Abstract Booklet

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The HB-2D Polarized Neutron Development Beamline at the High Flux Isotope Reactor
Neutron and X-Ray Scattering Studies of Hybrid Perovskites for Photovoltaic Applications

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Hybrid perovskites (ABX\textsubscript{3}) have attracted a great deal of attention recently as light absorbers for photovoltaics. In these materials the A site is occupied by organic cations, for example methyl ammonium (MA) or formamidinium (FA) cations, the B site is occupied by metals, for example Pb or Sn, and the X anions are halogens (I, Br, or Cl). Typical of perovskites, these materials exhibit a series of structural phase transitions involving rotations or tilts of the BX\textsubscript{6} octahedra, but with the added complexity that the inorganic framework is coupled to order-disorder transitions of the organic cations. We have used neutron diffraction, together with quasielastic and inelastic neutron scattering, to characterize the structures and dynamics of several of these compounds as a function of temperature. In addition, high resolution synchrotron x-ray diffraction measurements have been performed to investigate the structural phase transitions. These studies yield a detailed picture of the structures, dynamics, and structural phase transitions of these compounds, and provide a firm basis for understanding their excellent photovoltaic properties.
In phonon-mediated superconductors, the lattice features essential to the electron-phonon coupling are at the heart of the mechanism and need to be resolved. This is a key issue in the new class of BiS$_2$ based superconductors. The layered crystal structure plays an important role in this endeavor because of its potential to exhibiting a strong structure-property relationship due to its intrinsic disorder. The crystal symmetry has long been presumed to be tetragonal, $P4/nmm$. From first-principles calculations, it was suggested that the symmetry is most likely lower to $P2_{1}mn$. Meanwhile, band structure and spin polarization calculations proposed two yet different symmetries, the non-centrosymmetric $C2$ and the centrosymmetric $P2_{1}/m$. Here, we present evidence from single crystal synchrotron X-ray and pulsed neutron diffraction that challenges all suggested symmetries. The observed Bragg pattern from the BiS$_2$ planes arises from in-plane displacements of sulfur that morph into coordinated ferro-distortive patterns in the ab-plane. A previously proposed unstable antiferro-distortive phonon mode at $(\pi, \pi, 0)$ is therefore not consistent with the data and neither are the $A_1$, $E$ and $B_2$ Raman active modes. The pattern remains with electron doping but the displacements diminish in magnitude.
Science Productivity Process and Major Instrument Upgrades
K. W. Herwig, Instrument and Source Division, ORNL

The Science Productivity Process seeks to identify and act on opportunities that will deliver high-impact science and remove barriers that keep an instrument from being highly productive. It began as a pilot program with 4 initial instruments May, 2014. The program launched with full instrument participation across both the SNS and HFIR instrument suites in fiscal year 2015. The process and lessons learned will be described. Outcomes resulting in major investments in instrument upgrades planned for the current fiscal year will be presented.
Dopant Induced Solubility Control in Semiconducting Polymers

We demonstrate that the solubility of semiconducting polymers can be reversibly “switched off” and “switched back on” using addition and removal of high electron affinity molecular dopants. Using this technique, we are able to vertically stack and laterally pattern mutually soluble polymer layers, which are vital processing steps needed to expand the use of organic semiconductors. The key breakthrough is the development chemical and light induced techniques to remove the dopants from the polymer film. Optimization of these techniques has yielded diffraction limited film patterning with regular features of 200-300 nm. Several neutron scattering methods are critical to the determine the doping and dedoping mechanisms. Neutron vibrational spectroscopy (VISION) is used to determine the molecular structure of the doped polymer. Quasielastic Neutron Scattering (BASIS) is used to determine the temperature dependent molecular diffusion mechanism of the dopant in the polymer. Small angle neutron scattering is used to determine the temperature dependent aggregation of the polymer into nanofibers and also used to determine the size and density of the nanofibers. In combination we demonstrate a powerful new polymer patterning method and a systematic study of the mechanistic details at each stage of the process.
The Effects of Chemistry and Particle Morphology on the Transformation Characteristics of Metastable Austenite in Ductile Iron

Alan Druschitz  
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Abstract

Neutron diffraction studies at SNS using VULCAN have shown that the chemistry and/or particle morphology of metastable austenite in ductile iron influenced the strain at which the austenite transformed to martensite, and therefore, the overall mechanical properties. If the austenite transformed at low strains, the elongation at fracture of tensile specimens was significantly lower compared to alloys in which the austenite transformed at higher strains. Austenite stabilized with primarily carbon and manganese had a blocky particle morphology and transformed at low strains, austenite stabilized with primarily carbon, nickel and manganese had a mixture of blocky and acicular particle morphology and transformed at higher strains, and austenite stabilized with primarily carbon, nickel and copper (with a small amount of manganese) had an acicular particle morphology and transformed at the highest strains, and consequently had the highest yield strength, ultimate tensile strength and elongation at fracture.
MOLECULAR SHAPE TUNING WITH PRESSURE IN A SYSTEM COUPLED TO A CONTINUOUS PHASE TRANSITION: A NEUTRON DIFFRACTION STUDY

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The transition-metal complex trans-[Ni(cyan-κN)₂(NH₃)₄] (cyan = cyanurate-N) forms molecular crystals that undergo a continuous, or second-order, phase transition to permit continuous variation of the molecular shape. In a first report on this system [1] the phase transformation and accompanying molecular distortion were characterized as a function of temperature only. It was found that from the zero point of the transformation, at just above room temperature, to the lowest temperature studied, 13 K, the square of any of three distortion parameters varied linearly as a function of temperature, as expected for a continuous phase transition.[2] In the present study, pressure was added as a parameter and structure analyses were performed at T = 223 K, p = 2 kbar and at T = 20 K, p = 2 kbar. At T = 223 K the effect of increasing the pressure is greater than that at T = 20 K. It was further observed that the application of pressure at T = 20 K yielded a larger distortion than that predicted for T = 0 by the temperature-only study at ambient pressure. The implications of these results are discussed.

REFERENCES

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Work at the Intense Pulsed Neutron Source, Argonne National Laboratory, was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under Contract No. W-31-109-ENG-38.
Deterministically Nanostructured Surfaces for SANS Investigation of Trapped Nanobubbles

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Boiling is an effective mode of heat transfer in a wide variety of natural and industrial processes. In order to investigate nanoscale processes involved in initial stages of boiling, we have designed, implemented and investigated a model system in which nanobubbles can be controllably trapped near the surface. More specifically, deterministically nanopatterned surfaces were created using a combination of electron beam lithography and reactive ion etching and evaluated using small-angle neutron scattering (SANS). The nanostructures in contact with an aqueous phase exhibit 2D neutron scattering patterns that confirm the presence of trapped nanoscale bubbles. Comparison of SANS intensities obtained from samples in air and in contact with an aqueous phase (pure deuterium oxide, D₂O, or a contrast matched mixture of D₂O + H₂O) reveals formation of stable gaseous nanobubbles trapped inside the engineered nanocavities. The relative volume of nanobubbles depends strongly on the hydrophobicity of the cavity walls. In the case of hydrophobic surfaces, nanobubbles occupy up to 87% of the total cavity volume. The results demonstrate the high degree of sensitivity of SANS measurements for detecting and characterizing nano- and mesoscale bubbles with the volume fraction as low as \( \sim 10^{-6} \).
Visualizing Hydraulic Fracturing Processes and Assessing Effective Fracking Fluids using Neutron Imaging

Larry Anovitz, Hassina Bilheux, Phillip Bingham, Michael Cheshire, Victoria DiStefano, Richard Hale, Lindsay Kolbus, Joanna McFarlane, Ed Perfect

The combination of horizontal drilling and hydraulic fracturing has greatly increased the productivity of natural gas wells. However, these new techniques have raised concerns about the adverse environmental and social impacts of these practices, especially related to impacts on water resources. To address these issues, models are used to simulate fractures and fluid movement under downhole conditions. However, these models suffer from the requirement to make a multitude of generalized assumptions that are highly dependent on microscale fluid-rock interactions. The use of neutron imaging is a rapidly developing capability that can be used to verify and modify these critical modeling parameters.

Neutron imaging at HFIR CG-1D and NIST has been used to:
   (1) Establish a successful calibration using computed tomography for quantifying water/fracking fluid in samples from Eagle Ford, Marcellus, and Mancos shales and,
   (2) Investigate the uptake of water and brines within fractured samples using radiography with 10 ms temporal and 50 µm spatial resolution.

Uptake data show an initial dependence of water front height with the square root of time, as expected under conditions of capillary flow. The rates change as the fractures become complex deep within the shale samples. Differences in uptake have also been observed for DI water and saturated NaCl solutions. These results demonstrate an experimental basis for utilizing neutron imaging to quantify the transport and displacement of fluids through porous media that will contribute to understanding formation wettability and fluid replacement, relevant to reservoir performance.
Ferroelectrics are used as electromechanical energy transducers in many technologies owing to their large piezoelectric properties, including sonar, medical diagnostic imaging, 3-D printing and energy harvesting. Due to environmental concerns regarding lead-based ferroelectrics, there are currently on-going efforts to develop lead-free alternatives. For many prototypical lead-free ferroelectrics such as BaTiO$_3$ and KNbO$_3$, which feature as end members in several proposed alternative alloy systems, the B atoms are locally displaced along directions that are different from the average electrical polarization vector. It is important to understand how these local atomic displacements order under the effects of changes in temperature or applied electric fields. Using neutron time-of-flight Laue diffraction and quasi-elastic-neutron scattering (QENS), we show the evolution of dynamic microscopic polar clusters (~10 nm) in a BaTiO$_3$ crystal near its paraelectric-ferroelectric phase transition point $T_C$, which have correlated $<$111$>$-type Ti displacements within {110}-type crystallographic planes. These polar clusters develop strong interfacial microstrains as $T_C$ is approached from above, which could be explained as a result of increase in microdomains population. Additionally, using in situ high-energy X-ray diffuse scattering measurements, we demonstrate for KNbO$_3$ single-crystals that applied electric fields along a nonpolar crystallographic direction also increases the correlation length for local Nb displacements from $\sim$1.6 nm to $\sim$7 nm. Critically for non-lead ABO$_3$ ferroelectrics, such nanoscale atomic orderings can induce greater lattice instabilities, as shown from inelastic neutron scattering measurements of acoustic phonons, and consequently enhance susceptibility for mechanical deformation. Taken together, the current results therefore indicate that local atomic displacement orderings can be an important tuning parameter for engineering enhanced electromechanical functionalities in lead-free ferroelectric ceramics.
Neutron Imaging of Intra-nozzle Fluid Dynamics of Fuel Injectors

Todd J. Toops¹, Eric Nafziger¹, Derek A. Splitter¹, Charles E.A. Finney¹, Hassina Bilheux², Louis Santodonato², Jean Bilheux², Alex E. Pawlowoski³, Anton Tremsin⁴ and Ronald Grover⁵

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Project Description:
This project utilizes high resolution neutron radiography to obtain intra-nozzle fluid dynamics of an automotive fuel injector, which will guide and validate data-intensive models of both internal flow and spray patterns. Fuel injector design in modern diesel-based compression ignition (CI) engines and recently developed gasoline direct injection (GDI) engines can have a dramatic impact on both combustion efficiency and emissions. The external spray dynamics are being extensively studied, but these approaches do not easily allow flow visualization inside the dense metallic injectors. Model validation needs a better understanding of fluid dynamics within the injector and in the dense region just outside of the orifice. The unique capability of neutrons to penetrate the metal injector and visualize hydrogen-rich fuel flow enables the connection of the internal and external flows to describe the physics of the spray. In particular, recent improvements of both the spatial resolution and neutron flux at the HFIR CG-1D imaging beam line enable the dynamic reconstruction of the fuel injection event; flux improvement through changes in optics. Our project developed and demonstrated the capability which allows the visualization of a 1 ms injection event with 20 µs temporal resolution. This will accelerate model development leading to improved injector design and vehicle efficiency.

