or predicted. They affect numerous physical properties (specific heat, thermal conductivity, optical response, ...), but are poorly understood. Currently half a dozen theories have been proposed to describe lattice dynamics at the nano- or mesoscopic level. With few systematic experimental studies, it is not possible to validate or even distinguish between various approaches. Neutron vibrational spectroscopy will play a fundamental role in this area. The results are essential, and urgently needed to understand the dynamical properties of nanoparticles for applications in optoelectronics, photovoltaics, thermoelectricity, and a host of other technological uses.

d. Molecular magnets

Molecular magnets are garnering the attention of organometallic chemists. Macromolecules exhibiting magnetic properties at the molecule level are of fundamental interest, but also hold enormous potential in the fabrication of compact magnetic recording devices with enormous storage capacity and density, as well as in the development of sensors. The coupling between magnetic properties and molecular dynamics/conformation remains unexplored. Generally speaking, there are no investigations of vibrational spectroscopy in radicals, molecules, or macromolecules exhibiting magnetism. There are very few examples of neutron vibrational spectroscopy in a magnetic field in the literature.

5. Liquids and solutions

Virtually all of chemistry takes place in solution. And yet we do not possess a microscopic theory of solubility, which would allow us to predict solubility or miscibility even qualitatively, let alone quantitatively. The pharmaceutical and chemical industries spend an enormous amount of time, money, and effort to measure solubility or develop new binary or ternary solvent systems. While the structure of liquids has received much attention, the nature of intermolecular interactions in solvents and solute-solvent systems is much less understood, especially the role played by hydrogen bonding in the liquid state. Even water remains an object of intense scrutiny by physicists and physical chemists. Neutron vibrational spectroscopy is -- in principle -- the ideal tool to observe all vibrational modes (torsions, bending, stretching) associated with hydrogen bonds. The main problem is the exchange of momentum with the molecular system. The recoil that results broadens and shifts vibrational modes. We have a theory of this effect, but additional theoretical developments are necessary to develop a practical correction scheme to process neutron vibrational spectra collected in liquids. Alternatively, the recoil problem could be mitigated experimentally by working at low momentum transfer.

Glass-forming systems, with many liquids among them, have been traditionally investigated by QENS. In general, QENS plays a special role in studies of liquids and solutions. Uniquely among other probes (NMR, dielectric spectroscopy, etc.), QENS signal shows a sensitivity to the scattering momentum transfer, from which the information can be derived on the geometry of the motions that give rise to the QENS signal. As we have mentioned above, a novel approach to the QENS data analysis from liquids has been adopted at BASIS and applied successfully and consistently to various bulk-like and confined fluids, from simple hydrocarbons to complex room-temperature ionic liquids. BASIS has played and plays a central role in the activities under the umbrella of the ORNL-based FIRST (Fluid Interface Reactions, Structures, and Transport) Energy Frontier Research Center.

Areas of technical development

1. Multifunctional instruments

Invariably, the interpretation of neutron vibrational spectra requires structural information in the form of molecular environment, crystal structure, molecular conformation, ... While this knowledge is sometimes available, it is not unusual for a user to face a situation where only limited information is available. This is the case when a material is disordered or poorly ordered, or when a sample is prepared in situ, or when a sample is irreversibly modified (even destroyed) during an experiment. In some of these situations, it is not possible to recover the sample or bring exactly the same sample to another instrument for structural characterization. The simultaneous determination of vibrational and structural determination then becomes advantageous or even essential. This can take the form of powder diffraction detectors, a small-angle detector, or pair distribution function capabilities. The purpose is not to compete with more specialized instruments, but to complement the inelastic data in a timely and efficient fashion, especially in fragile samples.

We also note that in modern crystal analyzers, the elastic line is relatively narrow. By designing new instruments or modifying existing instruments to allow for a reasonable dynamic range in neutron energy gain and optimizing further the width of the elastic line to 40 micro-eV or better, one could obtain an instrument usable for simultaneous neutron vibrational spectroscopy and quasielastic neutron scattering. The possibility of measuring fast diffusion phenomena and identifying molecular moieties by vibrational spectroscopy would open up new possibilities in surface science (catalysis, porous materials, intercalated compounds) and other fields.

The conceptual design of BRAINWAVES (see dynamical range in Figure 1) will address simultaneously the quasielastic and inelastic spectra on a single sample with a “single shot”. This will particularly benefit INS/QENS studies of soft matter, which is generally characterized by broad, overlapping quasielastic and low-energy inelastic excitations, which are difficult to study through “piecemeal” measurements. The BRAINWAVES will combine the energy resolution of a backscattering spectrometer such as BASIS with the accessible energy transfer of a vibrational spectrometer such as TOSCA/VISION while, importantly, providing coverage over a range of momentum transfers. Besides, BRAINWAVES will feature a small beam size, shared by some other spectrometers described below and amenable to samples available in limited quantities and high-pressure experiments that require a limited sample volume. The JANUS instrument concept is a direct/indirect INS spectrometer that allows dual operation.

2. *In-situ/in operando*

The preparation of fragile samples in situ presents a number of advantages. *In situ* gas adsorption on surfaces is a prime example of the application of the technique and is becoming increasingly popular in neutron vibrational spectroscopy. The synthesis of samples such as clathrates that are not recoverable at ambient conditions is another example of the use of *in situ* synthesis techniques.

A natural extension of this approach is to use neutron vibrational spectroscopy to observe materials in operando. Examples abound: cation transport in solid electrolytes, piezoelectric materials in a DC or AC electric field, electrode processes, proton transport, magnetoelastic effect, etc. Once a steady state is established upon the application of an external field, materials dynamics can be compared to its state in the non-driven material. The potential of this approach is enormous and relies in part on the penetrability of neutrons through the equipment needed to establish the external excitation and the advantage of neutrons in probing the bulk of a material in operando.

3. Weak scatterers

Small sample sizes and/or weak scatterers would broaden the range of samples usable for neutron vibrational spectroscopy. Traditionally the technique has favored the use of materials containing hydrogen because of the large incoherent neutron scattering cross section of hydrogen. High power neutron sources alleviate the problems associated with the absence of hydrogen in a sample by enabling data collection in reasonable amounts of time. Background is the other issue that will require attention to produce high quality spectra with weak scatterers. This entails the development of sample holders, collimators, and shields specifically geared for these situations.

The proposed STS instrument SPHIINXS (SPHerical Indirect Inelastic Xtal spectrometer) has small and weak scattering samples in mind. By using a focusing guide to 5x5 mm^2 and positioned at 60 meters from moderator, it will provide unique and unparalleled capabilities. Two other spectrometers proposed for the STS, BRAINWAVES and MINTBARS, are expected to feature the same small beam size.

4. High pressure

Pressure is a thermodynamic parameter in increasingly high demand with users. Pressure is clean perturbation on a given system: it brings atoms closer together. The consequences of this perturbation can be extremely complex, but the perturbation is clean. Pressure is of interest to the earth sciences in general to induce phase transitions, determine equations of state, produce chemical reactions or changes in oxidation levels, or stabilize unusual states of minerals. Catalysis is another area of research in which the use of pressure is of interest.

The development of pressure cells for neutron vibrational spectroscopy at high pressure lags the demand from users. This is in contrast with the use of diamond anvil cells in x-ray or optical spectroscopy. Inelastic neutron scattering has specific requirements beyond those typically encountered in DAC work:

- Larger sample volumes are needed, which tends to limit the maximum reachable pressure. Currently small cells exist up to 20 kbar (2 GPa). This is a major limitation for the Earth Sciences.

- The pressure in the cell should be adjustable remotely. Compact DACs are easily removed from the beam for pressure adjustment, then cooled and heated again. This is more cumbersome in neutron scattering. Gas or liquid cells permit pressure adjustment remotely, but are limited to about 10 kbar.

- Similarly, remote pressure measurement is needed. In the absence of diffraction, a pressure marker with a known equation of state is not usable. (See multifunction instrument section above, however.)

The proposed STS instrument, XTREME-X (EXTReme Environment Multi-Energy Spectrometer with Xtal analyzers) has been conceived having high pressure/high magnetic fields in mind. By arranging the crystal analyzers on a plane and using a number of them in series, combined with a focusing guide and the innovative use of parahydrogen as a filter of higher reflections, it will allow INS studies on high pressure systems routinely. Following will be a high profile research filed that this technology will enable.

Phase diagram of molecular hydrogen under pressure is still not fully understood. Hydrogen is the simplest of molecules. However its properties are completely dominated by the quantum nature of the molecule. In particular the observation of the structural and dynamic properties of hydrogen can only be done indirectly. From a structural point of view, X-ray diffraction is not useful because hydrogen contains only one electron, in the case of neutrons, the incoherent cross section of hydrogen is too much of a problem, so neutron structural studies are done on deuterium. It has to be noted that from a quantum point of view a proton is a fermion and a deuteron is a boson, as a consequence the spin statistics of both molecules is different. Spectroscopic methods like Raman and IR are commonplace. However, they study mostly the stretch of the hydrogen molecule (in high pressure studies) and therefore they are indirectly assessing the phases. INS is a direct proof of the interatomic separation and the spin arrangement of the hydrogen atoms in the molecule. It does provide direct measurement. High pressure studies, in the Mbar range would be the ultimate challenge for INS, in principle it will provide unequivocal evidence of metallization of hydrogen under pressure.

