Book of Abstracts

SNS and HFIR

Neutron Sciences User Meeting

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Oak Ridge National Laboratory
High Flux Isotope Reactor
Spallation Neutron Source
U.S. Department of Energy
Office of Science

Plenary Speaker Abstracts

Advancing the Science of Oxyanion-Based Superprotonic Conductors

Sossina M. Haile

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Superprotonic solid acid electrolytes, materials with chemical and physical properties intermediate between conventional acids (*e.g.*, H_3PO_4) and conventional salts (*e.g.*, Cs_3PO_4), have emerged as attractive candidates for fuel cell and other electrochemical applications. Key characteristics of these materials are tetrahedral oxyanion groups linked by hydrogen bonds, and a polymorphic structural transition to a disordered state at moderate temperatures. Rapid oxyanion reorientation and dynamic disorder of the hydrogen bond network facilitate high proton conductivity in the high temperature phase. Materials exhibiting a superprotonic transition include $CsHSO_4$, $Cs_3H(SeO_4)_2$, CsH_2PO_4, and $Cs_2(HSO_4)(H_2PO_4)$. Here we review the present state of understanding of proton transport mechanisms and the factors governing the transition behavior as gathered from a range of measurements techniques, highlighting the critical role of neutron scattering for determining structure and evaluating dynamics. We focus in particular on CsH_2PO_4 due to its technological value in near-commercial fuel cell demonstrations. Dramatic changes in phase behavior and proton conductivity of the base material can be induced by only minor changes in chemistry, suggesting routes for tuning behavior to achieve desired outcomes.

Stroboscopic Neutron Scattering and Magnetic Relaxation in Spin Ice*

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Event mode neutron detection offers unique opportunities for probing dynamic materials properties over time scales ranging from 10 μs to hours that are so far largely unexploited. Driving a sample periodically with a suitable perturbation (magnetic, electrical, optical, or mechanical), each detected neutron reflects the state of the sample when it was scattered. This makes it possible to add a sample time dimension to virtually any neutron scattering experiment where the time of interaction can be inferred from the neutron detection time. Both continuous and pulsed source instruments can thus be retrofitted for stroboscopic scattering and they offer complementary capabilities for perturbations with distinct time structures and duty-cycles.

After reviewing the state of the art and discussing future opportunities, I shall describe our recent use of stroboscopic neutron diffraction to probe the response of spin-ice to abrupt changes in the applied magnetic field [1]. The experiment was conducted on a new class of ultrapure $Ho_2Ti_2O_7$ single crystals and when combined with AC SQUID magnetometry, it covered almost 10 decades of time scales. The experiment resolved apparent discrepancies between prior measurements on more disordered crystals and revealed a thermal crossover between distinct relaxation processes. Magnetic relaxation at low temperatures ($T<1$ K) is associated with monopole motion through the spin-ice vacuum, while at higher temperatures, relaxation occurs through reorientation of increasingly spin-like monopolar bound states. Spin fractionalization is thus directly manifest in the magnetic relaxation dynamics of spin ice on the second time scale, which is accessible with stroboscopic neutron scattering.

* Work supported as part of the IQM EFRC funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under award no. DE-SC0019331. Development of the time-resolved neutron scattering methods was supported by the Gordon and Betty Moore Foundation's EPiQS Initiative under GBMF4532 and GBMF9456.

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Solution structures of an intramembrane aspartyl protease and its lipid bilayer environment obtained via SANS

Raquel L. Lieberman

Sepcic-Pfeil Professor

School of Chemistry & Biochemistry

Georgia Institute of Technology

Membrane-bound enzymes are notoriously challenging to study biochemically, and for most classes, basic structure-function questions remain unanswered. Membrane-bound enzymes require a lipid environment for function, which can be challenging to mimic in the lab. In this talk, I will show how my lab has used small angle neutron scattering (SANS) to better understand the organization of intramembrane aspartyl proteases (IAPs), integral membrane proteases that use aspartates to hydrolyze substrates within the water-depleted hydrophobic lipid bilayer, in different lipid-mimicking environments. I will describe how we used contrast matching of different components, as well as deuterating the IAP and selected other components, to isolate the signal of interest. Our studies provide new insight into the oligomerization of IAPs in connection to enzymatic properties. More broadly, a similar SANS approach with contrast matching could be useful for other membrane-bound protein and enzyme systems.

Investigating the stability of monoclonal antibodies in solution and at interfaces using NSE, NR, & SANS with applications in formulation science.

Norman J. Wagner
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Unidel Robert L. Pigford Chair in Chemical and Biomolecular Engineering
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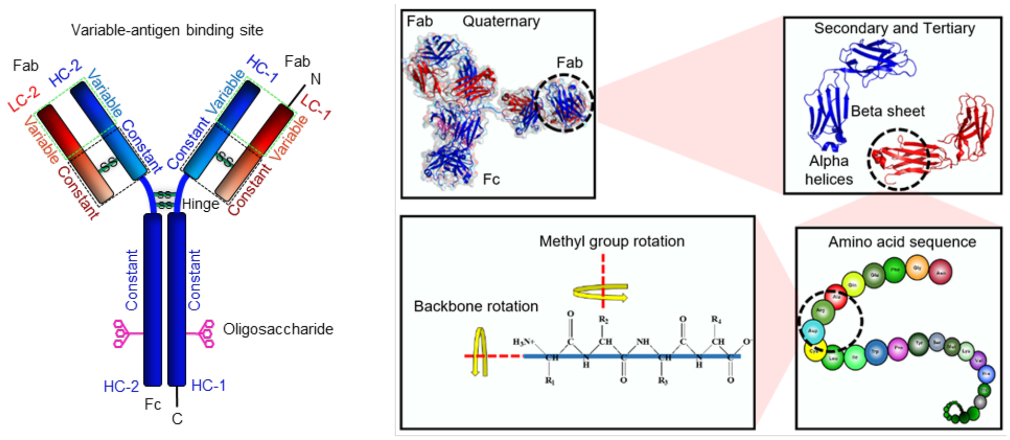
Biophamaceuticals comprise over 100 billion USD in global sales and have revolutionized human health care. Neutron scattering measurements are uniquely positioned to answer some key questions in the biopharmaceutical industry as they cover length scales from the nanoscale to the microscale as well as pico-to-100 nanoseconds dynamics. I will discuss the use of neutron techniques to aid in the development of biopharmaceuticals by providing examples from our work on the use of neutron measurements to solve fundamental questions concerning monoclonal antibodies and their formulations. This includes studies of excipients as well as mAbs in solution and at interfaces. Examples include recent studies using neutron spin echo to determine the internal dynamics of the NIST standard mAb, as well as industrial mAbs, in solution. The adsorption of mAbs at surfaces and interfaces are probed using a variety of surface methods, including NR. Opportunities for new multimodal methods combining surface rheology and neutron and x-Ray reflectometry are also discussed.



A) Artistic rendition of the quaternary structure of NISTmAb (IgG1) with two Fabs and one Fc linked via di-sulfide hinges. B) Ribbon quaternary NISTmAb structure with van der Waals surface, tertiary beta sheets and secondary alpha helices formed due to interactions between polar, nonpolar and neutral amino acid groups, and primary structure contains chemical groups (*e.g.*, methyl groups) that can rotate and fluctuate. NISTmAb structure figures are based on the NISTmAb composite model PDB and created with PyMOL version 2.3.0. Figure couresty of Dr. Jannat Nayem.

Inspiring the next generation of neutron scatterers

Allyson Fry-Petit
California State University, Fullerton

Performing neutron experiments for the first time often ignites a passion for performing experiments at user facilities; however, for many, that opportunity is not realized until graduate school. Several faculty at primarily undergraduate institutions have made it their focus not only to utilize these facilities but to provide opportunities to students in undergraduate and masters programs to experience neutron measurements firsthand. Thus igniting a passion that hopefully will direct a more diverse pool of scientists to utilize neutrons in graduate school and their future careers. This talk will cover the differences in performing experiments with less experienced students versus doctoral students and the spectrum of PUI institutions that aim to engage students in these types of transformational experiences. We will also discuss the role of remote experiments in undergraduate and masters student engagement. Lastly, we will provide time for discussion on how we as a community can support the development of neutron scientists at earlier stages of their academic journey.