Results and Accomplishments:
The project has achieved all of the major tasks that were proposed, and the team has successfully captured a series of radiographs with 20µs resolution that clearly show internal and external fuel injection using both commercial-intent and commercial injectors. This effort required the synchronization of the fuel injector system with the microchannel plate (MCP) detector. The project progressed through logical steps with the new detector and the newly built injection system:

- full 3-D reconstructions of the static injectors
- synchronization of the commercial injectors with the detector while triggering the injector under dry conditions
- building a fuel delivery system, spray chamber, and fuel recovery system
- designed to operate with commercial and prototype injectors up to 150 bar rail pressure
- spray chamber can be operated at absolute pressures as low as 0.2 bar, i.e. sub-ambient, and currently has a maximum pressure of ~4 bar.
- spray chamber that can be heated to over 100°C while flowing up to 60 L/min sweep gas.
- operation for at least 50 hours for each condition to achieve the necessary statistics for proper visualization

Two generations of systems were operated for over 350 hours of combined beam time during three campaigns at HFIR. We were able to successfully capture two video sequences of sprays that clearly show the fuel in the injector, flow around the pintle when injection starts, fuel spray leaving the injector during the 1.2 ms trigger, and followed by a slow emptying of the injector sac that occurs over 0.3-0.6 ms. This last feature is a key phenomenon that is known to occur in injectors, but the internal visualization has not been shown to occur with commercial gasoline injectors until now. This technique will thus allow the quantitative analysis of this phenomenon and how it is affected by injector design and injection conditions.
Self-assembly and molecular ordering of solution-state conjugated polymers

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Abstract
Controlling the assembly structure and functional expression in solution of conjugated polymers holds great potential for enabling enhanced organic optoelectronic and sensory materials. We have designed a conjugated polymer consisting of a hydrophobic thiophene backbone and hydrophilic, thermo-responsive ethylene oxide side groups, which shows a step-wise, multi-dimensional assembly in water under a simple thermal control. In addition, by incorporating the polymer into phase-segregated domains of an amphiphilic surfactant in solution, we demonstrate that both chain conformation and degree of molecular ordering of the conjugated polymer can be tuned in hexagonal, micellar and lamellar phases of the surfactant solution. The controlled molecular ordering in conjugated polymer assembly is demonstrated as a key factor determining the electronic interaction and optical function. Small angle neutron and x-ray scattering, optical absorption and emission and transmission electron microscopy are applied to characterize the solution structure and molecular ordering of conjugated polymers.

Reference
J. Zhu et al. Nanoscale 2015. DOI: 10.1039/C5NR02037A

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J.Z. and Y.H. acknowledge support of ORNL Laboratory Directed Research and Development Program (LDRD) project. This research was conducted at the Center for Nanophase Materials Sciences and the Spallation Neutron Source, which are sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract no. DE-AC02-06CH11357.
Using Neutron Reflectometry to Determine the Effects of a P3HT Brush Functionalized Substrate in Organic Photovoltaics

Elizabeth E. Bickel, Jameson L. Tyler, Sarah E. Russell, Zach Seibers, Mark Dadmun, S. Michael Kilbey, John Ankner, Candice Halbert, Holly A. Stretz

Controlling and characterizing the morphology of the active layer in organic photovoltaics (OPVs) is essential for improving process efficiency in OPV roll to roll manufacturing. We report the effects of the modification of a Si substrate with a poly(3-hexylthiophene (P3HT brush) followed by P3HT film deposition, where the brush represents a neutral surface in terms of interactions with [6,6]-hexyl-C_{61}-butyric acid methyl ester (PCBM) on PCBM distribution. Gas Expanded Polymer (GXP) annealing (a high pressure CO\(_2\) annealing method) was employed versus thermal annealing. Changes in P3HT crystallinity and π-π stacking after thin film annealing were observed via X-ray diffraction, UV-Vis spectroscopy and contact angle measurements. Neutron reflectivity, which is sensitive to the PCBM depth profile, suggests that an annealing pressure oscillation range of 875-900 psi caused the PCBM to distribute more uniformly throughout the film compared to an as-cast non-functionalized sample. In the presence of the P3HT brush, P3HT film capping and wetting layers formed at the air and substrate interfaces respectively. The efficacy of such surface modification for altering PCBM distribution throughout a bulk heterojunction is compared to other reports of surface-modified P3HT/PCBM films post-annealing, spanning hydrophobic, neutral, and hydrophilic surfaces. Using PCBM attractions to a surface modification to direct PCBM stratification represents a useful direction for manufacturing control of continuous nanoparticle polymer thin film morphological control.
We introduce the recently commissioned VISION spectrometer at the Spallation Neutron Source. The instrument configurations, currently available sample environment, and capabilities are described, together with several recent examples of data collected on VISION.
Characterization on Cellulose Nanocrystals (with different surface chemistry) Particle Interaction and Microstructure Growth

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Abstract

Cellulose Nanocrystals (CNCs) are obtained from natural cellulose fibers by acid catalyzed hydrolysis to produce crystalline nano-scale rod-shaped particles. Our work is to elucidate the oriented self-assembled structures that are associated with acetic acid-hydrolyzed CNC dispersions, which are markedly different from other CNC and liquid crystal colloidal phases. In this work, Small Angle Neutron Scattering (SANS) will be used to determine the dimensions (with polydispersity) of individual CNC rods and characterize the microstructure growth. The colloidal stability of CNC aqueous suspension is determined by inter-particle forces such as steric repulsion, electrostatic repulsion (indicated by charge value from structure factor). The evolution of CNCs microstructure formation will be studied by investigating the structure dimension with increasing concentration. Potentially, shape model from form factor such as Parallelpiped model can still be applied to determine the initial aggregates (or polydomain) dimensions and geometry. Cellulose Nanocrystal aqueous dispersions with different surface chemistry in a series of different concentrations has been characterized by SANS to study the aggregates formation and microstructure formation. Cellulose Nanocrystal with sulfate group (CNC-SA) showed a uniform particle size distribution through 0.1%vol to 1.5%vol, which is due to its high surface charge potential, followed by aggregation in an end-to-end configuration. Cellulose Nanocrystal with acetate group showed the dimensions larger than that of single nano-rod at low concentrations of 0.1%vol, which indicates microstructure formation. The aggregate height does not change with increasing concentration, however the width does increase as the concentrations increases from 0.1 %vol to 1.5%vol. The length is above 400 nm and could not be accurately reduced due to the limitations of the model. The dimensions data has a good agreement with the aggregate size measurement in the CNC-AA dried film. The unchanged height and increase in the width dimension is consistent with the thin-sheet-like structure observed by Scanning Electron Microscope imaging on the dried films. Samples of Cellulose Nanocrystal (with different surface chemistry) mixture dispersion with different mixing ratios and concentrations showed multi-stages of aggregation size changing through the increasing of concentration.
Key words: Cellulose nanocrystal, aggregate, colloidal assembly, phase behavior
Pressure-Induced Polymerization of CN⁻ investigated by in-situ Neutron Diffraction and Neutron Pair Distribution Function

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KEYWORDS high pressure, cyanide, neutron diffraction, pair distribution function, polymerization.

ABSTRACT Pressure-Induced Polymerization (PIP) of charged monomers like C≡C²⁻ and C≡N⁻ under several tens of GPa is usually accompanied with significantly enhanced conductivity. This means conductive polymers with ionic skeletons and functional cations can be synthesized. The critical pressure for reactions is usually above 30 GPa for alkali metal cyanides, while for transition metal cyanides like Prussian blue and K₃Fe(CN)₆ the critical pressure is often below 10 GPa, like 2-3 GPa, which is important for synthesizing large amount of sample. To figure out the effect of the transition metal on the reaction, the crystal structure and electronic structure of K₃Fe(CN)₆ under external pressure is investigated by in-situ neutron diffraction (SNAP, SNS), in-situ X-ray Absorption Fine Structure (XAFS) and neutron pair distribution functions (PDF, NOMAD, SNS) up to ~15 GPa. The cyanide anions react following a sequence of approaching-bonding-stabilizing. The Fe(III) brings the cyanide anions closer, which makes the bonding progress at a low pressure (2-4 GPa). At ~8 GPa, an electron transfers from the CN to Fe(III), reduces the charge density on cyanide ions and stabilizes the reaction product of cyanide. From this study we can conclude that bringing the monomers closer and reducing their charge density are two effective routes to decrease the reaction pressure, which is important for designing novel PIP conductor and excellent materials.
Using Neutrons to Study Fluid-Rock Interactions


Recovery of hydrocarbons by hydraulic fracturing depends on complex fluid-rock interactions that we are beginning to understand using neutron imaging and scattering techniques. Organic matter is often thought to comprise the majority of porosity in a shale. In this study, correlations between the type of organic matter embedded in a shale and porosity were investigated experimentally. Selected shale cores from the Eagle Ford and Marcellus formations were subjected to pyrolysis GC, Differential Thermal Analysis/Thermogravimetric analysis (DTA/TGA), and organic solvent extraction with the resulting affluent analyzed by GC-MS. The pore size distribution of the microporosity (~1 nm to 2 µm) in the Eagle Ford shales was measured before and after solvent extraction using small angle neutron scattering (SANS). Organics representing mass fractions of between 0.1 to 1 wt.% were removed from the shales and porosity generally increased across the examined microporosity range, particularly at larger pore sizes, approximately 50 nm to 2 µm. This range of pore sizes reflects extraction of accessible organic material, including remaining gas molecules, bitumen molecules, and kerogen derivatives, indicating where the larger amount of organic matter in shale is stored. An increase in porosity at smaller pore sizes, about 1 to 3 nm, was also present and could be indicative of
extraction of organic material stored in the inter-particle spaces of clays. Additionally, a decrease in porosity after extraction was attributed to swelling of pores with solvent uptake that occurred in a shale with high clay content and low maturity. The extracted hydrocarbons were primarily paraffinic, although some breakdown of larger aromatic compounds was observed in toluene extractions. The amount of hydrocarbon extracted and an overall increase in porosity appeared to be primarily correlated with the clay percentage in the shale, with the results being complicated by solvent interactions with the pore matrix. This study complements fluid transport neutron imaging studies, to explain the physics and chemistry of fluid-rock behavior.
Predictive Power of Density Functional Theory in Finite-Temperature Hydrogen Adsorption/Desorption Thermodynamics with Corrective Energies and Potential Surfaces

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For the past few decades, density functional theory (DFT) has been widely employed to study the gas adsorption properties of surface-based/nanoscale structures. However, recent indications are sufficient to raise questions about the trustworthiness of the literature values, especially in terms of the DFT exchange-correlation (XC) functional. Using hydrogen adsorption on metalloporphyrin-incorporated graphenes (MPIG) as an example, we performed a benchmark study on the XC functional dependence of their thermodynamic properties of hydrogen adsorption, explicitly including entropic as well as energetic contributions [1]. We find that thermodynamic properties are strongly XC functional dependent, with high dependence not only for the energetic but also for the entropic contributions. Using chemical potential as a descriptor we identify required calculational accuracy with which DFT can serve as a predictive tool for experimental guidance.

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References

From neutron nanoscience to direct-write nanofabrication at the Center for Nanophase Materials Sciences

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The Center for Nanophase Materials Sciences (CNMS) at Oak Ridge National Laboratory (ORNL) is a national user facility that provides the research community with access to expertise and equipment to address the most challenging issues in nanoscience. Industrial, government and academic researchers from around the world may access capabilities in functional imaging, atom-precise synthesis, and nanofabrication, at no cost through peer-reviewed proposals or at-cost for proprietary or intellectual property protected research. Located adjacent to the Spallation Neutron Source at ORNL, CNMS offers the neutron science community diverse complementary capabilities such as selective deuteration, sample environments for multi-modal measurements, fabrication of templates for neutron reflectivity experiments, or any other materials science capabilities to complement neutron results. Theoretical and supercomputing approaches, which are also available to neutron science users, range from deep-data methods for imaging to computational prediction of functional and physical properties in nanostructures. The CNMS pioneers a range of unique nanoscience techniques including direct-write nanofabrication using electron and ion beams, and spatially resolved quantitative measurements of physical properties (e.g., band excitation scanning probe microscopy, scanning transmission electron microscopy). He-ion microscopy and atom-probe tomography are offered as unique cutting-edge nanoscience tools. As one of the five Department of Energy Nanoscale Science Research Centers (see nsrcportal.sandia.gov), CNMS makes all of these capabilities, and the staff expertise to fully benefit from them, available free of charge to users who intend to publish the results, as described at cnms.ornl.gov.