5. Thin films

Because of the small amount of active material in a thin film, such samples have always presented a challenge for spectroscopy. Scraping the film prior to neutron vibrational spectroscopy to increase the volume of sample and minimize scattering from the substrate modifies the film, for example by relieving any stress or defect structure that may exist only when the film is interaction with the substrate. A more systematic approach ought to be developed to enable the use of thin films as samples.

[No technical suggestions were offered during the discussion.]

6. Transients and fast phenomena

Neutron scattering is an intensity-limited technique. As such it is not suitable to observe fast, transient phenomena. In some cases, it might be possible to observe fast phenomena with neutrons if a sample is excited with an external field (light, electric field, ...) synchronized with the neutron beam. For example, a pulsed laser synchronized with the pulsed neutron beam (with a variable delay) could excite a photosensitive molecule. The induced change in molecular conformation would then be reflected in a change in vibrational state, which would be observable with neutrons. Such an approach is common in fast laser spectroscopy (pump-probe systems) and might be accessible to neutron vibrational spectrocopy if the observed phenomenon has the proper time scale. Neutrons as a probe have the advantage of being completely orthogonal to many pumping systems (e.g., laser). The technical challenges are to design pumping (excitation) systems compatible with the typical environment of a sample on a given neutron beam line and to synchronize the excitation with the beam.

7. Slow dynamic processes.

Many technologically important systems are glass-formers. As a glass-forming system approaches its glass transition temperature in the course of cooling down, its viscosity grows tremendously, from the microscopic (picosecond) to the macroscopic (100 s and longer) time scale. Likewise, the diffusion coefficient, which is related to the viscosity through the Stokes-Einstein relation, decreases dramatically on cooling down toward the glass transition temperature. However, in many systems, a remarkable breakdown of the Stokes-Einstein relation occurs, oftentimes below ca. 120% of the glass transition temperature, when the diffusion becomes much faster than one would expect from the measured viscosity. Understanding the origin of such a breakdown would be of much fundamental interest and also of great practical importance for the systems where the improved transport properties are desired, especially when the structural relaxations slow down due to low temperature or high packing density. However, this will require the much higher energy resolution than presently available at backscattering spectrometers, sufficient to probe the relaxations on the time scale of nanoseconds to tens of nanoseconds. To this end, the mica-based backscattering spectrometer with ~ 200 neV energy resolution proposed for the STS is poised to open unique scientific opportunities in the area of technologically important glass-forming materials where traditional spectroscopic technique are invariably limited by their lack of the spatial resolution capabilities. MINTBARS will feature the same small beam size and the momentum transfer range as BRAINWAVES in QENS regime; these two spectrometers combined together will provide unprecedented coverage over 7 orders of magnitude in energy transfer (that is, relaxation times).

8. Libraries, databases

Unlike other techniques (x-ray, FTIR, Raman) for which extensive libraries of structures, diffraction patterns, and spectra exist either in book-form or as online databases, neutron vibrational spectroscopy is limited in terms such resources. An effort at ISIS is underway to produce a database of spectra. It includes currently a few hundred spectra. Non-specialists often find the interpretation of neutron vibrational spectra to be difficult. A database would go a long way in terms of making the technique more user-friendly and more immediately accessible to a broader range of users and potential users. At a high throughput instrument such as VISION, a large database could be assembled over several run cycles provided an automated sample change become available.

<u>What is needed to achieve our goal?</u>

1. Automatic sample changers
2. Batch treatment of data
3. Gas-handling manifold
4. Pressure cells
5. Collimation, gauge volume definition for imaging (local vibrational spectra)
6. Hyphenated techniques (NVS-diffraction; NVS-SANS; NVS-NMR; NVS-pdf; NVS-Raman)
7. Deuteration
8. Sample environment integration in DAQ (e.g., transients; synchronization with beam)
9. Polarization
10. Sample preparation/characterization labs

III. Session Reports

B. Materials Science and Engineering

Participants:

Yan Gao (GE Global Research)
Iuliana Cernatescu (Pratt & Whitney)
Cev Noyan (Columbia University)
Anton Tremsin (University of California, Berkeley)
Raj Vaidyanathan (University of Central Florida)
Andrew Payzant (ORNL)

Presentations:

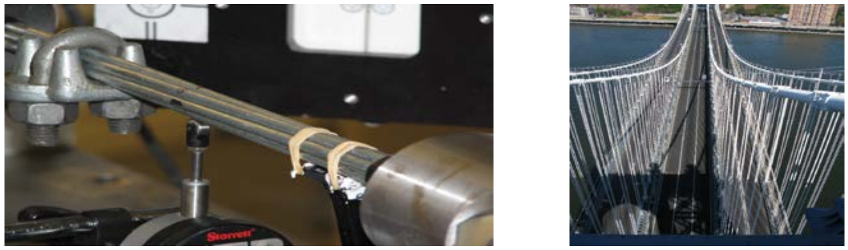
Yan Gao: *“Characterization at National User Facilities: Industrial perspective”*

Dr. Gao provided an industrial research perspective on user facilities, and then followed with a discussion of how next-generation neutron techniques might be employed for solving important industrial problems. Techniques such as imaging, microscopy, and stress mapping were highlighted. A strong case was made for an investment in developing comprehensive and user-friendly data analysis software, which he described as a major bottleneck at present in getting from data to results. He stressed that being “advanced” is good for science, but for industry it is essential to provide data that is reliable, repeatable, and reproducible.

Residual Stress: a never-ending pursuit by industry. Yan Gao described the use of neutron research at GE Global.

Cev Noyan: “*Some issues in engineering materials and systems*”

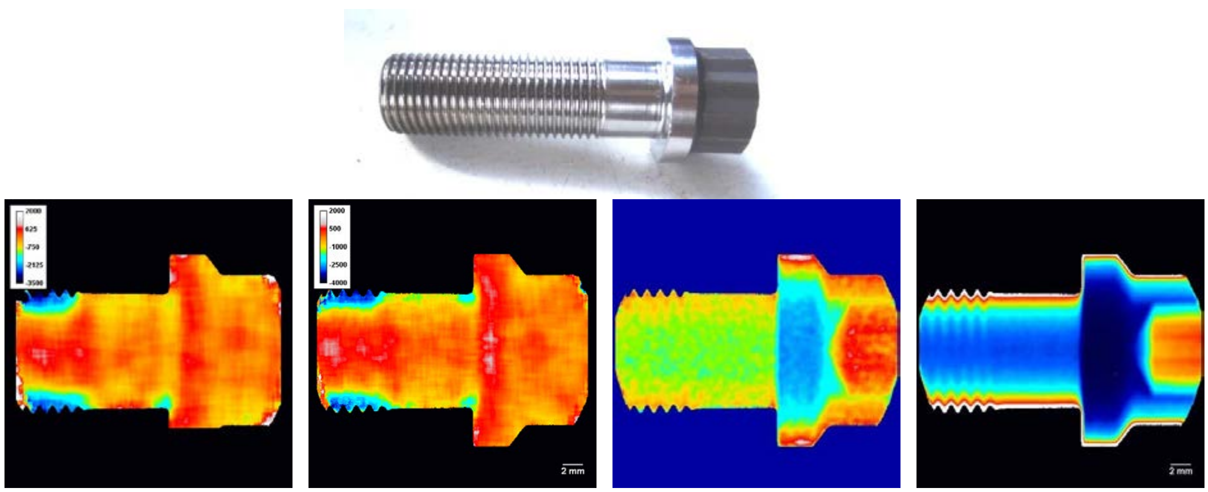
Dr. Noyan began with the relationship between basic research and applied/industrial research, where the objective of basic research is “understanding nature”, and applied research is “controlling nature”. This places different requirements for a neutron user facility to serve both communities. Dr. Noyan then gave an applied science/engineering example based on his neutron diffraction studies of suspension bridge cables, and concluded with a perspective on how user facilities can best support investigation of applied science problems with great importance to society



Studying Suspension cable used in bridges for failure mechanisms using Neutron Diffraction.

Anton Tremsin: "*High resolution energy resolved neutron imaging and resonance transmission analysis*"

Dr. Tremsin provided a review of the recent rapid developments in energy-resolved neutron imaging, with particular emphasis on Bragg edge and resonance absorption features that enable non-destructive 2-D and 3D characterization of elemental/isotopic composition, crystallographic phases, orientation texture, stress, and temperature at pulsed neutron sources. It is now possible to map these differences at spatial resolution of tens of microns. Even magnetic fields can be imaged using polarized neutrons, as recently demonstrated at HZB (Berlin). The presentation generated much discussion, and the It was noted that these detectors are not only applicable to dedicated "imaging beamlines" such as VENUS, but may be added to existing beamlines such as VULCAN to provide complementary information to the existing infrastructure.