Invited Speaker Abstracts: Quantum Materials

Antiferromagnetic-ferromagnetic homostructure and Dirac magnons in CrI3 van der Waals magnet

Author:

Despina Louca

Van der Waals (vdW) Dirac magnon system CrI3, a potential host of topological edge magnons, orders ferromagnetically (FM) (Tc=61 K) in the bulk, but antiferromagnetic (AFM) order has been observed in nanometer thick flakes, the latter enabling large tunneling magnetoresistance. Its structure is monoclinic (M) at room temperature, and it undergoes a layer-sliding transition to a rhombohedral (R) phase below ~180 K. The transition is often inhibited, in which M-type layer stacking persists to low temperatures, an effect that is prevalent in thin films and powders. We report neutron scattering measurements on a powder CrI3 sample where over half of the structure remained M-type even down to 5 K. Elastic measurements showed that an AFM transition is clearly present below ~50 K, coexisting with the FM order of R-type stacking, demonstrating the coexistence of two types of Dirac magnons. Inelastic measurements showed a decrease in spin wave energy relative to reported R-phase data, which is consistent with a smaller interlayer magnetic coupling in M-type stacking. A gap is present at the Dirac point, suggesting that the same factors which open a gap in the R phase, resulting in potentially nontrivial magnon topology, may be present in the M phase as well. Signatures of the mixed M/R stacking can also be seen in magnetization data, in the form of a coercive field that decreases to zero above ~50 K. Thus, we show that the mixed M/R stacking provides a natural homostructure of AFM and FM layers in the bulk as well as in thin films.

Electronic liquid crystal state in a kagome lattice antiferromagnet

Author:

Pengcheng Dai

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A nematic phase originates from a state where elongated molecules in liquid crystals exhibit no crystalline positional order but are aligned with their long axes approximately parallel to form directional order with twofold rotational (C_2) symmetry. In some quantum materials and twisted bilayer graphene, correlated electrons can also exhibit an electronic nematic phase, in which the electronic degrees of freedom are spontaneously broken into the C_2 symmetry, often as part of complex intertwined phases with profound impacts on their properties. While two-dimensional (2D) kagome lattice metals consisting of corner-sharing triangles exhibit many interesting phases, an electronic nematic phase with C_2 symmetry has only been reported in weakly electron correlated, non-magnetic AV3Sb5 (A = K, Rb, Cs); no such phase is known in correlated magnetic kagome lattice metals. Here, we report the discovery of an electronic nematic phase in the kagome lattice magnet FeGe, in which antiferromagnetic (AFM) spin correlations form one-dimensional (1D) stripes in the structurally distorted 2D kagome plane below T_N, phase separated from the AFM ordered phase analogous to spin-charge separated liquid-crystalline stripes in copper oxides. The C_2 symmetric nematic phase and associated lattice distortions compete with the A-type AFM order on warming to T_N and become isotropic paramagnetic scattering with restored C_3 kagome lattice symmetry above T_N. These results provide an unprecedented example of an electronic nematic phase that competes and coexists with magnetic order within a broad temperature range below T_N. This is in stark contrast to the theoretically predicted nematic phase at temperatures intermittent between an electronic crystalline solid and isotropic (disordered) liquid for quantum materails.

“Neutron Scattering: A Vital Probe to Study Quantum Magnets”

Author: Sara Haravifard

“Frustrated magnetism is a fruitful frontier in the contemporary field of quantum magnets, wherein mutually incompatible interactions, driven by the arrangement of the magnetic ions and their exchange couplings, can lead to a variety of exotic phenomena. Due to the dependence on lattice geometry, materials with specific lattice structures may offer untapped opportunities for the exploration of new and exotic physics. Recently, rare-earth-based triangular lattice compounds have garnered renewed excitement, where experimental techniques such as neutron scattering have proven vital in providing insight into their physical properties. In this talk, we will present the results obtained for a new family of rare-earth-based triangular lattice compounds using neutron scattering and will provide an overview of the future research directions for these interesting systems.”

Probing magnetism in intrinsic magnetic topological insulators via neutron scattering

Ni Ni
University of California, Los Angeles

Magnetic topological material provides a great platform for discovering new topological states, such as the axion insulators, the Chern insulators, and the 3D quantum anomalous Hall (QAH) insulators. Recently, MnBi2Te4 was discovered to be the first material realization of an intrinsic antiferromagnetic topological insulator (TI) where the QAH effect was observed at a record high temperature in its two-dimensional limit. Since the interplay of themagnetism and band topology determines their topological natures, understanding and manipulating the magnetism inside magnetic TIs will be crucial. In this talk, I will discuss how neutron scattering experiment has helped to understand the magnetism and chemical defects in this intrinsic magnetic topological insulator family.

TITLE

Spin-liquid-like state in ferroelectric $TbInO_3$ with a nearly triangular lattice

Valery Kiryukhin

ABSTRACT

Hexagonal $TbInO_3$ exhibits a nearly triangular lattice (TL) of non-Kramers Tb^{3+} magnetic ions (eight 4*f* electrons). It has been discussed as a spin-liquid candidate material. We present inelastic neutron scattering studies in single crystals of $TbInO_3$. At low energies, a broad and apparently gapless continuum of magnetic excitations, located at the TL Brillouin zone boundary, is observed. The data are well described by the uncorrelated nearest-neighbor valence bonds model. At higher energies, a broad excitation branch dispersing from the TL zone boundary is observed. No signs of static magnetic order are found down to the temperatures two orders of magnitude smaller than the effective interaction energy. The fluctuating magnetic moment exceeds two-thirds of the Tb^{3+} free-ion value and is confined to the TL plane. These observations are consistent with a TL-based spin liquid state in $TbInO_3$. Interestingly, $TbInO_3$ is a ferroelectric whose symmetry supports non-reciprocal effects, including those in the magnetic subsystem. Observation of such effects is so far hindered by the domain structure of single crystal samples. We discuss the topological domains in $RInO_3$ and ways of controlling their size and type, and present novel techniques of antiferromagnetic domain imaging, including dynamic studies.

Invited Speaker Abstracts: Functional/Energy Materials

Using Neutron Scattering to Reveal Complex Dynamics of Ions in Energy Materials

Olivier Delaire
Thomas Lord Department of Mechanical Engineering and Materials Science,
Physics Department, Chemistry Department,
Duke University

A better understanding of atomic motions in solids is critical to design improved materials for a wide range of energy applications. Neutron scattering provides us with key insights into a wide range of atomic dynamics in solids, from fast ionic diffusion in solid-state electrolytes to phonon propagation and thermal transport in thermoelectrics, or electron-phonon coupling and phase transitions in metal-halide perovskites for photovoltaics and optoelectronics. Our group combines state-of-the-art neutron and x-ray scattering techniques together with atomistic materials modeling to probe and rationalize atomic dynamics. This presentation will highlight results from our investigations of atomic dynamics in several classes of materials impacted by strong anharmonicity and a proximity to lattice instabilities, such as halide perovskite photovoltaics, thermoelectrics, and superionic conductors [1-6]. In these materials, we have found that one needs to properly account for the effect of strong anharmonicity, which disrupts the quasiharmonic phonon gas model through large phonon-phonon coupling terms. Large phonon amplitudes can also amplify the electron-phonon interaction and lead to renormalization of a material's electronic structure. Similarly, phonons of the host framework couple with hopping of mobile ions in superionic conductors, and significantly impact the bulk diffusivity. Such interactions, often neglected in textbooks, remain insufficiently understood but could open the door to new and improved material functionalities. By mapping spatio-temporal correlations throughout reciprocal space, complex atomic dynamics can be studied in detail. Our first-principles simulations enable the quantitative rationalization of these effects, for example with ab-initio molecular dynamics simulations and machine-learning accelerated simulations.