[The CNMS at Oak Ridge National Laboratory is a DOE Office of Science User Facility.]
The synthesis of Polyacetylene single crystal under high pressure and varying temperature

Under high pressure (up to tens of gigapascal), the double and triple bonds in unsaturated molecules can undergo additional reactions and produce polymers following topochemical pathways. Acetylene is the simplest alkyne, widely applied in chemical industry, and its doped polymer, polyacetylene is an important conductive polymer with the highest conductivity. However, under high pressure, the polymerization product of acetylene may vary from the “normal” polymers obtained at ambient pressure. In this project, we plan to prepare single crystals of pressure-induced polyacetylene from single crystal acetylene under proper temperature and pressure, and determine its crystal structure. We also plan to determine the reaction pathway by comparing the direction of the polymer chains and the orientation of the acetylene crystal, determine the atomic distances between the neighbored molecules from the crystal structure of acetylene at reaction pressure, and understand the reaction mechanism accordingly. For a further step, we plan to apply higher pressure on the pressured-induced polyacetylene crystals to initiate the polymerization of the double bonds and obtain novel carbon materials. We will also determine the structure of the “poly-polyacetylene” and study the reaction process and the possibility to produce carbon materials like graphane.
Neutron diffraction studies of hexafluorobenzene under high pressure

Aromatic compound is a kind of most thoroughly investigated organic compounds. Benzene (C₆H₆), as the simplest aromatic molecule, has attracted great attention as their unique chemical properties and its wide application. Under high pressure (up to 30 GPa), the raman spectra indicates that benzene undergo four pressure-induced phase transition and has a transformation to a polymer after static pressurization up to 30 GPa. Hexahalobenzene, like hexachlorobenzene (C₆Cl₆) and hexabromobenzene (C₆Br₆) crystal were also studied and different pressure-induced phase transitions were presented. Recently, we have studied the raman spectra of hexafluorobenzene (C₆F₆) and some new pressure-induced phase transitions has been observed. We then plan to use neutron diffraction in the study of hexafluorobenzene and predicate the unique properties of neutron interactions in solids. Three aspects of these interactions are of particular importance for the reason that neutrons are often highly penetrating, possess scattering cross sections which do not decrease with increasing scattering angle and neutron scattering cross sections do not vary systematically with atomic number. These aspects lead to a number of possible advantages for the characterization of phase change of C₆F₆.
The reaction mechanism of acetonitrile under high pressure investigated by in-situ neutron diffraction

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Particular interest has been focused on the chemistry of nitriles under extreme condition because the importance of C-N bond for the synthesis of abiotic amino acid and super-hard materials.1-2 The acetonitrile (CH$_3$CN), the simplest organic nitrile was selected as the model compound to explore its reaction process under high pressure. In our study, the CH$_3$CN is compressed to 25 GPa and a black powder with the characteristic D and G bands in its Raman spectra was obtained. The neutron pair distribution function (PDF) result shows this material has a graphene skeleton with the ordering in 2-3 nanometer range. The spectroscopic, crystallographic studies and metadynamic calculation shows a hydrogen atom transfer reaction was involved in the polymerization process. The crystal structure closed to the reaction pressure obtained from the in-situ neutron diffraction shows the acetonitrile keeps the orthorhombic structure ($Cmc_2$). The hydrogen bonding between the methyl and cyano groups (-C≡N...H-CH$_2$-) arranges the molecules into diamond type network, which facilities the hydrogen transfer reaction but hinders the direct addition reaction between the cyano groups. The critical reaction distance (1.98 Å) of the hydrogen abstraction reaction obtained from the Rietveld refinement results will provide a crucial reference for design and tailor the solid state reaction at microscopic level.

References:

In Situ Functionalization of Azlactone-based Polymer Brushes

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Abstract (229 words)

Reactive modification of polymer thin films provides a useful route to confer new properties to the underlying material, with the range, strength and type of interaction across the interface dictated by the display of functional groups decorating the surface. To address the links between design, in situ functionalization and properties, layers of end-tethered polymer chains, or polymer brushes, were created by grafting chains of poly(4,4-dimethyl-2-vinylazlactone) (pVDMA) onto silicon substrates. The pendant azlactone rings of pVDMA readily react with nucleophiles, allowing in situ functionalization to be studied through the use of ellipsometry and neutron reflectivity measurements as a function of parameters that set brush structure. The results indicate that the grafting density of chains and size of the functionalizing agent play major roles in governing the extent of functionalization, and with all but the smallest functionalizing agents, reactive modification is incomplete. In addition to developing an average view of the in situ functionalization, the sensitivity of neutron scattering methods to isotopic substitution (of D for H) provides insight into the location of functional groups installed within the pVDMA brush by reactive modification. These studies provide perspectives on the relationship between extent of reaction in the confined environment, display of functional motifs, and swelling properties of the interfacial layer, as well as insight into general strategies that can be used to tailor frictional, adhesive, or biomimetic properties of polymer thin films.
Interface and Morphology Engineering in Organic Solar Cells

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Abstract:

Advances in materials design and process engineering led to organic solar cells (OSCs) with both higher efficiency and excellent stability. However, in order to further increase the cell power conversion efficiency (PCE), it is very important to realize well-optimized absorbing layer morphology and high-quality interfaces for efficient charge generation and transport, respectively. The neutron facilities at Spallation Neutron Source (SNS) provide us the unique opportunity to study nanoscale structure and characteristics of materials both in liquid and solid states, which helps in rational cell design. In this work, we answered an important question why inverted OSCs yield better performance compared to conventional OSCs using neutron reflectometry and small-angle neutron scattering techniques at SNS. This work provides important insight and guidelines for further enhancement of PCE by materials and interface engineering.

The aim of our research is to characterize the effects of macromolecular crowding on an intrinsically disorder protein (IDP). The majority of biophysical studies use solutions that are dilute relative to \textit{in vivo} conditions. By conducting studies in solutions at concentrations comparable to those of the cellular environments, we may further our understanding of how proteins behave in biologically relevant conditions. While lacking well-defined structures, IDPs are recognized as playing key roles in cellular signaling processes. FlgM is an IDP that acts as a negative regulator of flagellin synthesis. It is readily expressed and robust, making it an excellent system for studying the effects of crowding on IDPs. In June of this year perdeuterated flgM was expressed and purified on-site at ORNL in collaboration with Kevin Weiss. SANS experiments were conducted at the EQ-SANS diffractometer in collaboration with Christopher Stanley. Over a concentration range of 75-450mg/mL, four crowders were used: dextran, ficoll, BSA, and lysozyme. Ensemble optimization modelling (EOM) is used to characterize the conformational ensemble of flgM in dilute and crowded conditions. Initial analysis suggests that as crowder concentration increases, the average flgM radius of gyration first decreases and subsequently increases. This is an indication of attraction between protein and crowder. Circular dichroism experiments have also been performed showing an increase in helical content of flgM as the concentration of dextran or ficoll is increased. Complementary to this, relaxation NMR experiments are used to ascertain the internal dynamics and conformation of flgM in dilute and crowded conditions.
Unraveling the dynamics of aminopolymer/silica composites

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Abstract

The structure and dynamics of a model branched polymer, representing poly(ethylenimine), is investigated through molecular dynamics simulations and neutron scattering experiments. The monomer concentration, solvent quality and polymer confinement were varied in the simulations. Comparison between the calculated structural and dynamical properties of the unconfined polymer and those confined within an adsorbing and non-adsorbing cylindrical pore, representing the silica based structural support of the composite, were also undertaken. The simulations show a direct relationship in the structure of the polymer and the non-monotonic dynamics of the polymers as a function of monomer concentration within the adsorbing cylindrical pore. However, the non-monotonic behavior disappears for the case of branched polymer within a non-adsorbing cylindrical pore. The simulation results are in good agreement with quasi-elastic neutron scattering (QENS) studies of branched poly(ethyleneimine) and mesoporous silica (SBA-15) of commensurate size.
Nanodiamond (ND) inherits most of the superior properties of bulk diamond and delivers them at the nanoscale. Recent studies demonstrate that ND has excellent properties needed for the drug delivery platform, such as high biocompatibility, the ability to carry a broad range of therapeutics and release them in a controllable fashion, dispersability in water and scalability, and the potential for targeted therapy. Here we investigate the change in the tRNA dynamics on ND surfaces relative to the freestanding RNA using neutron scattering technique and molecular dynamics (MD) Simulations. The dynamics of hydrated tRNA on ND surfaces are compared with that of freestanding hydrated tRNA molecules and dry tRNA on ND surfaces at the molecular level within the time range of picosecond to several nanoseconds. Both experiments and simulations show faster dynamics of tRNA on ND surface compared to that of the dry tRNA on ND surfaces or freestanding RNA molecules. We attribute the faster RNA dynamics on ND surfaces to the de-confinement of RNA molecule from adsorbed water leading to a rapid dynamics compared to the “heterogeneous dynamics” of hydrated RNA in the absence of ND.

References
Membrane Domain Formation on Nanostructured Scaffolds

C. Patrick Collier, Fred Heberle, John Katsaras, Bernadeta Srijanto, Bob Standaert

The spatial organization of lipids and proteins in biological membranes seems to have a functional role in the life of a cell. Separation of the lipids into distinct domains of greater order (lipid rafts) and anchoring to the cytoskeleton are the two main mechanisms for organizing the membrane in cells. However, these domains are not visible with optical microscopy and are transient, making them difficult to study. There are no experimental membrane models that can maintain nanoscopic domains in identifiable positions for experimental study. To address this deficiency, we are developing a fundamentally new type of model membrane: a lipid bilayer floating on a nanostructured scaffold. Similarly to a cytoskeleton, the scaffold will nucleate domains and impart order at defined locations while allowing free diffusion in the bulk of the bilayer. This will result in the generation of a planar bilayer that maintains its native fluidity around suspension points defined by the structure of solid supports. This system is the first of its kind capable of systematically studying the influence of a static “cytoskeleton” on lipid membranes of defined composition. The platform is suitable for interrogation by a number of powerful experimental methods, including atomic force microscopy (AFM), fluorescence microscopy and neutron reflectometry.

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Dynamics of Molecular Associates in Hydrogen Bonding Liquids

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Many liquids,\textsuperscript{1} although homogeneous at the macroscopic level, present significant structuring at the nanoscopic level. Such structuring takes place over nanometer length scales which are however larger than the intermolecular distance. A typical signature of this phenomenon is the existence of a prepeak in the static structure factor, a feature at Q values smaller than the First Sharp Diffraction Peak (FSDP). Hydrogen bonding liquids, such as alcohols but also the fragile glass-former m-toluidine, form characteristic supramolecular associates originating a prepeak in their structure factor. Coherent Quasielastic Neutron Scattering (QENS) measurements allow investigating the dynamics of these structures at the molecular level.

QENS data were collected, on several hydrogen bonding systems including methanol, 2-propanol, m-Toluidine,\textsuperscript{2} and methanol/water mixtures, on samples differing also for their isotopic composition, in a Q range encompassing both the prepeak and the First Sharp Diffraction Peak (FSDP), thus allowing to study the molecular dynamics at length scales corresponding to the first neighbor and inter associates distances. Through these measurements, the lifetime of the molecular associates and how this is related to the main structural relaxation can be established, as a function of temperature. These results are discussed within the framework of current theories.\textsuperscript{3}

\textsuperscript{1} Mesostructure and Dynamics in Liquids and Solutions; \textit{Faraday Discussion}; 2013; Vol. 167.
Investigation of physical and chemical hydrogels by neutron scattering

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Hydrogels are 3D networks of polymer chains able to adsorb and retain large amount of water. Depending on the nature of the cross-linker, physical or chemical gels can be obtained. Hydrogels are useful for numerous applications, from food and cosmetic products to drug delivery, contact lenses production and tissue engineering. Recently, they have been also used as new confining systems for cleaning formulations (micellar solutions and microemulsions) for application to cultural heritage conservation[1]. Understanding the structure and transport phenomena in hydrogel matrices is of great interest in view of the final application. Neutron scattering techniques are able to investigate both the hydrogel structure and dynamics. A recent QENS investigation[2], will be presented showing the possibility to disentangle the dynamics of water from the dynamics of the network in physical and chemical hydrogel. Concurrently, small angle experiments are used to study the hydrogel nanostructure. All results will be discussed along with data obtained from complementary techniques in order to have a complete picture of the hydrogel system and to show the confining action imposed by the polymer matrix to the continuous medium.