Strain 4.16Å edge	Strain 4.14Å edge	Edge Height	Edge Pedestal

Bragg edge imaging: Strain mapping of Ni bolt with high spatial resolution. Work carried out at ISIS

Break out session discussions

For the purpose of this document, we have classified "materials science and engineering" (MSE) to include neutron imaging and tomography of functional components, small angle neutron scattering to characterize the microstructure of hard matter, and spatially-resolved neutron diffraction for study (primarily) of microstructure and mechanics in metals, alloys, and ceramics. While there are x-ray based analogs for these techniques, neutrons provide important advantages in many systems that make them either a complementary or sometimes unique characterization probe.

Such MSE instrumentation needs are presently met at HFIR with the CG-1D Imaging, the CG-2 GP-SANS, and the HB-2B Residual Stress instruments. The strong user demand for such instruments is demonstrated by the fact that comparable instruments have been built at all major reactor facilities around the world and are heavily oversubscribed. At pulsed sources, a similar array of instruments is found – "engineering diffractometers" such as SMARTS (Lujan), Engin-X (ISIS), VULCAN (SNS), etc. Pulsed-source imaging beamlines are comparatively recent additions at facilities including JPARC, ISIS, and the planned VENUS instrument at SNS. The HIPPO beamline at Lujan was in many aspects unique in providing fast and accurate orientation texture mapping with a variety of possible sample environments (cryo, pressure, high temp, applied load, etc.).

Emerging Areas of Impact

1. Infrastructure Stewardship

The nation's bridges, railways, power transmission lines, pipelines, etc., are ageing faster than they are being replaced. Prof. Noyan made an emphatic case for the need for advanced materials characterization techniques, specifically including neutron diffraction and imaging, in order to ensure that the computational models presently used to determine the safety of such structure are experimentally validated, and to provide the data necessary to build such models. It is clear from the example of stress distributions in suspension bridge wires that any serious attempt to investigate these problems will require significantly more neutron instrument time than is possible today, and that additional instruments would need to be built to meet this demand.

2. Development of Advanced Propulsion Materials

These include alloys, ceramics, and composite materials for automotive, aerospace, and marine applications. Essential to this area is the ability to conduct full microstructural characterization closely coupled with computational models to realize specific mechanical properties under operating conditions.

3. Advanced Materials Processing

Additive manufacturing (or 3D Printing) is a rapidly growing method of making parts and assemblies out of plastic or metal directly from a CAD drawing. This method can be highly efficient but the highly directional thermal processing has the potential to introduce significant hidden defects and residual stresses that impact the performance. Neutron imaging and residual stress mapping presently provide nondestructive characterization of these phenomena at spatial resolutions on the order of tens of microns (imaging) and mm (stress). Achieving higher spatial resolution was identified as a key advance here.

Magnetic field processing of alloys was another area of potential growth. In recent years it has been shown that high temperature processing of certain alloys, especially steels, can be strongly impacted by magnetic fields such that phase transformation temperatures (e.g. austentite-martensite) can be shifted. For in-situ characterization studies, neutrons appear to provide significant advantages in terms of sample environment and experimental infrastructure.

4. Advanced nuclear fuels and radiation tolerant materials

Neutron-based characterization was deemed essential to support development of improved reactor materials. Critical capabilities would include time-resolved evolution of defects and precipitates in reactor alloys using SANS, etc. This will require an ability to safely handle radioactive materials in solid, powder, or liquid form at the instruments. This will necessitate establishing modified/new procedures, potentially new software, raise additional materials accountability issues, much of which will be export controlled. Access to a hot cell and skilled tech support will also be needed.

5. Energy Storage and energy conversion integrated systems

A distinction was noted between studies of the crystal chemistry of energy storage, conversion, and/or transport materials, which would fall under the chemistry section of this report, and in-situ studies of assembled functional multicomponent systems, such as working batteries, fuel cells, photovoltaics, or thermoelectric modules, which fall under MSE. The latter would include in-situ lithium mapping in batteries, water transport in PEM fuel cells, using imaging, SANS, or diffraction mapping instruments.

6. Materials by Design / ICME

The issue here was how to couple neutron experimental data to models for verification and/or validation.

7. Materials Under Extreme Environments

Materials responses to extremes of temperature, pressure, and applied fields – or combinations of these, are of great interest to the applied science/engineering community, just as to the basic science community. Success in this area requires a skilled Sample Environment team, closely working with beeline scientists to enable in-situ studies using neutrons. Studies on more conventional functional materials such as piezo-electrics, magnetic shape memory alloys, etc., will directly benefit from an infrastructure designed to study materials under extremes.

Selected Problems

1. 3D Neutron analysis / microscopy

What is needed is a technique to probe interior microstructure at high resolution (e.g., 1-15 µm). This might include microstructural characterization using neutron resonances for composition-resolved particle/grain size, shape, and orientation, and also high-resolution strain and deformation mapping using Bragg edges. The energy range for resonances is much greater than for Bragg edge and imaging work may benefit from another dedicated instrument at STS.

2. Online virtual instrument

A great deal of valuable neutron beam time is used for sample alignment and evaluating planned experiments. Having useful interactive tools available to users online will enable better experimental design, and an opportunity to fully plan/test all steps in the data acquisition process before the user comes to the beamline.

3. Dynamic Studies

In-situ studies of great value to MSE include the formation of magnetic domains in transformer steels and how they to the microstructure development, solidification from the melt in castings and welds, single crystal growth, evolution of microstructure under load and/or temperature, etc. SANS in particular is expected to be invaluable for such studies.

4. Characterization of internal temperature distributions in complex assemblies

Real-time, in-situ studies of internal temperature distributions in operando would provide unique data of high value to develop robust, reliable, computational models of heat flow in working systems. This is particularly valuable for materials that are operated close to phase boundaries, and in composite materials/assemblies where the thermal conductivities of the constituent parts are very different. Ideally such characterizations would span multiple techniques (e.g., neutron resonance imaging, lattice parameters (CTE), etc.) at spatial resolutions of mm to µm, depending on the application.

5. Multiscale characterization, and multimodality

It will be important to provide capabilities to study alloys, composites, etc., using <u>simultaneous</u> multiple techniques, including diffraction, N-CT and X-CT imaging, SANS, reflectometry, thermal analyses (DTA/DSC/TGA), etc., across a considerable range of dimensions (nano-, meso-, micro-, and macro-scales). At the VISION beamline there is already a capability to simultaneously collect inelastic spectrometry data in parallel with elastic diffraction data, and this multi-modality can be applied to many other beamlines – VENUS and VULCAN being prime examples. For SANS, adding stress/strain, shear, rheometry, and stop flow sample environments will enable in-situ studies of chemical synthesis of materials processing.

6. Characterization of radiation damage across multiple scales

As part of the effort to develop better materials for reactor fuels and structural components, it is essential to have access to neutron characterization tools. This requires MSE beamlines specifically designed to handle hot (radioactive) samples.

7. High throughput texture analysis

One of the most active instruments at the Lujan Center was HIPPO. The success of HIPPO highlights the critical need for a next-generation instrument for studies of texture, and texture evolution under pressure/temperature/etc. Both bulk and localized mapping capabilities are needed, and some aspects may be better suited to one instrument design over another – imaging versus diffraction, for instance.

8. In-situ corrosion studies

Corrosion is primarily a surface phenomenon, and so may appear well suited to reflectometry, but one also needs to consider identification of hidden corrosion in bulk assemblies, or in complex shapes. Both bulk characterization and spatially localized mapping may be useful.

9. Coupled sample environments

For parametric studies it will be essential to provide combinations of sample environment, including multiaxial stress, temperature, magnetic field, electric field, controlled atmosphere and humidity, etc. In the case of temperature it will be essential to not only control temperatures over a wide range from cryogenic to high temperature, but also to enable rapid rates of heating and cooling.

What is needed?

1. Live data analysis that feeds directly back to data acquisition:
    a. “expert” systems to optimize experimental setup and data analysis
2. Entirely new modes of user access
    a. Requires routine “rapid access” review and processing
    b. Needs a new paradigm to measure impact
3. Ability to easily handle unique samples (both in and out)
    a. large/heavy samples
    b. “hot” (radioactive) samples
    c. proprietary samples (rare but occasionally needed)
4. Applied/Industrial research with neutrons would greatly benefit from some analog to the German Fraunhofer Institute to support closer collaboration between industry and laboratory staff (not just neutron science staff, but also modeling, microscopy, mechanical properties, etc., experts at ORNL. This has been done via EERE, FE, NE, SBIR, and WFO arrangements, but rarely closely coupled to the theme of neutrons for industry. Possibly the Joint Institute for Neutron Sciences (JINS) could step up to fill some aspects of this need.
5. Need for more outreach - frequent workshops, seminars, etc., to grow the community. There are many projects that would benefit from using neutrons that we are not reaching at present.
6. A multi-moderator target design (STS) will facilitate development of multimodal capabilities
7. Development of high-resolution neutron microscopy, imaging, and tomography beamlines, including epithermal neutrons for resonance imaging/tomography. Polarized

beams might expand measurement options including an ability to map magnetic fields on the micro-scale.