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Development of transmission measurements capability at VISION spectrometer

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Kemal Ramic

Co-author:

Jesse Brown

Historically, for the purposes of neutronics calculations using Monte Carlo neutron transport codes, the free gas approximation has been used to model the scattering of neutrons in the thermal energy range (below 5 eV) for many materials. However, this approach is known to inadequately reproduce neutron scattering at these energies. Until recently, only a limited number of materials had available thermal scattering law (TSL) evaluations in the Evaluated Nuclear Data Format (ENDF) libraries for this energy range. With advancements in atomistic modeling techniques, such as molecular dynamics, ab-initio molecular dynamics, and density functional theory, TSL evaluations have become available for many more materials. Validating nuclear data in the thermal neutron energy region requires several forms of benchmarks, ranging from differential (INS measurements) to quasi-integral (total cross-section as determined by transmission measurements and pulsed-neutron-die-away (PNDA) measurements) benchmarks. Currently, high-precision transmission measurements in the thermal energy region are only available in the US at the Gaerttner Linear Accelerator located at Rensselaer Polytechnic Institute (RPI), which is difficult to access and expensive. To address this issue, we have started developing transmission capability at the VISION beamline at the Spallation Neutron Source (SNS). This will provide a second location to perform transmission validation measurements, and it will also serve as a location to perform both double differential scattering measurements and quasi-integral benchmarks. Capability to measure high-temperature transmission will also be unique in the US.

Residual Stress and Stress Relaxation Cracking Susceptibility in Stainless Steel Welds

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Abstract: Stress relaxation cracking (SRC) has been reported as one of the main mechanisms contributing to failures in austenitic steels in multiple countries in heat-affected zone (HAZ) and weld metal, particularly in HAZ without post weld heat treatment (PWHT). A fundamental understanding of the failure conditions can be achieved by combining finite element modeling, residual stress mapping, thermodynamic calculations, thermomechanical experiments, and metallurgical characterizations. In this study, the cracking susceptibility of 347H stainless steel weldments made with matching and alternative filler metals was evaluated. The susceptible microstructural characteristics and critical threshold residual stress/strain as a function of temperature for SRC was identified for HAZ of 347H and different weld metals. Finite element models validated by neutron diffraction measurement were used to reveal the impacts of plate thickness and joint geometry design on the evolution of residual stress and susceptibility to SRC.

In situ neutron diffraction study of oxygen motion

Allyson Fry-Petit
California State University, Fullerton

To understand the complex structural evolution of oxygen transport membranes such as $La_{0.9}Sr_{0.1}Co_{1-x}Fe_xO_{3-\delta}$ ($x = 0, 0.25, 0.75, 1$)(LSCFO) under industrially relevant conditions *in situ* neutron diffraction data was collected and quantitatively analyzed via Rietveld refinements. Both temperature and gas atmospheres were modulated, and the weight percents of all intermediate phases were determined. These experiments led to a structural mechanism in the cobalt-rich phase that transforms the perovskite structure into the layered Ruddlesden Popper phase through exfoliation of the layers and liberation of a B-site oxide. Cobalt-rich phases formed reduction products at earlier temperatures than iron-rich phases and showed significantly different phase transitions during reactions, providing mechanistic insights into what phases are catalytically active at specific conditions. All systems showed redox cycling despite multiple structural phases being present throughout the redox process. This study gives insight into the structural changes accompanying redox reactions in oxygen transport membranes and how to utilize *in situ* diffraction measurements to study these systems under extreme conditions.

Influence of Interlayer Cation Ordering on Na^+ Transport in P2-type $Na_xNi_yMn_zO_2$ for Sodium-Ion Batteries

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The P2-type $Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ (PNNMO) has been demonstrated as a promising positive electrode material for sodium ion batteries. The structure is composed of two (2) alternating layers of transition metal octahedra and face-sharing prismatic (P) sodium sites that result in fast Na^+ diffusion, which is attractive to enable fast charging and discharging. Within individual transition metal layers, the Ni^{2+} and Mn^{4+} ions in PNNMO are known to exhibit a honeycomb-like ordering[1] as a result of their different size and valence (Fig 1). The Na^+ ions and vacancies in PNNMO are also known to exhibit a 'large zig-zag' ordering, which is absent in $Na_{2/3}Ni_{1/4}Mn_{3/4}O_2$ (NM13). The intralayer ordering (within individual layers) is well known to influence the Na transport properties, but interlayer (between several layers) ordering has not been systematically investigated. We show that by altering the interplanar ordering via previously demonstrated controlled Li doping strategy[2] ($Na_{2/3-x}Li_yNi_{1/3}Mn_{2/3}O_2$; PNNMO: x = y = 0: LFNy: x=0, y=0.05,0.1,0.2; LSNx: x = y = 0.10) we can achieve enhanced Na diffusion kinetics without disrupting the Na/vacancy ordering. The interlayer cationic stacking sequence in honeycomb ordered P2 structures is explained in terms of ABAB and/or ABCABC interlayer stacking modes (Fig 1) using neutron powder diffraction (NPD). Simulations incorporating cationic stacking faults (ABC-like regions) in the mostly ABAB ordered PNNMO material can explain the disorder evident in the NPD pattern. A simulated clustered faulting model is proposed to explain the NPD pattern of LFN samples, which have ABAB and ABCABC-type clusters. Quasielastic Neutron Scattering (QENS) establishes the association between the interlayer ordering schemes and Na^+ diffusion properties. Thermally disrupting the Na^+/vacancy ordering changes the diffusion mechanism in PNNMO. QENS further suggests that Na^+ diffusion can be enhanced by the incorporation of ABCABC ordered domains via Li doping without disruption of Na^+ vacancy ordering. However, the electrochemical rate performance is not predictable solely on the basis of the diffusivity measured by QENS. Synthesis methods to control the interlayer cation ordering could be a valuable direction for the development of high-power electrode materials.

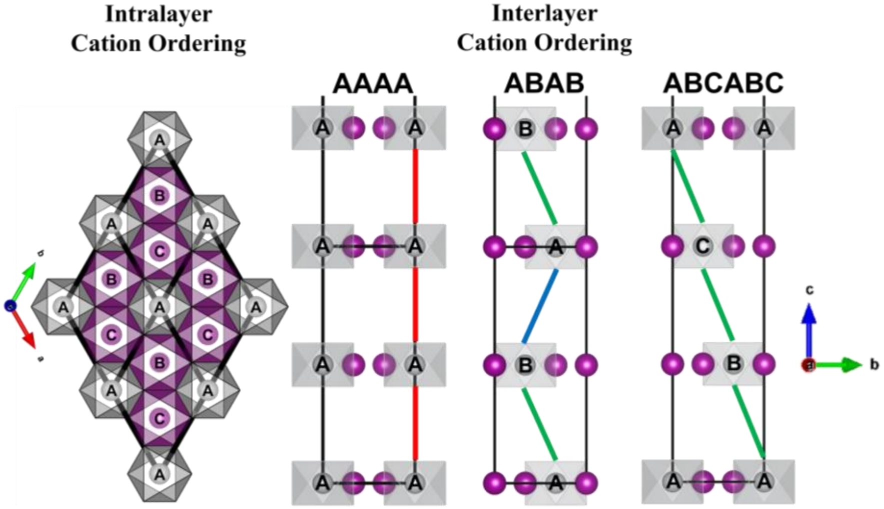

Figure 1. The intralayer Ni^{2+}/Mn^{4+} honeycomb ordering and different interlayer ordering schemes.