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References:
Using Small-Angle Neutron Scattering (SANS) to Investigate the Supramolecular Organization of Stimuli-Responsive Amphiphilic Polythiophene Block Copolymers

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Understanding the effects of supramolecular organization on π-conjugated materials is critical in design of next generation optoelectronic and sensing devices. We describe the synthesis and properties of the amphiphilic polymer system, which was specifically designed to study details of photoexcitation energy migration and its control in conjugated polymers. Hydrophobic and hydrophilic polythiophene block copolymers attached to a central low-energy gap perylenedicarboximide (PDCI) unit demonstrated the ability to manipulate energy transfer by changing molecular organization through external stimuli such as solvent polarity or temperature. Small-angle neutron scattering (SANS) experiments using selective deuteration of the specific parts of the block copolymers were used to study pre-organization in solutions where highly ordered bicontinuous morphologies were seen in hydrophilic “bad” solvents while larger less defined structures were observed in a hydrophobic “good” solvent. The details of the structural studies via SANS experiments will be described in this presentation.
A low resolution structure of CESA1 catalytic domain of Arabidopsis thaliana Cellulose Synthase Complex: Evidence for CESA trimers


Abstract

The cellulose synthesis complex (CSC) is a large multisubunit transmembrane protein complex responsible for synthesis of cellulose chains and their assembly into microfibrils in plants. This work reports a structural study of recombinant catalytic domain (residues 341 – 845) of Arabidopsis thaliana CESA1 (ATCESA1CatD) that was over-expressed and purified from Escherichia coli. Using a two-step procedure, it was possible to purify monomeric and trimeric forms of ATCESA1CatD, providing the first experimental evidence supporting the self-assembly of CESAs into stable trimeric complexes. The conformation of monomeric and homotrimeric ATCESA1CatD were studied using small-angle neutron scattering (SANS) and small-angle X-ray scattering (SAXS). A series of ATCESA1CatD trimer computational models were compared with the SAXS trimer profile to explore the possible arrangement of the monomers in the trimers. Four candidate trimers were identified with monomers oriented such that that newly synthesized cellulose chains project towards the cell membrane. In these models, the class specific region (CSR) is found at the periphery of the complex and the plant-conserved region (P-CR) forms the base of the trimer. This study strongly supports the hexamer of trimers model for rosette CSC that synthesizes an 18-chain cellulose microfibril as the fundamental product of cellulose synthesis in plants.
Understanding the effect of deuterated conducting polymer and solvent additive on the performance of organic photovoltaics

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Although deuterated organic semiconductors have been widely employed in neutron reflectivity/scattering to study interfacial phenomena in organic electronic devices such as organic photovoltaics, there is still no clear understanding of the possible impacts of deuterium substitution on the optoelectronic properties of the organic semiconductors. Here, we report a study of the isotopic effects of deuterium substitution on the structure, morphology and optoelectronic properties of regioregular poly(3-hexylthiophene)s (P3HT) with an approach that combines the synthesis of deuterated materials, optoelectronic properties measurements, theoretical simulation and neutron scattering. Selective substitutions of deuterium on the backbone or side-chains of P3HT result in distinct optoelectronic responses in P3HT/[6,6]-phenyl-C61-butyric acid methyl ester (PCBM) photovoltaics. Specifically, the weak non-covalent intermolecular interactions induced by the main-chain deuteration are shown to change the film crystallinity and morphology of the active layer, consequently reducing the short-circuit current. However, side-chain deuteration does not significantly modify the film morphology but causes a decreased electronic coupling, the formation of a charge transfer state, and increased electron–phonon coupling, leading to a remarkable reduction in the open circuit voltage.

Secondly, adding solvent additive has been demonstrated to be an effective method to optimize the bulk heterojunction morphology, and improve the efficiency of OPV. However, the key information of the nano-structural evolution occurring in the transformation from casting solution to thin photoactive film is still lacking. We investigate the effects of the processing additive diiodooctane (DIO) on the morphology of high efficient PBDTTT-C-T:PCBM and PTB7:PCBM OPVs, starting in the casting solution and tracing the effects in the spun-cast thin films by using neutron/x-ray scattering, neutron reflectometry and other complementary characterization techniques. Our results reveal that DIO has no observable effect on the structure of polymer donor and aggregation of fullerene acceptors in solution, however in the spun-cast films, it significantly promotes their molecular ordering and phase separation.

This research was conducted at the Center for Nanophase Materials Sciences and the Spallation Neutron Source, which are sponsored at Oak Ridge National Laboratory by the Division of Scientific User Facilities, U.S. Department of Energy.

Studies on the Intrinsically Disordered N-Termini of R67 DHFR using Small Angle Neutron Scattering (SANS)
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Abstract
Dihydrofolic reductase (DHFR) catalyzes the NADPH dependent reduction of dihydrofolate to tetrahydrofolate, which serves as a source for one-carbon donation in cellular metabolism. R67 (DHFR) is the plasmid-encoded DHFR that confers resistance against trimethoprim, which is a potent inhibitor of E. coli chromosomal DHFR. R67 DHFR is a homo-tetrameric protein with four β-barrel monomers that form a single active site pore in the center. The crystal structure indicates the 16-18 amino acid sequence at the N-terminus of each monomer to be intrinsically disordered. Removal of these residues results in a truncated protein, which is almost fully active, although somewhat less stable.

We investigated whether the disordered N-terminal sequence might undergo coupled binding and folding upon ligand binding using SANS. Formation of the binary complex with the oxidized cofactor (NADP⁺) and ternary complex with the substrate (DHF) resulted in comparable radii of gyration suggesting minimal, if any changes in the overall shape of the protein.

We studied the hydration of R67 DHFR in presence of osmolytes (glycine betaine and DMSO). Osmolytes cause neutron contrast variation and the water molecules (hydration shell) that are responsible for osmolyte exclusion can be examined by SANS as they have a different scattering intensity than the protein, bulk water and the osmolyte solution. Our study found around 1200 water molecules hydrating the full-length protein in the presence of betaine as well as DMSO.

We did not observe compaction of the overall structure in the presence of glycine-betaine as the radius of gyration (Rg) of the protein did not show a significant change upon osmolyte addition. The disordered N-termini seem to mostly remain disordered and maintain a large radius of gyration.

We are using a program called SASSIE, which creates a series of random models of the N-terminus using a Monte Carlo simulation and calculates SANS profiles for these conformations. The best fits obtained upon comparing these theoretical profiles to the experimental data, would generate an envelope representing the space occupied by the N-termini. This will give a better insight into the ensemble of states sampled by the 18 disordered residues.
Structural biology of cellulolytic enzymes–mechanistic insights into hydrolysis and oxidative chain cleavage

Wm. Brad O’Dell, Annette M. Bodenheimer and Flora Meilleur

Cellulolytic enzymes are vital to the production of ethanol from cellulose-rich feedstocks. The high cost of these enzymes is a burden to commercial-scale ethanol production. We are studying cellulose hydrolyzing and cellulose oxidizing proteins to gain mechanistic insights that can inform future engineering of enhanced enzyme efficiency. We are investigating Trichoderma reesei cellulbiohydrolase I (Cel7A) with a particular focus on protein–cellulose interactions during the hydrolysis reaction. We are also studying a cellulose oxidizing system from Neurospora crassa consisting of the polysaccharide monooxygenase PMO-2 and the cellobiose dehydrogenase CDHIIA. Recombinant expression of N. crassa enzymes from the yeast Pichia pastoris provides the potential for ²H-labeling for neutron crystallography and small-angle scattering studies. Crystals suitable for neutron diffraction are being pursued so that we may directly observe the protonation states of catalytic residues and/or ligands. Neutron crystallography experiments will be conducted on the IMAGINE diffractometer (High Flux Isotope Reactor, Oak Ridge Natinal Laboratory), which is also discussed.
Nanophase soft matter including polymers, organic materials, inorganic-organic hybrid systems, biological and biomimetic materials are of great interest in fundamental research towards medical and energy-related applications. Neutron techniques and transmission electron microscopy (TEM) are highly complementary tools in revealing the static and dynamic nanostructural details from these emerging materials of enormous importance. Neutron techniques provide indirect, reciprocal space information, which is often better companioned by direct imaging and real space measurements in TEM. However, in conventional TEM, the imaging of these materials suffered severely from low contrast associated with their low atomic numbers and high electron beam sensitivity resultant from the nature of the weak binding forces. To overcome those obstacles, Center for Nanophase Materials Sciences (CNMS), which is located right next to SNS, established a user facility for soft matter TEM that is highly complementary to neutron research in SNS and HFIR at ORNL. We are equipped with a FEI Vitrobot Mark IV cryoplunger and Zeiss Libra 120 TEM with LaB$_6$ filament, in-column Omega filter, cryogenic chamber, and optimized design for soft material imaging. Cryo-TEM, low-dose electron diffraction, low-dose lattice imaging, and energy filtered TEM have been pursued in thin film, bulk, and solution-state for nanophase soft materials such as star-shaped copolymers, conjugated block copolymers, surfactants, surfactant-dispersed nanoparticles, polypeptide-b-polystyrene copolymer, elastic block copolymers, biorenewable composites, proteins, cancer-fighting dendrimers, lithium-conducting polymer electrolytes, etc. In this presentation, we will showcase previous and on-going efforts in coupling the soft matter TEM capability at CNMS to neutron enabled experiments (at SNS and HFIR) such as neutron reflectivity, small angle neutron scattering, and neutron spectroscopy for the advancement of nanophased soft matter research. Our examples include deuterated copolymers, active layers in organic solar cell, organic-small-molecule-based semiconducting crystals, bottle-brush copolymers, porous carbon materials, waterborne polymeric micelles, and others.
QENS and Molecular Dynamics investigation of Dynamics of RNA on hydrophilic Nanodiamonds

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RNA and Nanodiamond (ND) both are useful for applications in nano-biotechnology, especially for drug-delivery. The architecturally flexible RNA with catalytic functionality has been considered as potential candidate for treatment of life-threatening diseases like cancer. On the other hand, ND with its functionalizable side groups and high surface are actively considered for biomedical applications such as bactericidal materials and cancer treatment. Combination of these two into RNA-ND nanocomposites is therefore a rational approach toward developing a potential new generation, in vivo, drug-delivery system. The enhanced material properties can only be achieved if fundamental understanding of the structural and dynamical behavior of this system at the nanoscale is fully resolved. To obtain such understanding we investigated the dynamics of RNA on ND surface by integrating large-scale molecular simulations that resolve atomistic details with neutron scattering that provide information on dynamical behaviors. In this work, we used quasi-elastic neutron scattering experiments on hydrated/dehydrated RNA-ND nanocomposites at low temperature in order to determine the dynamics of RNA on the ND surface. The results obtained show faster RNA motion on the ND surface compared to a ‘freestanding’ RNA. Large-scale molecular dynamics simulations enabled us to understand the underlying physics for the faster dynamics; the faster RNA motion in the nanocomposite is due the weaker heterogeneous dynamics of the RNA in the presence of ND compared to the freestanding one.