8. With the closure of the Lujan User Program, it is expected that the already high user demand for engineering materials on VULCAN will significantly increase. In order to accommodate this work, it is recommended that the VULCAN instrument be fully commissioned, adding five detector banks that were in the original instrument plan but not yet implemented. This will serve two purposes – to reduce the time needed per user project from increased detector coverage, plus enable science that cannot be done with current detectors (such as local structure evolution under stress in bulk metallic glass, complex functional oxide mechanical response, and texture, strain pole figures under complex loading and processing, etc.

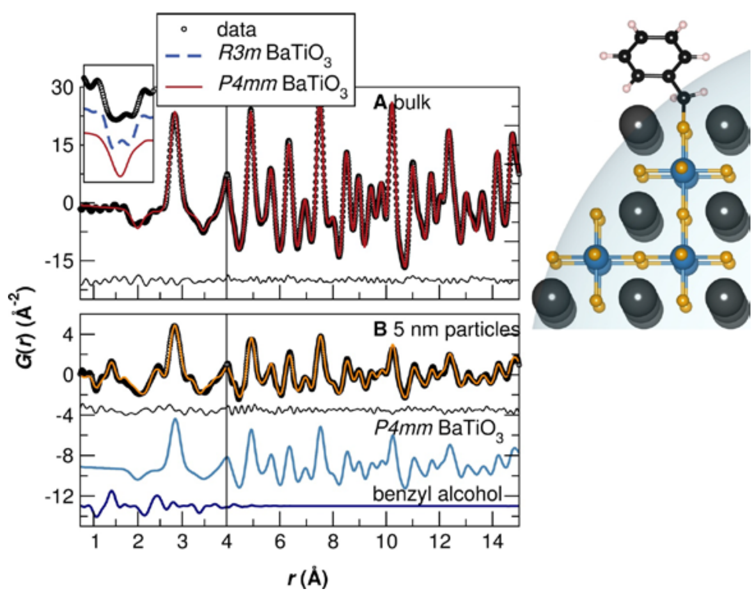
C. Structural Chemistry

Participants:
Ram Seshadri,
Nancy Ross,
Brian Toby,
John Parise,
Ken Poppelmeir,
Angus Wilkinson,
Mike Toney,
Hanno Zur-Loye
and Ashfia Huq

Presentations:

Ram Seshadri: *"Materials by design: Understanding from synchrotron x-ray and neutron studies provides key inputs"*

Understanding structure is the basis for learning everything else was the theme of Ram Seshadri's presentation. By picking several examples from his laboratory, which included nano particles, catalysis, non-metal to metal transition, charge ice and solid-state white lighting; he showed that understanding the structure of materials is absolutely crucial to understand their performance. For the level of complexity of the systems of interest, nothing less than the highest quality X-ray and neutron diffraction data often combined, along with modeling and analysis tools, is sufficient.

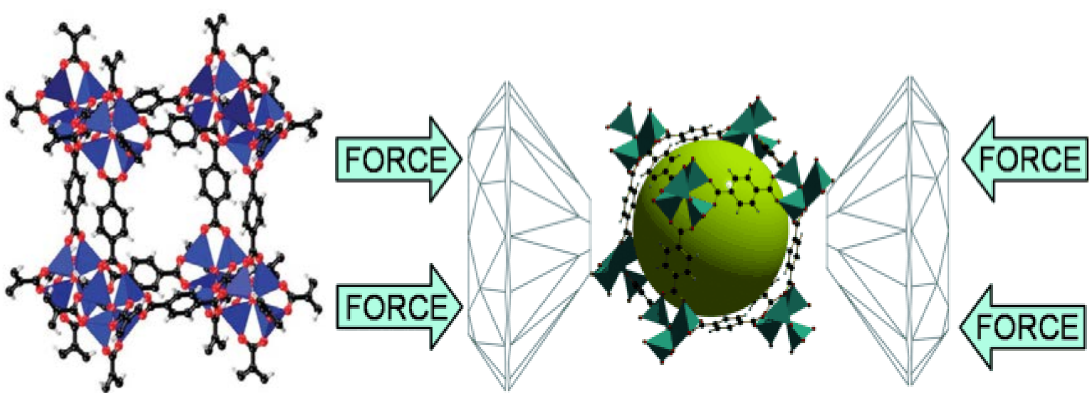


Capped $BaTiO_3$: Capping groups observed by neutron scattering for the first time; for any polydisperse nanoparticle system.

One of the most classic examples of this is the CuO based high Tc superconductors. He pointed out the need for the availability of high resolution high Q neutron diffraction data to carry out neutron Pair Distribution Function (PDF) analysis that allows one to probe local distortions in crystalline compounds and has also proven to be an ideal tool for studying size, shape and distribution of nano materials. In addition to the high quality data one also needs to sometimes use large box models such as Reverse Monte Carlo (RMC) algorithms to get to the true picture of mechanistic behavior. In the case of studying phosphors for solid-state white lighting, structural studies of some model compounds revealed that rigidity of the compound is important and that Debye temperature is a useful proxy for this. With that information in hand, multiple other structures were computed to synthesize numerous new materials for this application. This is a theme that resonated over and over again for various talks and discussions.

Nancy Ross: *"Materials under extreme conditions"*

"How does the earth's interior work?" This is one of the biggest science problems unanswered to date. Understanding the behavior of components that are predominately oxides and spinel compounds under high temperature and pressures provides a "window" into the Earth and planetary interiors. When either pressure or stress are applied to matter, atoms are brought closer together, ultimately altering a material's structural, electronic and mechanical properties in radical and unexpected ways. As a result, high pressure and temperature are very often used as tuning parameters to change the properties of various materials. Recent advances in artificial diamond production technologies, coupled with advancements in diamond anvil cell design for neutron diffraction has opened up a wide range of problems that can now be addressed by researchers around the world. Dr. Ross provided several such examples such as gas absorption mechanism in large pore structures such as zeolites and Metal Organic Framework (MOF) or studying the magnetic phase transitions using both elastic and inelastic neutron scattering. She put forward the following list of systems were high-pressure neutron scattering can have significant contribution in the next few decades.



Studying MOF using neutrons to find H_2 absorption sites. Pressure can be used for synthesizing other polymorphs of MOFs.

- The structures of complex hydrous phases and metal hydrides. Hydrogen bonding in organic and inorganic systems as a function of P and T (both high and low).
- Planetary ices; the structure, strength, and dynamics of ices under pressure, temperature and stress.

- Phase transitions: formation of new materials under pressure (e.g. superconductors such as metallic elemental sulfur and oxygen)
- Silicate melts, glasses at high P and T and the dynamics changes occurring during heating and pressurization, with implications for glass technology and for volcanic processes.
- The structure and dynamics of supercritical fluids and liquids.
- Influence of pressure and stress on magnetic properties at both high and low temperatures.
- The strength and rheology of materials and relationship to brittle and ductile failure. Following the rate of stress release as a function of time; stress and rheology in the mantle.
- The dynamics of protein folding and unfolding with implications for food technology and life at extreme conditions
- Stock pile stewardship: light elements at extreme conditions to provide data for verification of codes

Brian Toby: *"If you build it, will they come ?:Maximizing use of diffraction instrumentation"*

One of the most scientifically productive beamline at the advanced photon source is the powder diffraction beamline (11-BM). In its 7 years of operation since 2008 it has produced over 350 publications and despite the low-brilliance source and single-scientist staffing, became the most productive APS beamline in 2013. Brian Toby, in his presentation explained how the mail-in program, which accounts for over 50% of the operation of 11-BM was made into a success by the investment in automation in both hardware and software. He noted from his days in industry that the majority of the community who can benefit from structural characterization, be it X-ray and/or neutrons, need outreach and education about the power of these techniques, as user facility access is not a part of their regular repertoire of materials characterization techniques. Industrial scientists cannot afford the time or delay in proposing and scheduling a facility trip; many younger scientists do not have travel funds. 11-BM made its impact by growing the scattering community far beyond the traditional users of these facilities; the SNS and HFIR can follow suit to truly make an impact in both academia and industry. He noted the need to upgrade the existing SNS first target instruments to their original design criteria and also the immediate and high priority need to build another high-throughput powder diffraction beamline to accommodate displaced users from NPDF and HIPPO at The Lujan Center, which has recently been closed. Without this, there is no US facility to continue the PDF work initiated at the IPNS and continued at Lujan. Greater capacity is also needed to expand the user base. As long as instruments are highly oversubscribed, novice users will be out-competed by the existing user base.