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High pressure preparation and properties of helium containing fluoroperovskites

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In 2017, we reported that compression of $CaZrF_6$ in helium at room temperature, and pressures of less than 0.5 GPa, led to the formation of the defect perovskite $[He_{2-x}\square_x][CaZr]F_6$, and the incorporation of helium modified the material's negative thermal expansion.[1] Our subsequent work showed that $[He_2][CaZr]F_6$ likely forms at pressures ~ 1 GPa and that this materials is stable to high pressures unlike $CaZrF_6$.[2] Remarkably, this perovskite still shows negative thermal expansion and, on compression at low temperature, it shows a tilting transition typical of perovskites. This prompted an exploration of other frameworks that could incorporate helium to form new perovskites. The behavior of $NaNbF_6$, $CaNbF_6$ and ScF_3 in high pressure helium, as seen by high pressure diffraction and direct helium uptake/release measurements, will be presented.

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Invited Speaker Abstracts:

Biology & Life Sciences

The orientation of KRAS at the plasma membrane helps recruit RAF kinase

Andy Stephen
Frederick National Laboratory for Cancer Research

KRAS is a small GTPase that is frequently mutated in human cancers, particularly pancreatic, colorectal and lung cancer. Engagement of mitogens with transmembrane receptor tyrosine kinases result in the activation of KRAS from an inactive GDP to active GTP bound state. Localized on the inner leaflet of the plasma membrane, active KRAS-GTP serves to recruit RAF kinase to the membrane where it undergoes activation. Oncogenic mutations lock KRAS in the active GTP state resulting in dysregulated cellular growth and proliferation. We have used a combination of biophysical methods and computational simulations to investigate the molecular details of these first steps in signal transduction. Specifically, NMR and neutron reflectivity of KRAS bound to lipid mimetics coupled with coarse grained molecular dynamics simulations reveal that KRAS is predominantly extended from the membrane making only transiently interacts with the membrane. This orientation at the membrane allows KRAS to efficiently recruit RAF from the cytoplasm for activation at the plasma membrane.

Looking at rafts from different perspectives: Four techniques to detect lipid domains

Frederick A. Heberle, University of Tennessee

The organization of biological membranes into structurally and compositionally distinct domains (termed lipid rafts) is thought to play a crucial role in the life of a cell. Rafts are small and transient under most conditions, and their existence in resting cells has been controversial due to a lack of methods with appropriate spatial and temporal resolution. In this talk, I discuss four complementary techniques for probing the lateral organization of membrane lipids. Fluorescence microscopy provides direct, real-space images of coexisting lipid phases but is limited to domain sizes larger than the diffraction limit of visible light (typically a few hundred nanometers). Among techniques with nanoscopic resolution, FRET can detect lipid clustering on length scales as small as a few nanometers but relies on strong partitioning of the probes between ordered and disordered phases. Neutron scattering, when combined with selective lipid deuteration and contrast matching, is sensitive to domains larger than ~ 5 nm and provides a robust ensemble-averaged signal of lateral lipid heterogeneity, though quantitative information (e.g., domain size distributions) remains challenging to extract from the data. The most recent addition to the nanoscopic toolkit is cryogenic electron microscopy, a direct imaging technique in which the ability to visualize phase separation is provided by intrinsic thickness differences of ordered and disordered domains. Like SANS, cryo-EM does not rely on extrinsic probes that can perturb phase behavior, with the additional advantage of single-vesicle resolution.

Using neutron scattering to improve wood's durability

Nayomi Plaza
USDA Forest Service

Understanding and controlling water in wood is critical to both improving forest products moisture durability and developing new sustainable forest products-based technologies. While wood is known to be hygroscopic, there is still a lack of fundamental understanding on the nanoscale wood-water interactions that are necessary for increased moisture-durability and dimensional stability. Neutron scattering techniques, such as small angle neutron scattering (SANS) and quasielastic neutron scattering (QENS) are suitable to study the elusive nanoscale wood-water interactions and provide new insights. The main advantage of these techniques is that these can probe experimentally the nanostructure of both unmodified and chemically modified wood with minimal sample preparation and in situ humidity control. Using SANS, we have probed the effects of moisture induced swelling as well as chemical modifications on the wood nanostructure. Our studies have revealed that chemical modifications altered the water distribution inside the cell wall, and the most effective modifications at reducing brown rot fungal degradation also reduced the microfibril swelling. Additionally, QENS with in-situ humidity control have allowed us to probe the changes of bound water dynamics in both unmodified wood and chemically modified wood cell walls.

Protein Vesicle Characterization by Neutron Scattering

Julie Champion

Protein vesicles incorporating functional, globular proteins have potential in a number of bio-applications such as drug delivery, biocatalysis, and sensing. We have previously self-assembled protein vesicles from mCherry-zipper-ELP protein complexes where ELP is a thermo-responsive elastin-like polypeptide, zipper is a coiled-coil, and mCherry is a model folded protein. As we utilize these vesicles in different applications with different folded proteins, there is a need to understand and control vesicle self-assembly to tune their size, membrane structure, stability, and stimuli responsiveness. Control can be achieved through process conditions including temperature, protein and salt concentration, and heating rate or through protein specific parameters such as ELP sequence and molecular weight, molecular weight of folded protein (mCherry substitute), and ratio of folded protein to ELP. While light scattering and microscopy can be used for vesicle characterization, they do not give molecular level information. We have used small angle neutron scattering to understand the membrane structure of vesicles and state of the ELP component. With this understanding, properties can be controlled and the wide range of vesicle properties enable application of protein vesicles as versatile functional and responsive protein materials.

Small- and wide-angle neutron and X-ray scattering in characterization of pharmaceutical and biotech systems.

Evgenyi Shalaev, AbbVie, Irvine, CA

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Active pharmaceutical ingredients (API) represent a wide range of materials, from small organic molecules to enzymes, monoclonal antibodies, lipid nanoparticles, viruses, and cells. All pharmaceutical and biopharmaceutical dosage forms also contain inactive pharmaceutical ingredients (excipients) and solvents. The excipients cover similarly vast chemical space, including, e.g., water, salts, sugars, organic polymers, and even proteins such as human serum albumin. In addition to chemical diversity, the dosage forms (i.e., API+excipients systems) possess various levels of structural complexity, as they can be present as aqueous solutions in either liquid or frozen state, colloidal systems, suspensions, single- and multi-phase amorphous solids, crystalline mesophases, and highly ordered crystalline materials.

Development of novel drugs requires thorough understanding of the structural features of these systems on the length scale of angstroms to hundreds of nanometers. Therefore, small- and wide-angle neutron and X-ray scattering methods (SANS/WANS and SAXS/WAXS) represent essential tools in providing such information for all stages of drug development process, from early pre-clinical studies through 3 stages of clinical investigations and finally for development and manufacturing of commercial pharmaceuticals. For example, high-sensitivity synchrotron WAXS (sWAXS) has been used to detect onset of crystallization in amorphous pharmaceuticals while high-resolution sWAXS have been applied to study interaction of pharmaceutical proteins with ice during freezing. SAXS and SANS have been applied to monitor protein/protein interactions (as a pre-cursor to aggregation) during freezing and drying, while WANS provided pharmaceutically-relevant fundamental information on amorphous polyhydroxycompounds and their mixtures with water.

The presentation provides two examples of SANS and SAXS/WAXS studies of pharmaceutically-relevant systems. In one study, protein-protein interaction and crystalline and liquid-crystalline phases of excipients are monitored during freezing of model biopharmaceutical formulations, while second study outlines application of SANS/WANS, complemented with Infrared and Raman spectroscopy, for structural investigation of polyol/water glasses. The later study address fundamental questions, which are essential in understanding stability of amorphous pharmaceutical systems: (1) the existence of unfrozen water (i.e., partial or complete freezing inhibition) in aqueous solutions of cryo- and lyo-protectors at subzero temperatures; (2) water clusters and the chemical (in)stability of amorphous pharmaceuticals; (iii) small- and large-scale heterogeneities of amorphous pharmaceuticals.