Credit Line: This work was supported by the U.S. Department of Energy (DoE), Office of Basic Energy Sciences (BES), Materials Science and Engineering Division (MSED). This research used resources of the Oak Ridge Leadership Computing Facility at the Oak Ridge National Laboratory, which is supported by the Office of Science of the U.S. Department of Energy under Contract DE-AC05-00OR22725. M.G and J.M.B and V.E.L acknowledge the support from the Center for Accelerated Materials Modeling (CAMM) funded by the BES, MSED.
Three-Dimensional Structural Characteristics of Low-bandgap Polymer Based Solar Cells Processed with Solvent additives

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We present three-dimensional nanostructural changes in PBDTTT-CF:PC₇₁BM bulk-heterojunction with various amounts of 1,8-diiodooctane (DIO) as processing additive, and correlate the changes to device efficiencies by combining vertical phase morphology and surface imaging. For the films fabricated without DIO, depth-sensitive neutron reflectometry reveals the formation of PC₇₁BM enriched layers at the air/film interface. Atomic force microscopy (AFM) and transmission electron microscopy (TEM) images complement by visualizing surface aggregates of PC₇₁BM embedded in polymer:fullerene matrix. Addition of DIO remarkably changes the vertical phase morphology of the films, exhibiting nearly ideal structure with a thin PC₇₁BM enriched layer at the interface and well-mixed donor-acceptor bulk compact layer. In contrast, excess amount of DIO promotes formation of loosely packed vertical phase morphology with only a mixed-phase, which decrease the device performance. These results reveal how DIO processing additive can control the vertical phase morphologies of the films as well as the importance of having enriched phases in the film morphology for efficient device performances.
Selective Deuteration in Soft Materials

Macromolecular Nanomaterials Group

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Abstract: Substitution of deuterium ($^2$H) for protium ($^1$H) in organic and polymeric materials can provide contrast in neutron scattering experiments due to their different neutron scattering length densities. Strategic deuteration of soft materials can provide a powerful approach to elucidation of important structural and dynamic features in soft matters that would not be accessible by other techniques. The Macromolecular Nanomaterials Group at the CNMS has been developing an array of deuterated monomers, polymers, and molecular building blocks that are not commercially available. In addition, one of our objectives is to obtain a more fundamental understanding of the impact that substitution of $^1$H with $^2$H has on various properties (e.g., optoelectronic properties), in soft materials.

Acknowledgement: This work was performed at the Center for Nanophase Materials Sciences at Oak Ridge National Laboratory, supported by Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy.
IMAGINE, New Science and Capabilities at HFIR

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\textit{IMAGINE} is a new high intensity, quasi-Laue neutron crystallography beam line developed at the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL). \textit{IMAGINE} is a state-of-the-art facility for neutron-diffraction analysis of advanced materials and macromolecules. \textit{IMAGINE} is especially suited to pinpoint individual hydrogen atoms in protein structures, enabling neutron protein structures to be determined at or near atomic resolutions (1.5 Å) from crystals with volume < 1 mm\textsuperscript{3} and with unit cell edge of < 100 Å. Beam line features include novel elliptical focusing mirrors that deliver neutrons into a 2.0 x 3.2 mm\textsuperscript{2} focal spot at the sample position with full width vertical and horizontal divergence of 0.5° and 0.6°, respectively, and variable short and long wavelength cutoff optics that provide automated exchange between multiple wavelength configurations.

We will give an overview of the IMAGINE beam line at the HFIR, and present recent results from the instrument.

The acquisition and installation of \textit{IMAGINE} at the HFIR was funded by the National Science Foundation (NSF) under award No. 0922719. ORNL is managed by UT-Battelle, LLC, for the U.S. Department of Energy under Contract DE-AC05-00OR22725.
At CNMS we are able to prepare polymers using precision synthetic techniques and characterize their chemical composition and chain structure well, for subsequent work in solution, bulk, or thin films. There is a good opportunity for symbiosis with neutron experiments. We are just next door!

This poster is a collection of several past and present illustrative projects. Our synthetic strengths include both anionic and controlled radical polymerization. Precision anionic polymerization can afford polymers with unique topologies -- chosen and defined architectures such as graft or star copolymers. Controlled radical polymerization, such as RAFT, allows greater flexibility in monomer selection. We use these techniques to enable study of thin polymer films, or how polymers behave in solution or bulk, or other polymer properties. Moreover, films of polymers can be carefully prepared and characterized. Segregation of blends of brush and linear polymers can be followed by selective labeling.
New Capabilities at the ORNL Center for Structural Molecular Biology

Volker Urban, Sai Venkatesh Pingali, Shuo Qian, Hugh O’Neill, Kevin Weiss, Qiu Zhang, Paul Langan

Oak Ridge National Laboratory, Oak Ridge, TN 37831

The Bio-SANS instrument at the HFIR is ideally suited for studies of biomacromolecules including proteins, DNA/RNA, lipid membranes and other hierarchical complexes. The recently upgraded Bio-SANS detector has count rate capabilities (>10^6 Hz) that enable utilization of the full potential of the high neutron flux from the cold source. Furthermore, fixed high-angle detector banks to be installed in 2016 will improve the accessible scattering range by a factor of 10, especially critical for time-resolved studies of hierarchical and large biological systems. We have also developed a series of new sample environment capabilities that open untapped opportunities for the studies of biological systems using neutrons. These include a pressure cell to monitor chemical reactions in situ such as biomass pretreatment studies, a multi-position sample holder with rotational (tumbling) capability especially useful for studying suspensions, a humidity-controlled chamber critical for membrane studies, and a flow cell for systems that partition into multiple phases (e.g., microemulsions) with additional capability for flowing one or two phases during measurement. Furthermore, we can now perform grazing-incidence SANS in conjunction with a humidity chamber for studies of biomembranes and substrate-supported biosensors. In view of the constantly evolving sample environments for pursuing new scientific problems, the sample area has also been redesigned to enable flexibility in mounting a wider range of sample environments. The implementation of additional data reduction software, open source MantidPlot and streamlined operations together enhance the efficiency of the neutron scattering user experiments. Recent improvements to the Bio-Deuteration Laboratory at the SNS include a parallel bioreactor system that allows high-density cell growth with precise control and monitoring of dissolved oxygen, pH, agitation, and feeding rates as well as a new preparative scale bioreactor system for large-scale fermentations. Other capabilities that have been recently added to the suite of user laboratories include a Rigaku single crystal diffractometer, liquid handling robots for crystallization screening, and additional incubators for temperature-controlled protein crystallization.

The Center for Structural Molecular Biology (CSMB) is supported by the Office of Biological and Environmental Research Project ERKP291, using facilities supported by the U.S. Department of Energy, managed by UT-Battelle, LLC under contract No. DE-AC05-00OR22725. Research at Oak Ridge National Laboratory’s High Flux Isotope Reactor and the Spallation Neutron Source is sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.
User Laboratories at the SNS, HFIR, and JINS

Oak Ridge National Laboratory, Oak Ridge, TN 37831

Neutron experiments routinely require supporting laboratories that provide a safe and suitable environment for the preparation, handling, and further characterization of the samples of interest. In recent years, a number of laboratories have been developed at the SNS, HFIR, and JINS to accommodate these needs and to enable visiting researchers to make the most efficient use of their beam time. An overview of the activities and capabilities hosted by these user laboratories will be presented.
Entropic Effects in Polymer Thin Films

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Understanding structure and dynamics of polymers near interfaces is of great interest in the development of new technologies. In particular, reduction in conformational degrees of freedom of polymer chains near interfaces leads to counterintuitive effects in thin and ultrathin films. In this presentation, I will present our research in unraveling these entropic effects using combination of precision synthesis, neutron reflectivity experiments and modeling based on field theoretic methods. Examples based on the use of field theoretic methods for understanding the structure in the thin films and interpreting the neutron reflectivity profiles will be presented. These examples include thin films of polydisperse di-block copolymers, pH responsive polyelectrolyte brushes and helical brushes. It will be shown that usage of field theoretic methods coupled with precision synthesis and neutron reflectivity experiments provide unparalleled insights into physics of polymers near interfaces.
Modeling of time-of-flight INS intensity from phonons in single-crystals

The advanced inelastic neutron and synchrotron facilities around the world are adapted to experimentally measure phonons under different environmental conditions in the material. Combining experimental inelastic neutron/x-ray scattering measurements with first-principles simulations (e.g. density functional theory) is a powerful way forward to probe and rationalize the underlying atomic dynamics in systems of increasing complexity. This combined approach is also an opportunity to tackle challenging situations for first-principles calculations of phonons, such as anomalous (soft) phonon behavior in non-harmonic materials, strong temperature dependences of phonons, materials with strong electronic correlations, coupled spin-phonon systems, or systems with large interaction ranges.

In this talk, I will present the systematic development of lattice dynamics modeling in relation to soft phonon modes, calculating the interatomic force interaction range, and investigating the temperature dependence of phonons. In particular, I will discuss real-space modeling of the force-constants in analyzing the origins of strong electron-phonon coupling in Nb, strong temperature dependence of TO phonon mode in thermoelectric material SnSe, and the role of electron-phonon coupling and Te-doping in Mo₃Sb₇ which modifies the local bonding non-uniformly. All of these cases illustrate the importance of coupling experimental inelastic scattering with first-principles simulations to develop further insights into atomic dynamics.

Research was supported by the Center for Accelerating Materials Modeling of SNS data (CAMM), supported by the U.S. Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division and through the Office of Science Early Career Research Program (Delaire). The Research at Oak Ridge National Laboratory's Spallation Neutron Source was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy (DOE).

Collaborators: Olivier Delaire, Iyad I. Al-Qasir, Jennifer L. Niedziela, Jiawang Hong, Douglas L. Abernathy, Vickie Lynch, Chen W. Li
A neutron scattering kernel data evaluation framework for computation of model-dependent predictions is outlined and their uncertainties are obtained by fitting to double-differential cross section measurements and their uncertainties. We demonstrate the first component of this framework by performing molecular dynamics (MD) simulations using NAMD for light and heavy water using TIP3P and TIP4P interaction models. These MD trajectories are then processed using the nMOLDYN to compute the thermal neutron scattering kernel. We study convergence of the computed kernel with increasing number of water molecules. These computations of the scattering kernel will then be fitted to double-differential data measured at the SNS SEQUOIA detector. The fitting procedure is designed to yield optimized model-parameters and their uncertainties in the form of a covariance matrix, from which new evaluations of thermal neutron scattering kernel will be generated. In addition to heavy and light water, this framework will be used for other key thermal moderators [e.g. CH2, C2F4 (Teflon), C5O2H8 (Lucite)] of importance for Nuclear Criticality Safety applications. Two complementary fitting procedures will be considered: Generalized Least Squares and Monte-Carlo. We show how computation of sensitivities of the scattering kernel with respect to model parameters could be computed by a novel application of adjoint method to MD simulations.
High-temperature Sample Environment Template for Experiment Simulations on DGS Instruments

Hillary Smith, Jiao Lin, Doug Abernathy, Garrett Granroth, Brent Fultz

A template for a high-temperature sample environment for MCViNE simulations in the Virtual Neutron Facility framework has been developed to simulate the MICAS 1600°C furnace. MCViNE simulations currently support experiment simulation on several SNS DGS instruments, and the design of this template allows extension of simulations to elevated temperatures by easily adding this element to the sample assembly. Many layers of heat shielding are required for high temperature operation, greatly increasing the complexity of multiple scattering from these additional components. The template allows a sophisticated geometrical arrangement, and it can simulate the many layers of scatterers and reproduce contributions from multiple scattering.