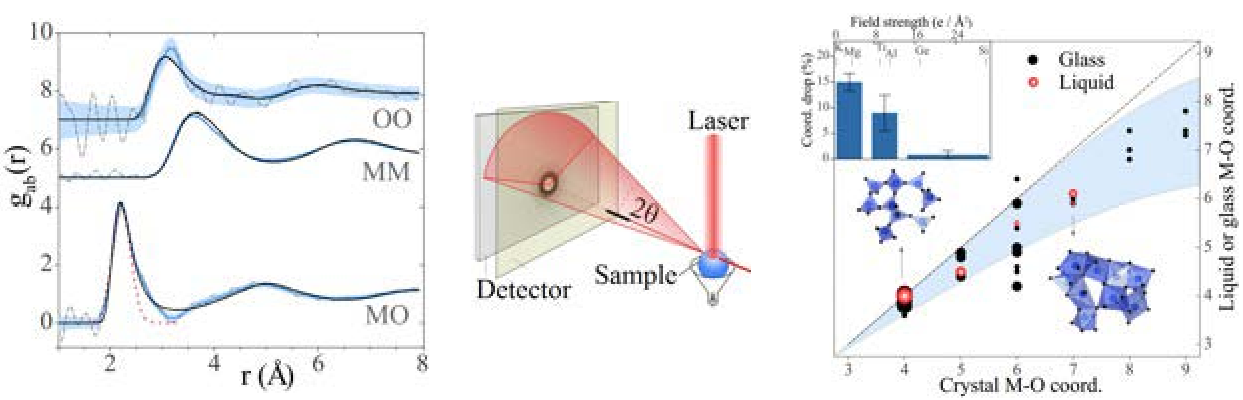
Brian ended his talk with recent work that is being carried out by him and collaborator Bob Von Dreele on a third generation Rietveld code called GSAS-II that is intended to better allow chemists, biologists, geoscientists, etc. with minimal crystallographic expertise to perform structural analysis with user facility data.

Ken Poeppelmeier: *"Accelerated Discovery of the Predicted Stable and Unknown ABX Phases"*

The Materials Genome Initiative is a multi-agency initiative designed to create a new era of policy, resources, and infrastructure that support U.S. institutions in the effort to discover, manufacture, and deploy advanced materials twice as fast, at a fraction of the cost. The materials genome project has launched several programs where large database of materials are being used to calculate and minimize structures of known compounds and predict new ones using various different theoretical techniques. ***Successful theory has led and will lead to prediction of large numbers of unknown stable (missing) compounds. Validation through the synthesis is the challenge for experimentalists.*** Dr. Poeppelmeier showed his groups work on using in-situ X-ray diffraction at the Advanced Photon Source on a system of compounds under various synthesis conditions, which greatly enhanced their ability to make new materials and find ideal conditions under which these new compounds form. He emphasized that for certain families of composition these in-situ measurements will be need to be carried out in neutron diffraction beamlines. In this emerging field of theory assisted materials discovery process X-ray and neutron diffraction will play a very important and complementary role.

John Parise: *"Sample environments for information poor systems"*

John Parise shared some of the success stories of experiments carried out at the NOMAD instrument where a complete set of pair distribution functions for an oxide melt was measured for the first time. This task was achieved with collaboration between Advance Photon Source, Spallation Neutron Source and a DOE SBIR grant to a small company called MDI to build a levitator to carry out these sets of measurements. He pointed out the complementary role that X-rays and neutrons played in solving this important problem. He also discussed the need for collaboration between national labs, academics and industrial scientists to develop realistic sample environment to study materials of technological importance.



Combine X-N PDF studies reveal the physical properties of high temperature oxide liquids determined by the coordination behavior of next neighbor pairs. Understanding of oxide liquids is essential in nuclear meltdown scenarios, evolution of planetary bodies, glass formation and crystal nucleation.

Mike Toney: *"Li ion Batteries"*

One of the most active fields of research in our current decade in energy storage materials is to improve both gravimetric and volumetric performance in Li ion batteries. It is envisioned that batteries will play a major role in our next generation energy storage, be it for mobile applications or balancing the electric grid. However, our current technology is not yet up to either task. Neutrons play a crucial role in understanding the structure of batteries at various different length scales due to its sensitivity to Li. Understanding where the atoms are, how Li exchange happens, how particle size and shape distribution effect the performance and what are the causes of failure in batteries are just some of the issues we will need to address for mass deployment of Li ion battery technology.

Hanno Zur-Loye: "*In-situ Neutron Diffraction Study of* $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ *Under High Temperature SOFC Operating Conditions*"

Hanno Zur-Loye presented some work done recently at powgen investigating the structure of a candidate Solid Oxide Fuel Cell (SOFC) electrode under operational condition. He emphasized that the true structure of materials are often different under *in operando* conditions compared to ambient state. Doing measurements in realistic environments can greatly enhance our understanding of these materials.

Break out session discussions

In the structural chemistry break out session we first tried to come up with some key question that we felt neutrons could contribute to and then explored what technical developments were needed to answer some of these grand challenges. The current instrument suites at SNS that support structural chemistry are both powder and single crystal diffractometers, which include POWGEN, SNAP, TOPAZ and NOMAD.

Areas of Novel Science

1. Glass Transition

Glasses are disordered materials that lack the periodicity of crystals but have the interatomic bonding associated with solids. They have quite distinct mechanical properties from crystalline solids. The most common way of making a glass is by cooling a viscous liquid fast enough to avoid crystallization. Although this route to the vitreous state — supercooling — has been known for millennia, there are many other routes to formation of glasses. The molecular processes by which liquids acquire amorphous rigidity upon cooling are not fully understood.

Liquids at extreme temperatures and/or pressures have immediate relevance to the behavior of nuclear reactors in melt-down, understanding the interiors of planets, and glass and metals manufacturing industries. As we try to capture the properties of metastable phases in functional materials, we need to look beyond equilibrium states of matter; such as perfect crystals. As nature has done, exploitation of non-equilibrium, metastable amorphous and disordered materials can provide new materials with novel and more tunable properties.

Liquids quenched from high pressures, for example, may form new amorphous materials with novel physical properties, analogous to the difference between diamond and graphite. Similarly many valuable drugs show acceptable bioavailability only when prepared in an amorphous state. Yet, we still know relatively little about the behavior of liquids at extreme and metastable conditions. Of particular interest are the conditions under which liquid-liquid transitions occur, and the formation of glassy and amorphous solids from different liquid states. For example, the behavior of water, the most important liquid at the Earth's surface, is highly debated in the deeply supercooled regime. This is highlighted by two recent articles in *Nature*. The first, Palmer *et al.* (Nature **510**, 2014, 385-) uses MD simulations to show that there are two distinct metastable liquids in the deeply supercooled regime (of the simulation). The second, Sellberg et al. (Nature **510**, 2014, 381-) shows experimentally the lack of any abrupt structural transition in the ambient pressure metastable liquid, down to 227K.

Experimentally reaching these interesting regimes require probing smaller samples (0.01-1.0 mm), and shorter times scales (<60 sec). For example, the structure and dynamics of technologically relevant silicate glasses evolve with rapid cooling rates ~100K/s. To probe such transient states, cyclical sample environments such as measuring a continuous stream of falling liquid drops, can help to expand the effective measurement timescales.

2. Chemical reaction mechanism

"How do atoms come together to make functional materials; in reaction systems involving solid-solid, solid-liquid and solid-gas interactions?" This is a question we will need to answer if we are to address the challenges posed by the materials genome project. To date, discovery of new materials are often serendipitous, even though they are guided by centuries of knowledge gains in chemistry. However, as our understanding of reaction mechanisms involving solids, liquids and gases improves and we have better computational tools, we can use theoretical guidance for synthesis of new materials. Modern methods in quantum mechanics have proven very successful in understanding and sometimes even predicting materials properties. Several groups around the world are now expanding these methodologies to predict crystal structures of unknown compounds by looking at the energy minimization landscape of known stable compounds, known metastable compounds and finally using this information to predict stable compounds that have not been synthesized. A few such groups that whose work was discussed were Artem Oganov's group in Stony Brook University, Gerd Ceder's group at MIT, Martin Jansen's group in Stuttgart. *In situ* powder diffraction (including PDF methods) is one of the ideal ways to identify both crystalline and non-crystalline intermediates during a reaction, which is invaluable for solving the phase formation puzzle. As described earlier in Ken Poeppelmeier's talk, use of in-situ diffraction measurements are establish reaction pathways and demonstrating synthesis conditions. While some of these experiments are possible now with existing synchrotron and neutron sources, but lack of sufficiently fast data collection prevents neutron use (usually the preferred tool) for many systems due the timescale of these reactions. This will be a major growth direction for instruments in design and construction around the world.