Biodeuteration of polysaccharides from microorganisms

Yue Yuan

Biopolymers are macromolecules produced from natural resources and have been considered as sustainable alternatives of petroleum-based polymers. ß-(1-4)-linked co-polymers of N-acetyl-D-glucosamine and D-glucosamine, known as chitin or chitosan, are natural occurring co-polymer and depending on the degree of deacetylation, the macromolecule has pH-dependent solubility. Therefore, it has been extensively studied and applied in material innovation in the food, agriculture, biomedicine, energy, and environments. However, the complexity of their macromolecular structures, heterogeneous properties, and impurities, as well as the lack of fundamental understanding of their interaction with other biomacromolecules (e.g., cellulose), limited their applications in large-scale functional material fabrication. Emerging tools and methods are needed to conduct research to study the structure-function relationship and molecular interactions between those carbohydrate polymers. Neutron scattering combined with deuterium labeling has been considered as a powerful tool to study biopolymer-protein combo. However, lacking selective biodeuteration protocol for chitosan created challenges in studying these carbohydrate composites or complexes with neutron.

In this study, we utilized microbial chitosan extraction methods to obtain chemicals comparable to conventional crustacean shell derived chitosan and explored D_2O and deuterated carbon source to conduct non-exchangeable deuteration in chitosan. The chemical composition and structure of protiated and deuterated chitosan were determined by Fourier-transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), and small-angle neutron scattering (SANS). It was found that the solubility of microbial chitosan is significantly impacted by the glucan content in the structure. This explained solubility problems observed in chitosan biodeuteration study using methylotrophic yeast, a routinely used microorganism for protein deuteration. With filamentous fungus *Rhizopus oryzae*, we not only produced a soluble chitosan with higher yield without needs of further deacetylation, but also developed a novel cultivation condition which reduces the deuterium toxicity for deuteration using deuterated glucose and H_2O medium. The position of the deuterons in the glucosamine backbone was confirmed by the ^1H and ^{13}C NMR characterizations. The results from Attached Proton Test (APT) in ^{13}C-NMR indicated that the deuterium incorporation of the amino glucopyranosyl ring at C3 – C5 positions was at least 60–80 %. However, the C2 position was deuterated at a much lower level (6%). This deuteration result is consistent with the glucose metabolic pathway in microorganism and provide further suggestions in biodeuteration approaches in regards of deuterated nutrition selection. Also, SANS showed that the structure of deuterated chitosan was very similar compared to the non-deuterated counterpart.

Publication: Biosynthesis and characterization of deuterated chitosan in filamentous fungus and yeast (https://doi.org/10.1016/j.carbpol.2021.117637)

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Invited Speaker Abstracts: Polymers, Colloids, & Complex Fluids

Dynamics of polyelectrolytes in semidilute aqueous solutions

Jacinta Conrad
University of Houston

Motivated by experiments showing unusual confined dynamics of nanoparticles in semidilute polyelectrolyte solutions, we investigate the structure and dynamics of unentangled semidilute solutions of sodium polystyrenesulfonate (NaPSS) using small-angle neutron scattering (SANS) and neutron spin–echo (NSE) spectroscopy. We examine the effects of electrostatic interactions and chain structure by varyingf ionic strength and polymer concentration, respectively. The SANS profiles exhibit a characteristic structural peak signature of polyelectrolyte solutions that can be fit with a combination of a semiflexible chain with excluded volume interactions form factor and a polymer reference interaction site model (PRISM) structure factor. We confirm that electrostatic interactions vary with ionic strength across solutions with similar geometries. The segmental relaxations from NSE deviate from theoretical predictions from Zimm and exhibit two scaling behaviors with the crossover between the two regimes taking place around the characteristic structural peak. The chain dynamics are suppressed across the length scale of the correlation blob and inversely related to the structure factor. These observations suggest that the highly correlated nature of polyelectrolytes presents an additional energy barrier that leads to de Gennes narrowing behavior.

Nanostructure and rheology of complex fluids at extreme shear rates

Ryan Murphy
NIST Center for Neutron Research

Spraying, coating, and jetting processes produce extreme flow velocities within confined geometries. High shear rates and stresses near the wall may induce reversible or irreversible changes within the fluid microstructure. To quantify these flow-induced changes, a capillary rheometer was developed to measure the viscosity and structure of complex fluids at high shear rates using small-angle scattering. Originally developed for small-angle neutron scattering, the same capillary setup and methodology was expanded recently for x-ray scattering, and enables significantly lower count times, improved sample and shear rate throughput, higher shear rates up to 107 s-1, and extremely confined flows within capillaries down to 500 nm. The rheometer design criteria, recent upgrades, and control improvements will be discussed. The structure-rheology relationships of various complex fluids will be highlighted, including worm-like micelles, lipid vesicles, polymer solutions, proteins, nanoparticles, and colloidal crystals. Expanding the measurement capabilities of capillary rheometry and small-angle scattering methods will continue to improve pharmaceuticals, coatings, lubricants, and fuel additives with enhanced flow-stability and rheological behavior.

Talk Title: Using Neutron to Study the conformation of semi-rigid semiconducting polymers

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Talk abstract:

In recent years, there has been a great deal of interest in organic semiconducting polymers due to their unique optoelectronic properties. These polymers are essential components in a variety of functional electronic devices, including organic photovoltaic devices, flexible displays, wearable sensors, neuromorphic computing, and bioelectronics. They are also being studied for their potential use in water splitting for hydrogen generation.

Despite significant progress being made in improving charge carrier mobility and optimizing energy bandgap, little attention has been paid to studying the physical properties of conjugated polymers, such as chain rigidity, molecular entanglement behavior, and glass transition phenomenon. However, these properties are critical for the development of the next generation of organic electronic polymers. The conformation of the polymer backbone, in particular, greatly affects the charge transport along the conjugated polymer backbone. Unfortunately, studying the single-chain conformation of these polymers in solution has proven to be a challenging task.

In my talk, I will provide an overview of our research efforts in studying the single-chain conformation of conjugated polymers in solution. We employ a wide range of characterization tools, with an emphasis on neutron scattering and deuteration labeling. Our approach involves first understanding the aggregation or de-aggregate state of the polymer chain. We then use the unique selective deuteration and contrast matching neutron scattering method to highlight a portion of the polymer chain of interest. Finally, we examine how different building structures impact chain rigidity and the resulting consequences on solid-state morphology and the properties of conjugated polymeric thin films.

Overall, this talk will shed light on the importance of studying the physical properties of conjugated polymers and the challenges associated with doing so. It will also highlight some promising research avenues that could lead to the development of improved organic electronic polymers.

Related publications:

1) Cao, Z.; Li, Z.; Zhang, S.; Galuska, L.; Li, T.; Do, C.; Xia, W.; Hong, K.; Gu, X. Decoupling Poly(3-Alkylthiophenes)' Backbone and Side-Chain Conformation by Selective Deuteration and Neutron Scattering. Macromolecules 2020, 53 (24), 11142–11152. https://doi.org/10.1021/acs.macromol.0c02086.

2) Galuska, L. A.; McNutt, W. W.; Qian, Z.; Zhang, S.; Weller, D. W.; Dhakal, S.; King, E. R.; Morgan, S. E.; Azoulay, J. D.; Mei, J.; et al. Impact of Backbone Rigidity on the Thermomechanical Properties of Semiconducting Polymers with Conjugation Break Spacers. Macromolecules 2020, 53 (14), 6032–6042. https://doi.org/10.1021/acs.macromol.0c00889.

3) Cao, Z.; Leng, M.; Cao, Y.; Gu, X.; Fang, L. How Rigid Are Conjugated Non-ladder and Ladder Polymers? J. Polym. Sci. 2021, No. August, pol.20210550. https://doi.org/10.1002/pol.20210550.

4) Chaudhry, S.; Wu, Y.; Cao, Z.; Li, S.; Canada, J. L.; Gu, X.; Risko, C.; Mei, J. Evolution of Chain Dynamics and Oxidation States with Increasing Chain Length for a Donor–Acceptor-Conjugated Oligomer Series. Macromolecules 2021, acs.macromol.1c00963. https://doi.org/10.1021/acs.macromol.1c00963.