The viability of the template was demonstrated by simulating a powder sample of bcc Cr and comparing the results to an experimental measurement performed on ARCS between 25 and 1250°C. The $S(Q,E)$ shows good agreement between simulated and experimental results and the phonon density of states integrated over all $Q$ reliably reproduces peak positions and broadenings. Scattering kernels for all elastic/inelastic and coherent/incoherent mechanisms are included in the simulation. The template provides the flexibility to turn these mechanisms on and off, allowing us to better discern the origin of features in the spectra. Similarly, components of the template can be used or removed in an attempt to understand the details of multiple scattering between the sample and the components. These results may suggest opportunities for the designs of components with lower backgrounds.
First-Principles Predication of Two-Dimensional Electrides

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Two-dimensional (2D) electrides have recently received increasing interest due to its promise for electron emitter, surface catalyst and high-mobility electronic devices. However, they are very limited in a few layered alkaline-earth nitrides and rare-earth carbides. Here, we extend the possibility of 2D electrides by structure predication, using density functional theory calculation in conjunction with particle swarm optimization algorithm. Simple-element compounds $A_2B$ ($A/B = \text{alkali metals/halogen, or}\ A/B = \text{alkaline-earth metals/VA, VIA, VIIA nonmetals}$) and $AB$ ($A/B = \text{alkaline-earth metals/halogen}$), which have nominal imbalanced oxidation numbers, were investigated. We find several new 2D electrides out of 90 candidates, and uncover that the stabilization of the 2D layered structure, which is required for the success of 2D electrides, strongly depends on the relative size of cation, in such a way that it has to be of similar or larger size than the anion in order to sufficiently screen the repulsion between the excess electrons and anions. We additionally identify the experimental conditions of temperature and chemical potential where the predicted 2D electrides are stabilized against the decomposition into compounds with balanced oxidation numbers. Our results will shed light on searching for new electrides and understanding on design principles of electrides for practical applications.
Monte Carlo Simulation of the ARCS Instrument Response Function

M.S. Bryan\textsuperscript{1}, T.R. Prisk\textsuperscript{2}, G.E. Granroth\textsuperscript{3}, and P.E. Sokol\textsuperscript{1}

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It is frequently necessary to account for instrumental resolution effects in order to correctly analyze and interpret neutron scattering data. However, in inelastic neutron scattering studies, it is often difficult or impossible to directly measure the instrumental resolution at finite energy transfers. Time-of-flight spectrometers, such as the ARCS instrument at the Spallation Neutron Source, pose special problems to analytical calculations of the instrument response function because the asymmetrical time-structure of the beam must be taken into account. In this presentation, we discuss recent measurements of the momentum distribution of liquid helium using the ARCS spectrometer. We have performed realistic neutron ray-tracing simulations of ARCS using the McStas software suite. This approach permits an accurate assessment of the instrument response and thereby allows a detailed comparison between theoretical models of the momentum distribution and the observed scattering. This scientific example illustrates the importance of computational modelling of neutron instrumentation to realizing the full potential and productivity of instruments at the SNS.
A correct account for the statistical weight of time of flight measurements is missing in earlier software approaches for neutron scattering data processing. This is particularly evident in the case of single crystal Laue scattering, when looking at diffuse signals. Recently, new algorithms were implemented in the Mantid package to overcome this problem. The expansion to inelastic scattering yields a vastly reduced memory footprint for the data, especially when using event based processing. Future work will include expansion to powder measurements, and data symmetrization.
Collective Excitations in the Frustrated Classical Spin Liquid MgCr2O4

Xiaojian Bai, Joseph M. Paddison, Martin Mourigal
School of Physics, Georgia Institute of Technology, Atlanta, USA

We study the spin dynamics of frustrated magnet MgCr2O4 in the cooperative paramagnet regime using inelastic neutron scattering on SEQUOIA at the SNS. The data shows strong local zero energy excitations indicating the appearance of emergent local structure in the network of corner-sharing tetrahedrons with antiferromagnetic interactions. We extract all the relevant exchange parameters in the Heisenberg model by fitting the instantaneous structure factor with a self-consistent Gaussian model. A set of real space correlators is consistently obtained by the Fourier analysis of the structure factor and the Reverse Monte Carlo refinement. A further fitting of the First Moment verifies independently all exchange parameters. We also perform the Fourier analysis for data in an energy resolved fashion and demonstrate the deviation from antiferromagnetic hexagon spin-loop model at finite energy. The large set of single crystals used for the experiment were grown by Seyed Koohpayeh and Jia-Jia Wen in Collin Broholm’s group at Johns Hopkins Institute for Quantum Matter.
Magnetic, electronic and lattice degrees of freedom in complex transition metal compounds

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This DOE EPSCoR program aims to build a major neutron scattering infrastructure capable of treating both soft and hard materials. The scientific focus is to understand the role of coupling between the important degrees of freedom in complex materials and its impact on the structure/property relationship. For hard materials, our goal is to tune dominant couplings that impact the magnetic, electronic, and phonon properties of complex transition metal compounds to enhance a critical property in order to discover new functionality. In particular, many of the most interesting materials display coupling both in their static and dynamical behavior, making neutron scattering the ideal tool to elucidate these fundamental relationships. Materials under investigation include Sr$_2$Ru$_{1-x}$Fe$_x$O$_4$, Sr$_3$(Ru$_{1-x}$Mn$_x$)$_2$O$_7$, Ba$_2$CoO$_4$, Ba(Mn$_{1-x}$Fe$_x$)$_2$Sb$_2$, Cu$_x$FeAs, Fe$_3$Ga$_4$, Ru$_{1-x}$Co$_x$Ge, and Sr$_{1-y}$MnSb$_2$. 

1-3 Department of Physics & Astronomy, Louisiana State University, Baton Rouge, LA 70803
Title:
Dimensional Crossover, Long-Range Order, and Magnetic Plateaus in Sheets of Magnetic Dimers

Abstract:
The interactions that define how spins arrange themselves in a material play a fundamental role in a wide variety of physical phenomena from quantum magnetism to quantum critical phenomena to exotic superconductivity. The Shastry–Sutherland model, which consists of a set of spin 1/2 dimers on a two dimensional square lattice, has played an influential role in developing this field. In this talk, I will present the results of the high-pressure neutron scattering studies performed on the physical realization of the Shastry-Sutherland model, SrCu2(BO3)2, which combined with computer modelling, show how true antiferromagnetic order can emerge with a crossover into the third dimension. We find a subtle symmetry change as a function of temperature for pressures above 4.5 GPa, linked to antiferromagnetism and the tilting of the dimers out of the plane. The inclusion of Dzyaloshinskii-Moriya interactions in the Shastry-Sutherland Hamiltonian helps explain the observations. Additionally, interest has focused on finite magnetization of SrCu2(BO3)2 at low temperatures, wherein the lowest energy of the three triplet states is driven to zero energy. At higher magnetic fields, plateaus have been observed in the magnetization, which have been interpreted in terms of preferred filling of the singlet ground state with increasing densities of triplet excitations. This is related to Bose-Einstein crystallization of the triplet excitations. I will present how pressure and magnetic field can be used as tuning parameter to drive the system across the quantum phase diagram.
Neutron Spectroscopy on the Most Complex Element: Plutonium

Marc Janoschek (LANL)

Magnetism is typically described in one of two extreme limits: In insulators electrons are treated as localized objects which carry a magnetic moment, whereas in the metallic regime magnetism is generally considered to arise from an instability of the Fermi surface. Strongly correlated electron systems typically display a duality between these two pictures. Electrons behave both itinerantly giving metallic like behavior, yet can also possess a large fraction of their spectral weight in high energy Hubbard-like bands that are more local in nature. This duality has been intensively studied from the charge perspective and continues to be an active area of research. However, this duality also is manifest in the spin degrees of freedom, and therefore neutron spectroscopy represents a powerful tool to gain insight in such electronic dichotomy as demonstrated by our recent measurements on plutonium (Pu) metal. Pu is arguably the most complex elemental metal known because its 5f electrons are tenuously poised at the edge between localized and itinerant configurations. This complex electronic structure leads to emergent behavior—all a direct consequence of its 5f electrons—including six allotropic phases, large volumetric changes associated with these transitions of up to 25%, and mechanical properties ranging from brittle α-Pu to ductile δ-Pu. Pu also exhibits a Pauli-like magnetic susceptibility, electrical resistivity and a Sommerfeld coefficient of the specific heat that are an order of magnitude larger than in any other elemental metal. Finally, while experiments find no sign for static magnetism in Pu, most theories that use the correct volume predict a magnetically ordered state. We have investigated the magnetic fluctuation spectrum of δ-Pu using the ARCS spectrometer at SNS [1]. Our study reveals that the ground state of plutonium is governed by valence fluctuations, that is, a quantum-mechanical superposition of localized and itinerant electronic configurations. Our results that are in quantitative agreement with dynamical mean field theory show that the magnetism in Pu is not "missing" but dynamic, and is driven by virtual valence fluctuations. Our measurements provide a straightforward interpretation of the microscopic origin of the large, Pauli-like magnetic susceptibility of δ-Pu. Finally, because the various valence configurations imply distinct sizes of the Pu ion, the valence-fluctuating ground state also gives a natural explanation for its complex structural properties and notably the large sensitivity of its volume to small changes in temperature, pressure or doping.

Giant electromechanical coupling of ferroelectric relaxors controlled by local-structure vibrations

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Understanding how inhomogeneous nanoregions form and enhance functional properties is an outstanding scientific challenge for a broad class of materials. Ferroelectric relaxors, for example, have electromechanical responses tenfold larger than industry-standard piezoelectric ceramic materials and have dramatically improved technologies ranging from medical 3D ultrasonography to sonar. The giant coupling is widely associated with the presence of polar nanoregions (PNRs) in these materials, but a microscopic explanation for how PNRs form or enhance coupling has remained elusive for decades. Using neutron scattering to characterize the lattice dynamics of ferroelectric relaxor materials, we discovered an Anderson-type phonon localization mechanism that explains the PNRs in terms of localized vibrations [1]. More recently, using neutron scattering measurements of the lattice dynamics and local structure, we find that localized vibrations also enable the giant coupling by softening the underlying macro-domain polarization rotations. An avoided crossing of the local vibrations and acoustic phonons drives this softening. Furthermore, the local vibrations and a component of the local structure align in an electric field and this focuses softening for particular shear modes, revealing a way to tune the ultrahigh piezoelectric response by engineering the elastic shear softening in these technologically important materials.


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Probing Molecular Magnetism by Inelastic Neutron Scattering


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Poster Abstract:

Inelastic neutron scattering (INS) has been used to determine the magnitude and sign of the zero-field splitting parameters $D$ of non-deuterated samples at CNCS including $d^5$ metalloporphyrins $[\text{Fe}^{III}(\text{TPP})X]$ ($S = 5/2$; $X = F, Br, I$; $\text{TPP}^2$ = tetraphenylporphyrinate) and $d^7$ $(\text{Ph}_4\text{P})_2\text{Co(NO}_3)_4$ ($S = 3/2$) which has shown properties of a single-ion magnet (SIMs). SIMs have been actively studied due to their potential applications in information storage and quantum computation. Inelastically scattered neutrons transfer energy to molecules in the sample, leading to transitions between the magnetic levels. The metalloporphyrin work completes a rare series of biomimetic halide compounds with magnetic excitations measured up to ~53 cm$^{-1}$. Studies on $(\text{Ph}_4\text{P})_2\text{Co(NO}_3)_4$ demonstrate that the use of an external magnet field in INS determines the sign of $D$. Increasing $D$ is crucial to improving the properties of SIMs. Preliminary data on two Co(II) SIMs have been collected on CNCS, VISION, and BASIS for $\text{Co(acac)}_2(\text{D}_2\text{O})_2$ and CNCS for $\text{Co(12-crown-4)}_2(\text{I}_3)_2$ to probe how to use INS to measure magnetic splittings larger than 50 cm$^{-1}$. Studying large magnetic splittings by INS is important because there is a lack of direct techniques to determine separations between magnetic ground and excited states in order to fully characterize SIMs.
Structural and Electronic Characterization of α-RuCl₃ Layered Compound

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Understanding interplay between structural distortions, electron correlations and spin-orbit coupling in strongly-correlated materials is crucial for a realization of novel quantum phases in these systems. Recently, neutron scattering experiments on α-RuCl₃ layered compound have demonstrated a realization of a magnetic phase proximate to exotic quantum spin liquid phase in this system [1]. Detailed evaluation of α-RuCl₃ lattice structure and nature of an insulating state in this system can provide essential ingredients for explanation of the observed magnetic behavior. However, there has been so far no comprehensive experimental effort targeting these properties. Here we report a detailed characterization of structural and electronic properties of α-RuCl₃ using a combination of X-ray diffraction (XRD), scanning transmission electron microscopy (STEM), and scanning tunneling microscopy (STM) measurements supported density-functional theory (DFT) calculations [2]. Our experimental structural analysis and DFT calculations show a compression of Cl octahedral ligand cage along the C₃ symmetry axes in each RuCl₃ layer, with the Cl-Ru-Cl angles equal to ≈86° across the shared edges. The lattice distortion is limited mainly to the Cl subsystem leaving the Ru honeycomb lattice nearly intact. The XRD and STEM analysis indicates that the c-axis ordering in RuCl₃ crystals is best described by the P3₁2₁ space group. The STM images show a formation of a triangular-like superlattice as a result of the shift of charge density maxima from Cl atomic centers. Non-uniform distribution of charge density within each triangular unit forms a distinctive long-range charge ordered (CO) pattern of a \( \sqrt{3} \times \sqrt{3}R30° \) symmetry. The volt-scale persistence of the CO and its correlation with the periodic lattice displacements indicate its origin in a strong electron-lattice coupling. Finally, we report observations of an energy gap \( \Delta \approx 0.5 eV \) at the Fermi level in the STM spectroscopy measurements. Presence of a persistent energy gap well above the temperature of a magnetically ordered phase suggests that RuCl₃ is a Mott-Hubbard insulator.