3. Chemistry and Physics of materials under extreme condition

"What is the makeup of earth's core and the core mantle boundary?" Our understanding of earth's core is very limited and understanding materials behavior under extreme temperatures and pressures provide a window into this grand challenge in geology. There are other questions such as "What is the composition of the light elements in the core of earth?", "What is the density of states (which allows physical property determination) of liquid iron under 2-3 Mbar pressure at high temperature 4000 K" that we believe can be addressed in the next decade using the new generation scattering instruments and sample environments such as laser heated levitators and diamond anvil cells.

The other extreme condition that is technologically relevant is the effect of high radiation fields. Understanding processes involved such as waste separation and sequestration, reactivity of materials and degradation mechanism in reactors can help us develop materials for next generation nuclear reactors as well as the tailoring materials properties through introduction of defects.

Finally extreme conditions also open up a new phase space to explore new materials synthesis that is not accessible under ambient temperatures and pressures.

4. The role of disorder determining properties of materials

Disorder and defects are often what gives materials their interesting physical and chemical properties such as fast ion conductors, semiconductors etc. Defects in crystalline solids are known to control atomic transport process and reactivity as well as have profound effects on their thermodynamic, spectroscopic and mechanical properties. Basic defect structures of simple systems such as ionic crystals like NaCl have been well studied, but challenges remain in more complex systems such as non-stoichiometric oxides, irradiated and implanted metals and semiconductors. The advent of PDF analysis has made great strides in tackling more formidable problems posed by atomic and electronic structure and transport properties of amorphous materials such as glasses and liquids. More recently these concepts developed for amorphous materials have also been used extremely successfully in understanding local structures and defects in crystalline solids. X-ray and Neutron diffraction is an absolutely integral part of these studies and the loss of user-mode access to the NPDF instrument at Lujan is already causing disruption in science among the user community. A cutting-edge technology the offers even greater advance is the combination of spectroscopy and diffraction through recent progress in dynamic PDF, where slices in $S(Q,\omega)$ are Fourier transformed for structural correlations. In the future, with the development of needed modeling techniques and improvements to instruments, these measurements could become routine in less than a decade. The combination of both static and dynamic PDFs will provide information about the role of disorder in determining materials properties for which there are no current experimental probes.

5. Fluid flow and reactivity in porous materials

Porous materials such as zeolites have an enormous impact in our daily lives. They are industrially relevant materials that have usage in agriculture, gas separations, waste-water treatment, environmental remediation, as catalysts in petrochemical industry and even in consumer product formulations. The new families of porous materials called metal organic frameworks (MOFs) that have been studied in the past decade are also expected to have usage in all of these areas as well as ion conduction and more. The basic understanding of guest migration and reactivity in these materials is crucial and since many of these require study of light atoms in the presence of high-Z metal ions, neutrons are very much key. Topics such as hydrocarbon recovery, CO_2 sequestration, and capture of environmental contaminants, to name a few, depend on having neutron facilities, along with appropriate sample environment control systems, to complete these studies.

6. How component and integrated materials in devices function under realistic environment

The materials discovery and characterization methods employed by structural scientists are now being used to understand the function of complex integrated devices operational conditions. An example of this, electrochemical cells require multiple electrode, electrolytes and interconnect components with numerous reaction interface surfaces. While it is important to understand how the individual components work, it not possible to understand how a battery works without understanding the interactions that occur when all these components are brought together. Neutrons, due to their high penetration capability, are an ideal tool to probe real devices under realistic conditions. However, what is currently missing is the availability of instruments that can be used to probe multiple time and length scales or allow combining multiple techniques such as imaging, diffraction and spectroscopy. As we move forward, we need to plan instruments that provide data in regimes currently inaccessible to meet these challenges.

7. Complex multifunctional materials

As scientists become more adept with materials by design, structures become more complex by necessity, as more functional components are drafted to tune a material to a particular purpose. Ultimately, the number of resolvable reflections that can be observed dictates the level of structural detail that can be learned about a material. In more complex materials, this is limited by instrumental resolution. The highest resolution powder diffractometers in the US (POWGEN and BT-1 at NIST) are not close to competitive with the ISIS HRPD instrument, despite subsequent decades of advances in optics, electronics and detector technology. Not every study requires ultimate resolution powder diffraction data, but when it is needed no other measurement can substitute and without this U.S. scientists will remain unable to compete in this area of research.

Areas of technical development

1. Detectors

There are currently four different detector technologies in use in the SNS instrument suite. With the exception of NOMAD and Corelli, all diffraction instruments use either the Li-glass scintillator-based Anger Camera or the LiF/ZnS scintillator-based wavelength-shifting fiber optic detector. Technological advances could obsolete each of these through improved spatial resolution, efficiency and count rates. Continued detector R&D, both for incremental improvements and for entirely new detector designs is an essential effort for the SNS to keep the facility competitive. Further, Neutron Sciences is lacking a testing environment that allows detectors to be validated outside of their target instrument. Just as the APS has invested in a new detector/optics metrology beamline, there needs to be a facility where detectors can be tested with instantaneous count rates and neutron spectra comparable to what they will see in service.

2. Multi probe instrumentation

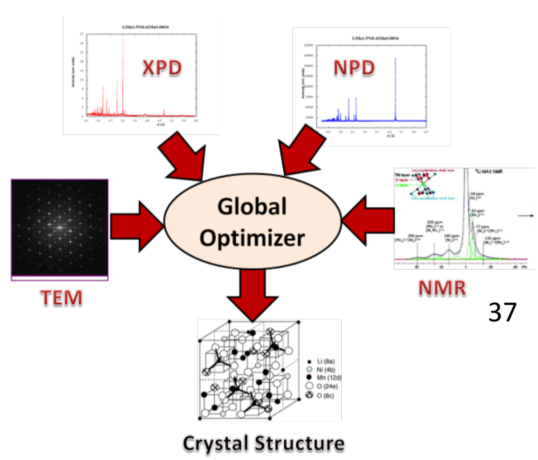
It has been mentioned earlier that several of the science goals require combining either multiple neutron techniques or neutron techniques with other probes (e.g. X-ray, NMR, DSC etc.). Workshops and continued R&D will be needed to advance these ideas to the point where they can be formulated into concepts for second target station instruments.

3. Integrated In-situ/in operando sample environment

Studying materials *in operando* has become the norm in most application oriented science endeavors. Neutrons have always had an advantage as a probe due to its high penetration. However, this advantage has started to erode due to lack of facility investment in deploying new technology. Where sample environment equipment has been developed, the design teams must consider the integration of these devices into the operation of each instrument where it will commonly be deployed. The retrofits have largely been adequate and have resulted in compromised or difficult to setup data collection conditions. Sample environment control will not be optional aspect of next-generation instruments, but will be a necessity for study of systems such as batteries. Sample environments design must be initiated as part of the instrument conceptual design and must be delivered together, not as an afterthought or on a contingency basis.

4. Software

The need to for good software and modeling tools simply cannot be overstated. The century of crystallographic studies of physics, chemical, geological and biological materials have shown the strength of modeling techniques to find where the



atoms are in materials we use in our daily life. Scattering data be it from electrons, photons or neutrons has tremendous amount of information that we can extract. Just like multimodal instrumentation, as we go forward one of our grand challenges will be acquisition and analysis of multi-modal data spanning many experimental techniques (e.g, TEM, XRD, NPD, spectroscopy, tomography) as well as theory, modeling and simulations. There are various challenges such as developing a frame work that allows access to data from multiple facilities seamlessly, global optimization codes, user friendly and accessible modeling tools etc.

For the past 4+ decades, diffraction analysis has involved use of computers to fit models to data. Likewise, computers have become ubiquitous for automating data collection. As research problems have become more complex, so have the models and likewise the quality of the computations. Fortunately, computers have become vastly more powerful and faster, so few computations are outside the realm of desktop computing. However, few scientists are educated as expert crystallographers, so increasing levels of expertise must be built into the software. At present, all software for structural analysis of TOF diffraction data (Rietveld and PDF) has been by experts for use by experts. For structural analysis to be open to the wide range of scientists with appropriate problems (from geosciences to catalysis to spintronics to drug-discovery) there needs to be an investment to develop software to suit users rather than educate users to master the complexities of the software. Where education is needed, web resources, videos, regional and topical workshops should bring experts to the potential users, rather than wait for them to come to a facility user meeting or crystallographic meeting. To date, fitting of TOF data has been a demanding task, usually taken on only after one is well versed with lab and synchrotron data. However, there is no fundamental reason why TOF data should be any more difficult to model than CW, if software is properly designed. Analysis software is a requirement for modern structural science and should be an investment that is planned as part of the initial instrument concept.