5) Cao, Z., Ma, G., Leng, M., Zhang, S., Chen, J., Do, C., Hong, K., Fang, L., & Gu, X. (2022). Variable-Temperature Scattering and Spectroscopy Characterizations for Temperature-Dependent Solution Assembly of PffBT4T-Based Conjugated Polymers. *ACS Applied Polymer Materials*, acsapm.1c01511. https://doi.org/10.1021/acsapm.1c01511

6) Cao, Z. *et al.* Probing single-chain conformation and its impact on the optoelectronic properties of donor–accepter conjugated polymers. *J. Mater. Chem. A* (2023) doi:10.1039/D2TA09389H.

Understanding the Properties of Porous Carbon Electrodes Far from Equilibrium

Jeffrey J. Richards

Advanced economies around the world are mounting a multifaceted response to the threat of climate change by transforming the way that electricity is produced and utilized. This includes new investments in technologies that use excess renewable electrons (produced by wind and solar energy) to manufacture commodities and fuels or store them at the grid-scale. Porous electrodes incorporating carbonaceous materials are central to these new technologies as they balance the flux of electrons through the carbon phase to the electrochemically active sites against the transport of dissolved or gaseous species within the pores. Small angle neutron scattering (SANS) has emerged as a critical tool to evaluate the properties of porous electrodes not only because the length scales accessible to SANS instruments align with the length scales of the carbon domains and the pores, but also because neutron methods permit the examination of these electrodes in their relevant electrochemical environments. As many of these electrochemical conversion processes are far from equilibrium the ability of SANS to permit *in situ* and *operando* experiments is critical to understanding how these electrodes perform and more importantly how they fail. In this talk, I will highlight work from our group and that of others using advanced SANS techniques to evaluate porous carbon electrodes and understand how their structural properties evolve under conditions far from equilibrium.

Quantitative Analysis of Multiphase Nanoscale Systems Using the Scattering Invariant

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Nanodispersed phases are found in structural materials, adsorbents and separation, energy storage devices and many other applications. The detailed structures of multiphase nanodispersed systems may not always be known, making application of form and structure factor models difficult. However, analysis of the scattering invariant can still yield interesting insights. In my presentation, I will discuss 2 examples of fluids and polymers inside porous materials, in which the analysis of the scattering invariant in conjunction with other characterization has yielded novel and unique insights into the physical state of the pore contained materials. In the first example, the density and volume of the sorption phases of simple fluids in nanopores will be calculated from the scattering invariant and the amount of fluids contained in the pores. The sorption phase density and its evolution with pressure and temperature provides detailed insights into the nature of fluid-solid interactions, and cannot be measured in volumetric or gravimetric sorption experiments alone. The second example considers a hybrid adsorbent, i.e., a CO2-capturing imine polymer dispersed inside silica or carbon nanopores. The dispersion of the imine polymer increases its surface area and capture activity. From analysis of the scattering invariant and separately measured TGA and N2 BET data, a detailed description of the pore-confined morphology was obtained. We show that the polymer-substrate interactions are very different for silica and carbon, which may explain the differences in CO2 sorption performance. We calculate the distribution of pore polymer between sorption film and plugs and determine the polymer blocked pore fractions as a function of polymer loading. The information can be used to tune substrate morphology and chemical composition, and polymer loading.

Rother, G., Vlcek, L., Gruszkiewicz, M. S., Chialvo, A. A., Anovitz, L. M., Banuelos, J. L., ... & Cole, D. R. (2014). Sorption phase of supercritical CO2 in silica aerogel: experiments and mesoscale computer simulations. *The Journal of Physical Chemistry C*, *118*(28), 15525-15533.

Rother, G., Tumuluri, U., Huang, K., Heller, W. T., Dai, S., Carrillo, J. M., & Sumpter, B. G. (2021). Interactions of an Imine Polymer with Nanoporous Silica and Carbon in Hybrid Adsorbents for Carbon Capture. *Langmuir*, *37*(15), 4622-4631.

Design & Engineering of Macromolecules for Sustainable Energy and Environmental Science

Guoliang Liu
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I will present a few examples of macromolecules for energy and environmental sciences. First, I will describe the synthesis of a new type of porous carbon fibers from block copolymers. Conventional syntheses of porous carbon fibers rely on blending polyacrylonitrile with sacrificial additives, which macrophase-separate and result in poorly controlled pores. Here we use the block copolymer microphase separation to synthesize porous carbon fibers with well-controlled mesopores and micropores. Block copolymers are directly converted to nitrogen and oxygen dual-doped porous carbon fibers. Owing to the optimized bimodal pores and interconnected porous network, the block copolymer-based porous carbon fibers exhibit outstanding ion transport properties and ultrahigh capacitances in supercapacitors. The use of block copolymer precursors revolutionizes the synthesis of carbon fibers. The advanced electrochemical properties signify that porous carbon fibers represent a new platform material for electrochemical catalysis, energy storage and conversion. Second, I will present the upcycling of plastic waste into high-value chemicals. We will discuss a tandem degradation-upcycling strategy to exploit high-value chemicals from PS waste with high selectivity. We first degrade PS to aromatics and then valorize the intermediate to high-value chemicals. Low-cost AlCl3 catalyzes both the reactions of degradation and upcycling at ambient temperatures under atmospheric pressure. The intermediates can advantageously serve as solvents for processing the solid plastic wastes, forming a self-sustainable circuitry. The low-value-input and high-value-output approach is substantially more sustainable and economically viable than conventional thermal processes. The cascade strategy is resilient to impurities from plastic waste streams and is generalizable to other high-value chemicals. Theupcycling to diphenylmethane was tested at 1-kg laboratory scale and attested by industrial-scale techno-economic analysis, demonstrating sustainability and economic viability without government subsidies or tax credits.

Poster Abstracts

Novel Inelastic Neutron Spin Echo Approach to Measuring Gruneisen Parameters

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Traditional neutron spectroscopy suffers inverse correlation between instrument resolution and neutron flux. For high resolution studies, low neutron flux necessitates larger samples compared to other similar scattering techniques, such as inelastic x-ray scattering. To resolve changes in dynamics, as induced by external pressure or temperature, large perturbations must be used, which can trigger phase transitions or non-linear responses of the frequency. For example, the Gruneisen parameter $\gamma = dln(\omega)/dln(V)$, a value that relates changes in a mode frequency (ω) to changes in volume (V), is challenging to measure with neutron spectroscopy due to its direct dependence on frequency measurement and the low achievable sample pressure due to large sample size. Often, pressures exceeding 1 GPa are needed to have any measurable change in mode frequency and fine details of phase transitions can be missed. In this study, we have developed a novel approach to solve two issues at once. First, we have used Inelastic Neutron Spin Echo (INSE), a neutron scattering techniques that offers exceptional resolution (< 10μeV) to detect small changes in neutron energy. Second, we have combined INSE with newly developed medium-pressure cell with large volume (~8 cm^3). This combination enabled detection of small changes in energy and relative lattice spacing (< 10^{-5}) at low pressures (to 0.1 GPa) in single crystal GaSb. GaSb was chosen as a suitable sample because of its *fcc* cubic structure with flat frequency bands at low energy (6 meV TA1, Γ-X and 5 meV TA Γ-L). This approach opens the possibility to study Grüneisen parameters with inelastic neutron scattering with relatively small perturbation in pressure.

The work was supported by the DOE Office of Science, Basic Energy Science, Early Career Research Program Award (KC0402010), under Contract No. DE-AC05- 00OR22725, and Materials Science and Engineering Division. This research used resources at the High Flux Isotope Reactor, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory.