[2] M. Ziatdinov et al., to be submitted.
A Structural Quantum Critical Point in LaCu$_{6-x}$Au$_x$

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The study of a quantum critical point (QCP) is one of the long-standing problems in condensed matter physics. Most of the previous studies to understand a QCP focus only on the magnetic aspects of the QCP. The structural quantum critical point (SQCP) — where the elastic degrees of freedom are associated with the quantum criticality — remains essentially unexplored. We study LaCu$_{6-x}$Au$_x$ as a potential candidate of the SQCP. The structural properties were studied using heat capacity, x-ray and neutron diffraction measurements. In agreement with the previous studies [1], LaCu$_6$ undergoes a continuous phase transition from an orthorhombic (Pnma) to a monoclinic (P2$_1$/c) structure at 460 K. The phase transition temperature ($T_{\text{St}}$) in LaCu$_{6-x}$Au$_x$ decreases linearly with Au-composition until the monoclinic phase is completely suppressed. An extrapolation of $T_{\text{St}}$ with Au-composition yields an SQCP at $x_{\text{SQCP}} = 0.3$. The phonon contribution to the heat capacity increases as LaCu$_{6-x}$Au$_x$ approaches the SQCP, which indicates the softening of an acoustic phonon associated with the structural instability at low-temperatures.

References:

Magnetic Excitations of the Quasi-1D Frustrated Ferromagnet LiCuSbO₄

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September 18, 2015

We use inelastic neutron scattering to study a powder sample of LiCuSbO₄, a quasi-1D ferromagnetic (FM) chain with anti-ferromagnetic (AFM) second nearest neighbor interaction and weak interchain coupling. Using spin-wave theory calculations we study how the anisotropy and ratio of coupling strengths along the chains affect the dynamic structure factors. Our results show that the \(J_1-J_2\) FM chain model with easy-plane anisotropy captures all the dominant features observed from the neutron scattering measurements on CNCS at the SNS and IN5 at the ILL. By including weak interchain interaction, the powder averaged spectrum can match the experimental data very well indicating that LiCuSbO₄ is a realization of the frustrated FM chain with strong \(J_1\). The sample used in this study was grown by Sian Dutton in Robert Cava’s group at Princeton University’s Institute for Quantum Matter[1].

References

Magnetic structure and its correlation to the possible Weyl state in topological semimetal Sr$_{0.92}$MnSb$_2$

**ABSTRACT**

Very recently, Liu et al. (arxiv.org/pdf/1507.07978, (2015)) discovered the first magnetic topological semimetal Sr$_{0.92}$MnSb$_2$, in which a possible Weyl state arising from time reversal symmetry breaking is expected. However, the origin of ferromagnetic (FM) behavior of this material has not been clarified. Determination of magnetic structure using neutron scattering is thus highly desired. By employing the four-circle neutron diffractometer technique at HB3A, HFIR, we found a long-range FM order with Mn moments along $b$-axis below $T_C=565$ K, followed by another magnetic transition to a canted C-type antiferromagnetic (AFM) order at $T_{FM-AFM}=304$ K. In the canted C-type AFM state, the Mn moments are aligned with the $a$-axis along with a canting toward the $b$-axis, leading to a net FM moment lying along the $b$-axis. The Mn moments along the $a$- and $b$-axes at 5 K are found to be 3.789(3) and 0.741(4) $\mu_B$, respectively. The discovered FM order in Sr$_{0.92}$MnSb$_2$, either the FM ordering at $304<T<565$ K or the FM component to the canted AFM order for $T<304$ K, is sufficient to break time-reversal symmetry likely creating a Weyl semimetal.
Proton Conducting Oxides - A Case Study of Disordered Fluorites

Solid-oxide electrolytes with high proton conductivity can facilitate a decrease in the operating temperature of solid oxide fuel cells -- in turn greatly improving the reliability and efficiency. Lanthanum Tungstate \((La_{28-x}W_{54+x}O_{54+\delta})\) -- LWO is a disordered fluorite material that exhibits high proton conductivity in the intermediate temperature range (400-700K). In this work, we describe neutron scattering experiments to investigate the LWO structure, bonding (in the presence (wet) and absence (dry) of protons), and proton transport mechanism of LWO.

Neutron powder diffraction data from POWGEN indicate LWO has a fluorite type structure with disorder in the material. The disorder is primarily due to O vacancies in the lattice. The nature and position of the vacancies and proton adsorption sites were analyzed by comparing the phonon density of states obtained from ab-initio models against inelastic neutron scattering (INS) spectrum obtained from the vibrational spectrometer VISION. Finally, the quasi-elastic neutron scattering data collected from BASIS provides information on the conduction mechanism inside LWO, by suggesting the presence of two different jump diffusion processes. Neutron scattering has provided critical information on proton adsorption & transport on this complex, disordered proton conductor.
Insights into Solid Oxide Fuel Cell Materials by In-Situ Neutron Diffraction

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The promise of direct and efficient conversion of chemical to electrical energy makes fuel cell development an area of great technological interest. Solid Oxide Fuel Cells (SOFCs) are one of the most promising technologies to meet this goal. However, current SOFCs operate at temperatures above 700°C. This high temperature increases costs and decreases cell lifetime. To overcoming this challenge we must develop materials that demonstrate high electrocatalytic activity and facile ion and electron transport at lower temperatures. A significant barrier to progress is a lack of experimental techniques that can probe the properties of these materials under high temperate working conditions in both oxidizing and reducing gas environments.

Neutron diffraction is one technique that can achieve this goal to reveal information relating to phase transition, order-disorder phenomenon, and the presence of anionic and cationic vacancies in crystalline oxides. Most powerfully, all of this information is collected in a single experiment over a wide variety of operating conditions. Analysis of these results enables visualization of diffusion pathways in ionic conductors, guiding future material development. This presentation will discuss results from a recently developed in-situ neutron diffraction cell developed for the POWGEN beamline at the Spallation Neutron Source, Oak Ridge National Laboratory. Results will be presented for a variety of materials to demonstrate the versatility of this technique.
Probing intercalation in Ti MXene using neutron scattering
Fluid Interface Reactions, Structure and Transport (FIRST) Center
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MXenes are a new family of exfoliated transition metal carbides and carbo-nitrides that show promise for applications in electrical energy storage (supercapacitors), fuel cells, chemical sensors or gas storage.[1] MXenes are created by etching Al from MAX phase materials, and may be composed of a wide range of early transition metals. These layered materials have high surface area and can be intercalated with ions or molecules. Key questions are how ions and reactive molecules enter into, move through and interact with the layers. It is possible that penetration of molecular reactants in electrochemical processes may be enhanced by the presence of intercalants which increase the interlayer spacing.

To study the role of water on interlayer structure and its dynamic, pristine and K-intercalated Ti₃C₂MXene have been studied by XRD, SANS, QENS and scanning probe microscopy. MXene has non-uniform stacks of MXene layers with gaps between them that hold the confined water with isotropic diffusion coefficient half that of bulk water. Intercalation of metal ions increase the c lattice parameter, taking up more water and giving improved homogeneity due to the formation of uniform stacking. The confined water may facilitate transport of the charges within the layers. QENS indicates a drop in the dynamics of the confined water after K-intercalation, due to the cumulative effects of ions upon the mobility of water in confinement. Contact resonance Atomic Force Microscopy (CR AFM) shows that cation intercalation into MXene leads to large volume changes. The attractive forces between the cations and the MXene sheet significantly increase the stiffness in the out-of-plane direction. While large K+ cations seem to have no influence on the mechanical changes, this effect was found to be enhanced when small cations such as Li⁺ were intercalated. The elastic modulus can thus increase by 15 GPa during the electrochemical cycling. The cation storage can therefore be imaged by monitoring the elastic coupling between the 2D sheets associated with the faradic reaction at the MXene/liquid interface.

To probe molecular interactions within the layers, we have performed INS studies of urea intercalation. INS vibrational and librational features clearly demonstrate the presence of intercalated urea. Comparison with spectra of bulk urea, Ti(urea)₆I₃ complex and urea intercalated Ti-MXene show how urea is affected by complexation and intercalation. In particular, variation in the -NH₂ deformation modes show H bonding interaction of the urea within the hydroxyl terminated Ti layers, and the librational modes indicate a confinement of the urea. Interestingly, INS shows the existence of trapped molecular H₂ in the pristine Ti-MXene that is detrapped as a result of intercalation.


This research was supported as part of the Fluid Interface Reactions, Structure and Transport (FIRST) Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences. Research was conducted at the Center for Nanophase Materials Sciences and Spallation Neutron Source, which are sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.
Title: 3D mapping of crystallographic phase distribution by energy-selective neutron tomography

Presenter: Dr. Dayakar Penumadu, University of Tennessee, Knoxville

Abstract: The study of crystallographic phase distributions and phase transformations is significant as these microstructural properties largely govern the global mechanical properties of advanced materials. Extensive studies of phase transformed materials are the focus of past and ongoing research, e.g. shape-memory alloys, recrystallization processes and materials exhibiting TRansformation Induced Plasticity (TRIP) effect. The available characterization methods (e.g. Electron Backscatter Diffraction, x-ray and synchrotron diffraction, optical microscopy) are destructive in their nature and/or a limited to the surface or small sized specimen. Diffraction Contrast Tomography and 3D-XRD, as employed at synchrotron sources, use the diffraction signal to produce three dimensional maps of grain shape and crystallographic orientation and are in principle capable of non-destructive phase mapping. However, those techniques are usually limited to small samples exhibiting a limited number of grains and more critically, the techniques are vulnerable when working with plastically deformed materials. The planned talk at SNS/HFIR user group 2015 will provide an overview on energy-selective neutron imaging approach that provides a non-destructive three dimensional representation of phase fractions by means of tomographic reconstruction. The method, which uses neutrons of selected wavelengths/energies to probe the energy dependence of the sample’s attenuation coefficient, is capable of mapping large volumes (cm³ range) with a (high) spatial resolution in the order of 50µm.

The presented technique uses energy-selective neutron transmission based radiography and tomography, by taking advantage of diffraction contrast due to Bragg scattering and the high penetration power of neutrons. The widely applicable technique is demonstrated for samples exhibiting strain-induced martensitic phase transformation (metastable 304L stainless steel), that have undergone controlled tension and torsional deformation. The distribution of austenitic and martensitic phase fractions within the three-dimensional reconstructed volumes agrees well with diffraction based measurements and transformation kinetics theory.