Additionally, as demonstrated by the success of 11-BM at the APS, an instrument that introduces no new technology and uses a bending magnet source well-behind the state of the art can still outcompete far more advanced facilities, provided that the instrument is exceedingly easy to access. That, in the case of 11-BM was achieved through automation and integration. Design of a workflow that maximizes availability and reduces staffing needs through deployment of decades-old innovations such as barcode scanners and web forms frees beamline staff from clerical chores and allows them to maximize their effort into producing real scientific value. Again, automation and workflow design are very difficult to retrofit, but instead perform best when designed as part of the construction instrument project.

<u>What is needed to achieve our goal?</u>

2. Fast tracked design and construction of the instrument RAPID that was proposed in the powder workshop held at ORNL in June 2013; this is now an urgent need due to the loss of NPDF.
3. A very high resolution powder instrument ($\Delta d/d \sim 10^{-4}$) at Second Target Station on a moderator providing primarily ambient-moderated neutrons.
4. Multi modal instrument
    a. Instrument capable of measuring multiple length scales (small angle + powder diffraction and high resolution elastic + inelastic scattering on the same instrument)
    b. Adding other simultaneous measurements capabilities (x-ray, calorimetric, gravimetric, NMR,…) for systems that are not easy reproduce.
5. Integrated and a wide variety of sample environments to do *in-situ/in operando* measurements that include but not limited to, extreme ranges of temperature and pressure, electrochemical cells and gas handling systems. It is critical that sample environments be integrated in all stages of the design of these instruments and not an afterthought.

To conclude the workshop report we collect together and summarize the principal findings and recommendations from the discussions and breakout sessions.

Principal findings of the Workshop

Chemical Spectroscopy

Advances in sources, better optics and optimized instrument design will result in a complete transformation of neutron vibrational spectroscopy giving access to novel science. Key findings include:

Ab-initio modeling of INS data: INS data allows the most stringent test of modeling capabilities available today. In conjunction with High Performance Computing it provides an outstanding tool for understanding structure and function of materials.

Neutrons provide crucial insight into chemical reactions and of catalysts in action: the ability to look at 3D systems in real reaction conditions and understand the kinetics and reactions is of outstanding importance. In addition small concentrations of hydrogenous compounds can be detected. High data rates would open up many important processes and give unprecedented insight into bond breaking and formation, functional group transformations and intermediates.

Broadening impact to new scientific communities: vibrational spectroscopy is a key technique for materials scientists, physicists, geologists, pharmacists, environmental scientists, engineers, etc. High throughput and modeling techniques can significantly open up the impact of neutrons which can deliver new capabilities to these fields.

Spectroscopy in complex molecular systems: spectroscopy gives fingerprints for atoms and molecules, their environments, as well as transport phenomena which can be combined with selective deuteration to gain understanding of complex interactions. Areas of future impact are identified as

- Advanced functional materials
- Porous materials and intercalation compounds
- Nanoparticles
- Molecular magnets.

Glasses and liquids: the underlying behavior of glasses and liquids is of intense importance but remain mysterious. With advanced modeling and data handling inelastic neutron scattering is poised to provide key insight into these.

New instrumentation is demanded: high intensity sources and focused beams are needed to study small samples, thin films, materials under extreme conditions and dilute concentrations. These would open up kinetics studies and 3D mapping in new ways accessing key science areas. In addition multimodal instrumentation is necessary to follow complex systems in realistic conditions which will also require advanced data handling and modeling.

***In situ* and *in operando* studies:** capabilities for sample growth in situ, a variety of probes and physical conditions, and in operando measurements are imperative to future science. Pumping conditions are important for the understanding of kinetics and will be increasingly needed with new capabilities for fast measurements.

Materials Science and Engineering

The demands for neutron capabilities in Materials Science and Engineering is very high and being driven by emerging challenges in infrastructure stewardship, advanced propulsion systems, advanced materials processing, nuclear fuels and radiation tolerant materials, energy storage and energy conversion integrated systems, materials by design/ICME, and materials under extreme environments.

3D Neutron analysis / microscopy: need is for characterization of interior microstructure at high resolution (e.g., 1-15 µm) including composition, particle/grain size, shape, and orientation, and also high-resolution strain and deformation mapping.

Online virtual instrument: Having useful interactive tools available to users online will enable better experimental design, and an opportunity to fully plan/test all steps in the data acquisition process before the user comes to the beamline.

Dynamic Studies: In-situ studies of great value include the formation of magnetic domains in transformer steels and how they lead to to the microstructure development, solidification from the melt in castings and welds, single crystal growth, evolution of microstructure under load and/or temperature, etc. SANS in particular is expected to be invaluable for such studies.

Characterization of internal temperature distributions in complex assemblies: Real-time, in-situ studies of internal temperature distributions in operando would provide unique data of high value to develop robust, reliable, computational models of heat flow in working systems.

Multiscale characterization, and multimodality: It will be important to provide capabilities to study alloys, composites, etc., using <u>simultaneous</u> multiple techniques, including diffraction, N-CT and X-CT imaging, SANS, reflectometry, thermal analyses (DTA/DSC/TGA), etc., across a considerable range of dimensions (nano-, meso-, micro-, and macro-scales) enable in-situ studies of chemical synthesis of materials processing.

Characterization of radiation damage across multiple scales: As part of the effort to develop better materials for reactor fuels and structural components, it is essential to have neutron characterization tools and beamlines specifically designed to handle hot (radioactive) samples.

High throughput texture analysis: There is a critical need for a next-generation instrument for studies of texture, and texture evolution under pressure/temperature/etc. Both bulk and localized mapping capabilities are needed, and some aspects may be better suited to one instrument design over another – imaging versus diffraction, for instance.

In-situ corrosion studies: Corrosion is primarily a surface phenomenon, and so may appear well suited to reflectometry, but one also needs to consider identification of hidden corrosion in bulk assemblies, or in complex shapes. Both bulk characterization and spatially localized mapping may be useful.

Coupled sample environments: For parametric studies it will be essential to provide combinations of sample environment, including multiaxial stress, temperature, magnetic field, electric field, controlled atmosphere and humidity, etc. In the case of temperature it will be essential to not only control temperatures over a wide range from cryogenic to high temperature, but also to enable rapid rates of heating and cooling.

Structural Chemistry

The field of structural chemistry makes seminal contributions to nearly every area of science. The revolutionary impact of materials by design and ability to explore systems under manifold environments and processes makes this field rich in compelling science problems for the future. The complementary properties of neutrons and xrays make them invaluable to these investigations.

Glass Transition: exploitation of non-equilibrium, metastable amorphous and disordered materials can provide new materials with novel and more tunable properties. This includes studies of transient states and needs new instrumentation to match measurement challenges.

Chemical reaction mechanism: "How do atoms come together to make functional materials; in reaction systems involving solid-solid, solid-liquid and solid-gas interactions?" Fast neutron diffraction instrumentation will allow the synthesis process to be studied, a key step in computationally directed materials discovery.

Chemistry and Physics of materials under extreme condition: Major materials challenges in extreme conditions are of outstanding importance from "How does the earth work at extreme temperatures and pressures?" to understanding the effect of high radiation fields for reactors, sequestration, and processing of waste. Finally extreme conditions also open up a new phase space to explore new materials synthesis that is not accessible under ambient temperatures and pressures.

The role of disorder determining properties of materials: Disorder and defects are often what gives materials their interesting physical and chemical properties such as fast ion conductors, semiconductors etc. Pair distribution function measurements, both static and dynamic, will provide information about the role of disorder in determining materials properties for which there are no current experimental probes.

Fluid flow and reactivity in porous materials: Porous materials such as zeolites have an enormous impact in our daily lives. Hydrocarbon recovery, CO_2 sequestration, and capture of environmental contaminants, to name a few, depend on advanced neutron facilities, along with appropriate sample environment control systems, to complete these studies.

How component and integrated materials in devices function under realistic environment: Neutrons, due to their high penetration capability, are an ideal tool to probe real devices under realistic conditions. To meet these challenges instruments that can be used to probe multiple time and length scales or allow combining multiple techniques such as imaging, diffraction and spectroscopy are needed.

Complex multifunctional materials

As scientists become more adept with materials by design, structures become more complex by necessity, as more functional components are drafted to tune a material to a particular purpose. To remain competitive it is essential that U.S. scientists have access to ultimate high resolution powder diffraction.

Recommendations

Chemical Spectroscopy

High Performance Computing should be vigorously pursued in conjunction with Neutron Chemical Spectroscopy.

Create software tools that open access to new communities and disseminate understanding of the technique.

Develop instrumentation capable of true in situ studies of chemical reactions, materials in action, and catalytic process

Multimodal instrumentation that combines diffraction, tomography, and inelastic methods along with other techniques for complex systems.

3D spectroscopic, diffraction mapping, and *in operando* capabilities are strongly needed.

Libraries and databases are needed to provide reference spectra and models that can be mined and utilized in future science.

Materials Science and Engineering

Live data analysis that feeds directly back to data acquisition: adoption of “expert” systems to optimize experimental setup and data analysis

Develop entirely new modes of user access: Requires routine “rapid access” review and processing and a new paradigm to measure impact.