Advancing neutron diffraction for accurate structural measurement of light elements at megabar pressures

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Over the last 60 years, the diamond anvil cell (DAC) has emerged as the tool of choice in high pressure science because materials can be studied at megabar pressures using X-ray and spectroscopic probes. In contrast, the pressure range for neutron diffraction has been limited due to low neutron flux. Recently, we have developed a neutron DAC that addresses this challenge and enables break-out of the previously limited pressure range. Key elements are ball-bearing guides for improved mechanical stability, gem-quality synthetic diamonds with novel anvil support and improved in-seat collimation. We have demonstrated a pressure record of 1.15 Mbar and crystallographic analysis at 1 Mbar on the example of nickel. Additionally, insights into the phase behavior of graphite to 0.5 Mbar have been obtained. These technical and analytical developments will further allow structural studies on low-Z materials that are difficult to characterize by X-rays and are now available to the SNS/HFIR user community.

High Temperature Checklist Implementation

Bekki Mills

Oak Ridge National Laboratory

Sample environment is an integral component of neutron scattering, enabling scientific users from around the globe to perform neutron scattering experiments under extreme conditions. The high temperature sample environment group provides several different forms of heating through complicated scientific equipment.

Historically, high temperature experiments have proven very difficult, and failures have been exacerbated due to lack of material consideration and planning. Over the past several years the high temperature sample environment group have developed and implemented a high temperature checklist, (HTCL,) which is required to be approved for all experiments that request a maximum temperature higher than 400 Kelvin. This presentation will discuss the process and considerations that are implemented in the HTCL as well as the increase observed in the reliability of the high temperature equipment, as well as the capability to perform more complicated experiments at high temperature.

VENUS on the Horizon: The Construction of the SNS Time-of-Flight Imaging Beamline

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Located at the Spallation Neutron Source (SNS), VENUS is an instrument optimized for wavelength-dependent neutron imaging techniques, namely Bragg edge and resonance imaging, across a broad range of neutron energies (from meV to hundreds of eV). The VENUS construction project started Fall 2018, establishing a detailed design of the major components and timeline for purchasing, testing, and installation. Completion of the VENUS instrument is anticipated during Fall 2024. This instrument comprises components such as a set of ¬10B4C apertures designed for both thermal/cold and epithermal neutrons, a suite of choppers (T0 and single disks), beam scrapers, filters. The principal detector at VENUS will be the micro-channel-plate Timepix (MCP TPX) detector. This poster provides an overview and status of the VENUS construction project, describes its main components, along with the beamline's anticipated capabilities.

Real-space local dynamics of molten inorganic salt studied by Van Hove Correlation Function

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Molten inorganic salts have attracted resurgent attraction because of their unique physicochemical properties and applications to energy-related advanced technology such as molten salt reactors. Despite its importance, knowledge about atomic-scale dynamics is scarce primarily due to the experimental difficulty. Conventional pair distribution function approach based on total neutron/X-ray scattering provides a snapshot structure of molten salts in real space, but the dynamical information is hindered in the spectra. We have recently developed an approach to studying the local dynamics using the Van Hove correlation function[1], which is a pair correlation function in real-space and time, based on inelastic neutron and X-ray scattering. In this presentation, we report our recent work on the real-space local dynamics of molten inorganic salt using this approach[2].

We used inelastic neutron scattering to obtain the real-space local dynamics of the molten salt of $MgCl_2$. Inelastic neutron scattering measurement was carried out at ARCS, SNS. Three energies, 20, 40, and 80 meV, were chosen as the incident neutron energy to balance the energy and angular resolution and the range of energy transfer and momentum transfer. The sample was put in thin-walled quartz (2.0 mm O.D. and 0.010 mm thickness) cylindrical cells covered by vanadium foil, then placed in the MICAS furnace to keep the sample's temperature at 875 ˚C. After the basic data reduction process, the dynamic structure factor $S(Q, E)$ was first converted to intermediate scattering function, $F(Q, t)$, by using the Fourier transformation over the energy transfer, E. After that, $F(q, t)$ was converted to the Van Hove correlation function, $G(r, t)$, by using the Fourier transformation over the momentum transfer, Q. The conversion into $G(r, t)$ enables us to distinguish the self-part and the distinct-part, which are overlapped in the reciprocal space. Our results depict the distance-dependent dynamics of molten salt on the picosecond time scale and demonstrate the capability of the developed approach to describe the locally correlated- and self-dynamics in molten salts.

Work by Y. S. and T. E. was supported by U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, Division of Materials Science and Engineering. Work by A.S.I., D.M., and S.D. was supported as part of the Molten Salts in Extreme Environments (MSEE) Energy Frontier Research Center, which is funded by the DOE Office of Science, Office of Basic Energy Sciences. A portion of this research used resources at Spallation Neutron Source, a DOE Office of Science User Facility operated by Oak Ridge National Laboratory.

1. L. Van Hove, *Phys. Rev.* **1954**, *95*, 249–262.
2. Y. Shinohara, A. S. Ivanov, D. Maltsev et al., *J. Phys. Chem. Lett.* **2022**, *13*, 5956–5962.

Understanding the effects of higher-order assembly on the structure of sulfite reductase

Author: Nidhi Walia

The redox state of sulfur determines its bioavailbility and its reduction to sulfide is required for assimilation of sulfur into amino acids and cofactors.The NADPH-dependent assimilatory sulfite reductase (SiR) is a metabolic enzyme that performs the six-electron reduction of sulfite to sulfide. *Escherichia coli* SiR is composed of eight flavoprotein (SiRFP, α) and four hemoprotein (SiRHP, β) subunits that associate in α_8:β_4 holoenzyme. This dodecameric assembly is unique because SiRs from other sulfur reducing organisms are dimers of reductase and oxidase subunits. Both SiR subunits are modular. SiRFP is a fusion between flavodoxin domain and a ferredoxin-NADP$^+$ reductase domain that assembles through its 52 N-terminal amino acids into an octamer. SiRHP is a monomeric metalloenzyme that houses the active site. Despite almost 30 years of effort across many laboratories, structures of SiR complexes have remained recalcitrant to X-ray crystallography and cryo-EM because of its structural heterogeneity aising from intrinsically disordered regions throughout the complex, including the flexible linker joining SiRFP's flavin binding domain. Thus we do not know how the domains assemble, which leaves a gap in understanding about how these domains coordinate to perform electron transfer. Here, we use neutron contrast variation (NCV) and small angle neutron scattering (SANS) to observe the relative subunit positioning within the SiR complex. To better understand the electron transfer mechanism, we have generated conformationally restricted variant of SiRFP that either locks its flavin binding domains in an open conformation by shortening the linker between domains, or in closed conformation by engineering disulfide bonds. SANS and NCV study reveal SiR's asymmetric complex, and the resulting maps supports a redundant, *cis/trans* mechanism of electron transfer between the reductase subunits as well as between the tightly or transiently bound reductase and oxidase domains.

Today's TTT Chart is Static. Should be Dynamic with A 3rd Axis

Paul Cheng, FuseRing, Inc

Much money is spent understanding residual stress but all global presentations examine samples w/ the best uniform location, no chance of confusion. Only clear cut well defined mathematical examples are displayed.

But the weakest, most prone locations are at the joints. Whether high energy or filler welds, one single pass, the RS modelling could be straight forward. But when there are multiple two or more passes, there is no modelling that this author is aware of. And not one scientist is willing to risk reputation examining the unknown.

The unknown can be by-passed w/ true solid state fusion welding. One shot, autogenous, automated and repeatable. No HAZ. Fine Grained base to base. RS pattern is uniform all around. OD, ID in compression. Across weld at center in tension. Resist embrittlement.

More interestingly crystalline structure forms sooner than traditional TTT Charts. By introducing a 3rd axis w/ shear & forge (dynamic condition), accepted crystalline formation can exist sooner. There is a 3D envelope, not 2D under static conditions.

There is no PhD studies anywhere in the world. Above statements are claims w/ no scientific evidence. But visual quality of this weld cannot be denied and is worth open forum discussions. A game changing new process is occurring right under our eyes but no research.