Related Publication:

Informing the Improvement of Forest Products’ Durability using Small Angle Neutron Scattering

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A better understanding of how wood nanostructure swells with moisture is needed to accelerate the development of forest products with enhanced moisture durability. Though, small angle neutron scattering (SANS) is well-suited to study wood nanostructure, it remains an underutilized tool in forest products research. Moisture-induced structural changes (1.3 – 600 nm) in intact and partially cut wood cell walls were investigated using SANS and a custom-built relative humidity (RH) chamber. SANS from intact wood sections cut from each primary orientation showed that wood scatters anisotropically across multiple length scales, and sample alignment must be carefully controlled. Tracking the swelling of the elementary fibril spacing (3 – 5 nm) as a function of RH, showed that the measurement of the elementary fibril spacing is independent of wood’s primary orientation; and that swelling of intact and partially cut wood cell walls only differs above 90% RH where partially cut wood cell walls swell more. Over the range of 25 to 85% RH, an increase of \textasciitilde16% in strain at the elementary fibril level revealed that the majority (\textasciitilde55%) of the transverse swelling of the S2 cell wall layer originates in the microfibrils. Hence, treatments meant to improve moisture-related dimensional stability must address swelling in the microfibrils. SANS also provided direct evidence of the creation of diffusion channels inside microfibrils during moisture sorption. Researchers can now use SANS to study wood protection treatments known to impart decay resistance and moisture durability and test their efficacy at the elementary fibril level.
Lithium ion battery technology has advanced significantly in the last two decades. However, future energy storage demands will require safer, cheaper and higher performance electrochemical energy storage. While the primary strategy for improving performance has focused on electrode materials, the development of new electrolytes has been overlooked as a potential means to revolutionize electrochemical energy storage. This work explores a new class of ceramic electrolyte based on a ceramic oxide with the garnet structure. The garnet, with the nominal formulation Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO), exhibits the unprecedented combination of high ionic conductivity (~1mS/cm at 298 K) and chemical stability against metallic Lithium. This presentation will discuss fundamental and applied aspects involving the development of garnet-based LLZO electrolyte. Specifically, the role that neutron diffraction plays in acquiring critical Li-ion site occupation will be discussed. The goal of this work is to correlate the atomic structure with transport data to hypothesize strategies for further increasing the ionic conductivity and to enable solid-state batteries.
Resolving the structure of Ti$_3$C$_2$Tx MXenes for energy storage applications and more

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MXenes are a recently discovered family of two-dimensional (2D) early transition metal carbides and carbonitrides. The 2D morphology, intercalation ability, good electronic conductivity, and tunable surface terminations make MXenes promising for energy storage and other applications, e.g., hybrid cells, electrochemical capacitors, sorption capacities for water purification systems, and supports for catalysts. The surface of the as-synthesized MXene has a mixture of moieties, including O, OH, and F, which adds versatility and complexity to this system. In this study, we describe and benchmark a novel way of modeling layered materials with real interfaces (diverse surface functional groups and stacking order between the adjacent monolayers) against experimental data. The structures of Ti$_3$C$_2$Tx MXenes (T stands for surface terminating species, including O, OH, and F) produced under different synthesis conditions were resolved for the first time using atomic pair distribution function obtained by high-quality neutron total scattering. The true nature of the material can be easily captured with the sensitivity of neutron scattering to the surface species of interest and the detailed “third-generation” structure model we present. The modeling approach leads to new understanding of MXene structural properties and can replace the currently used idealized models in predictions of a variety of physical, chemical and functional properties of Ti$_3$C$_2$-based MXenes.
Practical applications of using solid adsorbents for post-combustion carbon capture from flue gas depends upon CO$_2$ selectivity and fast kinetics of CO$_2$ adsorption/desorption rate, CO$_2$ regenerating efficiency, and stability and recyclability of the adsorbing material under the post-combustion conditions. Recently, we have created polymer-modified surfaces (viz. silicon) using dually-reactive BCPs comprised of glycidyl methacrylate (GMA) and deuterated vinyl dimethyl azlactone (dVDMA), PGMA-b-dPVDMA, and used neutron reflectivity to investigate thin film assembly and morphology. In this work, we build upon our earlier work in order to generate a functional surface for reversible capture and release of CO$_2$ (Figure 1).

The reversible capture and release of CO$_2$ by the amidine (MTHPBA) modified polymer surface were characterized by FTIR spectroscopy and QCM techniques as shown in Figure 2. Recently, our collaborative efforts at CNMS and SNS have led to the development of a unique multi-environment chamber to study via neutron scattering the effect of CO$_2$ capture-release on polymer thin films in-situ. This multi-environment chamber can achieve a base pressure of 10$^{-8}$ Torr and the CO$_2$ can be introduced to the chamber with a selective pressure from 0.01 Torr to 1000 Torr. Preliminary investigations with this new multi-environment chamber revealed that as cast films (~35 nm thick) segregates into four layers with a PGMA rich surface. Upon CO$_2$ exposure, the SLD of both the PVDMA and PGMA rich regions increase accompanied by an overall ~5% film contraction. Heating returns the film to its original thickness (Figure 3) thereby proving the reversibility of CO$_2$ capture-release process.

References


Towards a controlled growth of low-dimensional (hetero)structures and their (opto)electronic properties

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Substrates can have significant effects on the growth of nanoscale organic based semiconductors. Theory explains how the metal-incorporated crystalline organic nanowires (1D), films (2D), and nanoislands (0D) can be selectively grown by interaction with the substrates [1-4]. A precise description of intermolecular interaction and interaction with substrates is necessary to capture the formation of the experimentally observed molecular configurations. We have combined first-principles density functional theory (DFT) based approaches to effectively describe different levels of interaction. Here we present the prominent properties of 2D materials [5-10] and their interfaces [11-14] for energy and (opto)electronic applications. By combining DFT based approaches, we can effectively explore the configuration space of various 2D materials [5-14] and the effect of the interlayer registry [11] and the role of substrates on their electronic properties [13].

An aerodynamic sample levitator with laser beam heating was fully integrated with the NOMAD instrument in 2014. The new capability enables in-situ measurements of structures at extreme temperatures between 700 and 3000 °C in conditions that completely avoid contact with container surfaces. In addition to maintaining sample purity, the use of levitation enables deep supercooling and high degrees of supersaturation in liquids and it frequently enhances glass formation. The levitator is particularly useful for studying materials at temperatures of 1500 °C and above where chemical reactions with containers are major barrier to making measurements. There is currently very limited structural data on scientifically and technologically important glass and ceramic materials that require processing at high temperatures. The high neutron flux available at NOMAD and careful attention to lowering backgrounds also enables work with lower contrast isotopes, and understanding the structural role of selected cations and anions in extreme conditions of temperature and/or far from equilibrium.

The instrument has already been used to study a variety of liquids and solids at extreme temperatures. Examples of measurements made include total and isotopic difference functions for calcium silicates and Group II metal titanates, pure solid and liquid rare earth oxides, aluminum oxide, zirconium oxide, binaries based on magnesium, yttrium, lanthanum and zirconium oxides and high entropy metallic alloys. To date the scientific interest has focussed mainly on geological materials, glass formation, solid state phase transitions and anion sublattice disorder in crystals. Possible directions for future work include those which are already being pursued with high energy x-ray diffraction at the APS, namely effects of f(O_2)-induced oxidation state changes of cations on the structure of melts, high temperature disorder in nuclear materials and the temperature-dependent structural changes in supercooled liquids.
Chamber for Mechanical Testing in Gaseous Environments with Observation by Neutron or X-ray Scattering

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A gas-pressure chamber has been designed, constructed, and tested at a moderate pressure (3.4 MPa, 500 psi) and has the capability of mechanical loading of steel specimens for neutron and synchrotron x-ray scattering measurements. The chamber will allow a variety of \textit{in situ} neutron scattering measurements: in particular, diffraction, quasielastic, inelastic, and imaging, as well as synchrotron x-ray measurements with incident radiation energy above 80 keV. The chamber is compatible with load frames available at the user facilities at Argonne National Laboratory Advanced Photon Source, the NIST Center for Neutron Research, and Oak Ridge National Laboratory Spallation Neutron Source.

The primary motivation for the combined gas- and mechanical-loading chamber described in this paper is to study the effect of hydrogen embrittlement in steels. With hydrogen embrittlement, steels lose ductility and exhibit fatigue crack growth rates (FCGRs) 10 to 100 times larger in a H₂ environment compared to air\(^1-5\). Because of the fast diffusion of H₂ from the steels, the effect of hydrogen embrittlement presents only during exposure, and steel specimens will exhibit in-air fatigue crack growth rates shortly after being removed from a hydrogen environment (\(\approx 45 \text{ min.}\))\(^6\). Thus, any measurements designed to study hydrogen embrittlement and hydrogen-enhanced fatigue crack growth must be performed \textit{in situ}.

I. REFERENCES

Magnet Technologies for Neutron Science in Magnetic Fields Over 25 T

SNS/HFIR User Group 2015 Meeting

Dixon, Bird, Boebinger, Weijers

Abstract

The NHMFL recently delivered a 26 T hybrid magnet system to the Helmholtz-Zentrum Berlin (HZB) for completion of their new state-of-the art facility for neutron science, the High Magnetic Field Facility for Neutron Scattering. This HZB Series-Connected Hybrid magnet constitutes a 47% increase in field coupled with a 100% increase in solid-angle over other magnets available for neutron scattering. The magnet system, engineered and fabricated at the NHMFL, consists of a hybrid combination of water-cooled resistive coils and a superconducting solenoid with axis horizontal and a 30° conical bore (50 mm diameter at center). A peak field of 30 T can be realized with power upgrades.

The 26 T HZB SCH opens up a new experimental parameter space and raises the bar for future instruments requiring intense, continuous magnetic fields. While this has been made utilizing a hybrid approach, other methods of attaining higher magnetic fields exist. These technologies include magnets with only resistive coils or with only superconducting coils containing high temperature superconductor (HTS). The NHMFL is currently pursuing ultra-high field magnets using various types of high temperature superconductor and insulation configurations. A 32 T user magnet utilizing insulated YBCO HTS will be put into service at the NHMFL in 2016 for condensed-matter science. Designs have been made using similar magnet technology for neutron scattering applications which can produce 30 T in a conical configuration and 25 T in a split configuration. By reducing the amount of insulation on HTS, highly compact magnets show potential to reduce costs while achieving ultra-high fields. The latest concepts of these approaches are presented, with an emphasis on their technological maturity and relative costs.
In situ compaction of powders simultaneously characterized by GP-SANS and Impedance Spectroscopy Measurements

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Combining the collection of impedance data with SANS data to measure changes in electrical properties and changes in the size and volume distribution of scattering objects simultaneously during the compaction of a powder has not been attempted before. Such data is potentially very telling of how the different powders behave during compaction and may lead to standardization of electrical property-porosity correlation curves. Our recent series of tests focus on gathering in-situ measurements of the SANS vs Q curves and the impedance properties as a function of frequency for a variety of ceramic powders during compaction. To accomplish this, the powders are placed inside a custom-fabricated die mounted on a load frame, which was used to compact the powders. The metal punches, which apply pressure to the powders, also act as electrodes for the impedance spectroscopy measurements that are run in situ continuously during the compaction process. The entire load frame assembly is placed in the beam path of the GP SANS instrument at the HFIR to allow for the measurement of the porosity of the powders at specific discrete pressures. The ORNL SPICE package for the Igor software is used to reduce the data and the Irena software package for Igor is used to analyze the reduced data. The results clearly show sequential, concurrent decreases in resistivity as the applied pressure increases. Analysis of the SANS scattering results require further evaluation, but overall, the results demonstrate the potential of this new testing facility.
Expanding Pressure Capabilities for Neutron Science

Pressure changes the state, bonding and energy of matter more than any other variable. These effects have been extensively studied by spectroscopy and X-rays for many decades. For neutrons, pressure ranges have been very limited due to the required large sample volumes and limited neutron flux. We have shown at SNAP that the flux provided by SNS now allows diffraction experiments at thus unprecedented pressures in the megabar (100 GPa) range with excellent signal-to-noise patterns and relatively short exposure times. With the present development of very large diamond anvils by the CVD process it will be now possible to expand such measurements for other beamlines at SNS thus creating new opportunities for studying structural changes, bonding and dynamics of highly compressible hydrogen-rich materials.
The HB-2D Polarized Neutron Development Beamline at the High Flux Isotope Reactor

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The Polarized Neutron Development beamline, recently commissioned at the HB-2D position on the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory, provides a tool for development and testing of polarizers, polarized neutron devices, and prototyping of polarized neutron techniques. With available monochromators including pyrolytic graphite and polarizing enriched Fe-57 (Si), the instrument has operated at 4.25 and 2.6 Å wavelengths, using crystal, supermirror, or He-3 polarizers and analyzers in various configurations. The Neutron Optics and Development Team has used the beamline for testing of He-3 polarizers for use at other HFIR and Spallation Neutron Source (SNS) instruments, as well as a variety of flipper devices. Recently, we have acquired new supermirror polarizers which have improved the instrument performance. The team and collaborators also have continuing demonstration experiments of spin echo focusing techniques, and plans to conduct polarized diffraction measurements. The beamline is used to support a growing use of polarization techniques at present and future instruments at SNS and HFIR.