Ability to easily handle unique samples (both in and out): large/heavy samples, “hot” (radioactive) samples, proprietary samples (rare but occasionally needed)

An institutional approach to building collaborations between industry and laboratory staff is needed and would provide great benefits. Use of the Joint Institute for Neutron Sciences (JINS) could step up to fill some aspects of this need.

Need for more outreach - frequent workshops, seminars, etc., to grow the community. There are many projects that would benefit from using neutrons that we are not reaching at present.

A multi-moderator target design (STS) will facilitate development of multimodal capabilities

Development of high-resolution neutron microscopy, imaging, and tomography beamlines, including epithermal neutrons for resonance imaging/tomography is a priority.

Demand for engineering materials on VULCAN will significantly increase with the Lujan Center closure. In order to accommodate this work, it is recommended that the VULCAN instrument be fully commissioned, adding five detector banks that were in the original instrument plan but not yet implemented. This will reduce time needed per user project from increased detector coverage, plus enable science that cannot be done with current detectors (such as local structure evolution under stress in bulk metallic glass, complex functional oxide mechanical response, and texture, strain pole figures under complex loading and processing, etc.

Structural Chemistry

Fast tracked design and construction of the instrument RAPID that was proposed in the powder workshop held at ORNL in June 2013; this is now an urgent need due to the loss of NPDF.

A very high resolution powder instrument ($\Delta d/d \sim 10^{-4}$) at Second Target Station on a moderator providing primarily ambient-moderated neutrons.

Multi modal instrumentation

a. Instrument capable of measuring multiple length scales (small angle + powder diffraction and high resolution elastic + inelastic scattering on the same instrument)
b. Adding other simultaneous measurements capabilities (x-ray, calorimetric, gravimetric, NMR,…) for systems that are not easy reproduce.

Integrated and a wide variety of sample environments to do *in-situ/in operando* measurements that include but not limited to, extreme ranges of temperature and pressure, electrochemical cells and gas handling systems. It is critical that sample environments be integrated in all stages of the design of these instruments and not an afterthought.

Appendix I.

Frontiers in Materials Discovery, Characterization, and Application

Doubletree Hilton / Chicago-Schaumburg

August 2–3, 2014

AGENDA

(30 min talk + 10 min discussion)

Day 1—*Saturday, August 2, 2014*

Time	Event
8:30 – 9:00 a.m.	Badging and uploading of presentations
9:00–9:30 a.m.	**George Crabtree**, Argonne National Laboratory *Welcome and charge to the workshop*
9:30–10:00 a.m.	**Alan Tennant**, Oak Ridge National Laboratory *NScD plans (three source strategy at ORNL)*
10:00–10:40 a.m.	**George Crabtree**, Argonne National Laboratory *In-situ studies of Electrical Energy Storage Materials*
10:40–11:00 a.m.	BREAK
11:00–11:40 a.m.	**Yan Gao**, GE Global Research, NY *Industrial Perspective of using user facilities*
11:40 a.m.–12:10 p.m.	**Thomas Proffen**, Oak Ridge National Laboratory *Modeling*
12:10–1:30 p.m. (working lunch)	**Everyone** *Perspectives and Thoughts*
1:30–2:10 p.m.	**Luke Daemen**, Los Alamos National Laboratory *New frontiers in neutron chemical spectroscopy*
2:10–2:50 p.m.	**Ram Seshadri**, University of California, Santa Barbara *Materials by design: Understanding from synchrotron x-ray studies provides key inputs*
2:50–3:30 p.m.	**I.C. Noyan**, Columbia University, NY *Unique challenges in studies of engineering materials*
3:30–4:00 p.m.	BREAK
4:00–4:40 p.m.	**Nancy Ross** *Materials under extreme conditions*
4:40–5:20 p.m.	**Brian Toby**, Argonne National Laboratory *If you build it, will they come?: Maximizing use of diffraction instrumentation*
5:20–6:00 p.m.	**George Crabtree**, Argonne National Laboratory *Discussions and Summary*
6:00–8:00 p.m. (working dinner)	**Ashfia Huq**, Oak Ridge National Laboratory *Current Capabilities of CEMD*

Day 2—*Sunday, August 3, 2014*

Time	Event
8:00–8:15 a.m.	**Crabtree/Tennant** *Charge to breakout groups*
8:15–10:30 a.m.	Breakout sessions (Grand challenges, needs for SE, data analysis etc.) ***Session I: Chemical Spectroscopy*** *(Cook Room)* Moderator: **Luke Daemen** Recorder: **Thomas Proffen** ***Session II: Material Science and Engineering*** *(Lake Room)* Moderator: **I.C. Noyan** Recorder: **Andrew Payzant** ***Session III: Structural Chemistry*** *(McHenry Room)* Moderator: **Brian Toby** Recorder: **Ashfia Huq**
10:30–11:00 a.m.	BREAK
11:00 a.m.–12:00 p.m.	Reports from breakout sessions—*Presented by Moderators*
12:00 p.m.	Workshop adjourn (writing team meets in afternoon to draft report)

Appendix II.

List of Participants

Name	Affiliation
Albers, Peter	Aqura GmbH, Germany
Cernatesu, Iuliana	Pratt and Whitney
Crawford, Mike	DuPont Central Research and Development, PA
Daemen, Luke	Los Alamos National Laboratory
Gao, Yan	GE Global Research, NY
Hudson, Bruce	Chemistry, Syracuse University
Huq, Ashfia	Oak Ridge National Laboratory
Kolesnikov, Alexander	Oak Ridge National Laboratory
Noyan, I.C.	Materials Science and Engineering, Columbia University, NY
Larese, John	University of Tennessee, Knoxville
Parise, John	Department of Chemistry and Geosciences, Stonybrook University
Payzant, Andrew	Oak Ridge National Laboratory
Poeppelmeier, Kenneth	Chemistry, Northwestern University
Proffen, Thomas	Oak Ridge National Laboratory
Ross, Nancy	Department of Geosciences; Virginia Tech
Sawyer, Toni	Oak Ridge National Laboratory
Seshadri, Ram	Department of Chemistry & Biochemistry, University of California, Santa Barbara
Tennant, Alan	Oak Ridge National Laboratory
Toby, Brian H.	Advanced Photon Source, Argonne National Laboratory
Toney, Mike	SLAC and Stanford University
Tremsin, Anton	Experimental Astrophysics Group, University of California, Berkeley
Vaidyanathan, Raj	Materials Science and Eng Dept; University of Central Florida
Wilkinson, Angus	Department of Chemistry, Georgia Tech University
Zur Loye, Hanno	Department of Chemistry and Biochemistry, University of South Carolina

Appendix III.

First Letter of Invitation to Participants

As a leader in the field, we are inviting you to participate in a special workshop on "Frontiers in Materials Discovery, Characterization, and Application" to be held June 24-26, 2014, in Chicago, Illinois. The workshop will identify next-generation neutron instruments and measurement techniques needed to advance the discovery and application of materials into technology, emphasizing *in situ*, time-resolved, multi-modal, and multi-institutional research.

Workshop sessions will include plenary presentations on forefront areas of chemistry, materials sciences, and manufacturing that require capabilities for characterization beyond the current state of the art. Advances in characterization techniques will be discussed, including the prospect for greatly enhanced capabilities for neutron scattering applied to chemical and manufacturing problems. A report detailing the key findings of this workshop will be presented to DOE, in order to assist in defining the future course of Neutron User Facilities.

This workshop will be limited to approximately 40 participants and is by invitation only. Subject to time constraints, each participant will have an opportunity to contribute a short presentation, and all will participate in topical breakout sessions. There will be no registration fee, and local arrangements (food and lodging) will be covered. Also, a block of rooms at a local hotel will be reserved for the workshop. In order to facilitate the logistics of organizing the workshop, we would appreciate knowing if you are able to join us, by May 23, 2014. All responses should be emailed to Toni Sawyer (sawyertk@ornl.gov, 865-241-5176), who will make the travel arrangements.

We look forward to a vigorous and thought-provoking workshop.

Best Wishes,

George Crabtree
Workshop Convener

Alan Tennant
Workshop Facilitator

<u>Second Letter of Invitation (with revised dates) to Participants</u>

Thank you for your interest in the special workshop on *Frontiers in Materials Discovery, Characterization, and Application* in Chicago, Illinois. There was a great interest in the subject call. However, due to the short notice given, several major contributors are unable to attend. Because of this, the workshop has been rescheduled for August 2-3, 2014. At your earliest convenience, we would appreciate a response to this invitation. Your response should be sent to Toni Sawyer (sawyertk@ornl.gov, 865-241-5176) by Friday, June 13, 2014.

Thank you for your interest, and we look forward to your participation.

Sincerely,

George Crabtree
Workshop Convener

Alan Tennant
Workshop Facilitator

Appendix IV.

Acknowledgments

All workshop logistics were managed by Toni Sawyer (ORNL).