YMGO: Pseudo Quantum Spin Liquid modeling with SU(N)NY

Authors:

Martin Mourigal, Joe Paddison, Olivia Vilella

Ytterbium magnesium gallium oxide (YMGO) is a quantum spin liquid candidate with effective spin-1/2 ions on a triangular lattice, due to the crystal field ground state being a Kramer's doublet. As previously discussed in the literature, antiferromagnetic next nearest neighbor (NNN) interactions, spin space anisotropies, and disorder in chemical layers are all contained in this compound. Experiments have shown that there is no conventional magnetic ordering or zero-point entropy in YMGO. The triangular layers of YbO6 are sandwiched between triangular layers of magnesium and gallium, which are disordered and occur in a 60/40 split, respectively. The placement of the magnesium and gallium are not entirely random, but rather there is a probability distribution with how they are arranged. The model presented by our collaborator Dr. Paddison captures this disorder. The chemical disorder leads to a domino effect causing other types of disorder, including g-tensor and exchange disorder. The goal of my work is, based on models of g-factor and exchange disorder, to predict the high magnetic field response to validate these disorder models. In order to fully characterize the disorder in YMGO, we solved a multi-partite lattice with both linear spinwave theory and SUN(N)Y.

Microchannel Plates with Quad Timepix3 Readout (MCP/TPX3) Detector for High Spatial-Resolution Neutron Imaging with Time-of-Flight Capability

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Microchannel plates (MCPs) with quad Timepix3 readout have emerged as a promising neutron imaging camera for neutron imaging with time-of-flight (ToF) capability. The detector comprises of a pair of chevron-stacked MCPs coupled to quad Timepix3 readout in a vacuum enclosure. To make the detector neutron sensitive, one of the MCPs is doped with neutron absorbers with very high neutron capture cross-section such as ^{10}B and ^{157}Gd. The Timepix3 readout is triggerless event-by-event data driven and zero-suppressed readout. Each Timepix3 chip has 256×256 pixels, and each pixel size is 55×55 μm^2. It can record the time-of-arrival (ToA) and time-over-threshold (ToT) information of every hit in a pixel simultaneously, up to 80Mhits/s per chip. The timestamping of each hit enables the detector to do ToF imaging, which offers significant advantages over traditional neutron transmission imaging. The ToF capability allows the detector to perform more advanced neutron imaging techniques such as Bragg edge imaging and energy-resolved imaging. In this work, we present a neutron imaging camera capable of ToF imaging with a sub-55 µm spatial resolution using efficient clustering and peak fitting algorithm to sustain high event rates. The detector demonstrated a rate capability of $\leq$ 120Mhits/s, a neutron efficiency of $\geq$ 30% at 4.2 Å, sub-µs time resolution for thermal and cold neutrons, a gamma sensitivity of $\leq 10^{-2}$ and an active area of 28.2×28.2 mm^2.

Neutron Characterization of Residual Stress and Precipitate Evolution in Aluminum 2xxx Self-reacting Friction Stir Welds

Authors:

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2xxx series aluminums are age hardenable alloys which possess high strength and ductility, low density, good corrosion resistance, and stable cryogenic performance. [1] Their high strength-to-weight ratio and cryogenic stability make them ideal candidates in many structural aerospace applications such as the liquid propellant rocket fuel tanks on NASA's Space Launch System (SLS). For this critical application, joining thick plates reliably and without defects require a solid-state joining process known as self-reacting friction stir welding (SRFSW). This process greatly improves upon traditional fusion based processes and may reduce the effects of residual stress and joint softening (i.e. loss of mechanical properties). However, the frictional heat as well as the high shear and restraint conditions of SRFSW still result in a significant residual stress as well as coarsening and solvation of strengthening precipitates, each to the detriment of the mechanical properties of the assembly. [2], [3] The residual stress and precipitation state of a thick-plate aluminum 2219-T87 SRFSW were evaluated by two different techniques offered at the High Flux Isotope Reactor (HFIR).

High-resolution maps of the residual strain and stress states along the normal, transverse, and longitudinal directions were produced using neutron diffraction measurements taken at the High Intensity Diffractometer for Residual Stress Analysis (HIDRA). Residual stress was determined to have the highest tensile value in the heat affected zone (HAZ) in the longitudinal direction and largest compressive stress in the base metal (BM) region of the normal and transverse directions. These distributions followed the common pattern for SRFSWs with all directions displaying an 'M'-shaped profile across the weld. Mechanical properties were evaluated via microhardness testing across the transverse weld section and showed a 'V'-shaped curve across the weld with slight hardness recovery in the stir zone (SZ). Maximal and minimal microhardness values were observed in the base metal and thermomechanically affected zone (TMAZ), respectively. Microstructural evolution was recorded using optical microscopy and showed decreasing grain size from the HAZ to the SZ.

Precipitate evolution was determined on a transverse cross-section at General-Purpose Small-Angle Neutron Scattering Diffractometer (GP-SANS) and supported by microhardness, microstructural, and wide-angle x-ray scattering (WAXS) experiments. Two precipitates (θ and θ' – Al_2Cu) and one intermetallic (ω -Al_7Cu_2Fe) were identified via WAXS phase identification. SANS analysis suggested the precipitate morphology was of a plate/disc shape. The presence of two scattering geometries: one 2-9 nm and the other 20-60 nm was observed and correlates with θ' and θ, respectively. The identified θ and θ' precipitates coarsened from the BM to the HAZ before solutionizing in the SZ. Precipitate volume fraction decreased for θ' and increased for θ from the BM to HAZ and was qualitatively supported by WAXS. Precipitate volume fraction was highly correlated to microhardness and intensity. Supporting work with ultra small-angle x-ray scattering (USAXS) and small-angle x-ray scattering (SAXS) aligns well with the SANS data.

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Low Temperatures and Magnets: Principles and Best Practices

Victor Fanelli, Josh Pierce

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The demand for sample environment equipment and user-support will increase in the coming years at ORNL as major facility upgrades are underway at the High Flux Isotope Reactor (HFIR) and the Spallation Neutron Source (SNS).

Sample environment is an essential component of neutron scattering to performing neutron scattering experiments under extreme conditions. Therefore, it is crucial to maximize the efficient use of neutron beam time, while providing reliable performance of Low Temperatures and Magnets capabilities. Among the conditions impacting the support level to requested temperature, magnetic field and other sample environment demands, the complexity of sample environment, the equipment capacity and personnel resources are critical.

This presentation will discuss considerations for an experiment planning process and timing that will allow optimal use of the finite resources to satisfy requested sample environment in the experiment proposals, as well as timely preparation and test for both standard and novel experiment conditions, improving our group’s agility to respond to plan changes, needed upgrades and development of experimental capabilities.

Monte-Carlo Ray-Tracing Studies on Multiplexing Prismatic Analyzers for Implementation on MANTA at the High Flux Isotope Reactor

Authors:

Adam Aczel, Adit Desai, Garrett Granroth, Martin Mourigal, Gabriele Sala, Travis Williams

Though neutron scattering is now performed using a suite of techniques, the traditional triple-axis spectrometer first designed by Bertram Brockhouse in 1956 is still one of the best techniques to study a sample due to its versatility and compatibility with pressure cells and other restrictions. The latest development in triple-axis spectroscopy is the use of so-called multiplexing analyzer systems, seen at several neutron scattering laboratories and most recently at the Swiss Neutron Source's instrument CAMEA [2]. By using multiplexing analyzers, CAMEA is able to greatly improve upon the detection efficiency of a traditional triple-axis by using the combination of multiple analyzers and position-sensitive detectors to provide energy-resolved measurements. Our work aims to utilize this technology, along with a novel analysis technique, to push, to develop in-silico a next generation triple-axis spectrometer known as the Multi-Analyzer Neutron Triple Axis (MANTA).

MANTA makes use of both "local" multiplexing, in which analyzer crystals set to different Bragg wavelengths are placed behind each other, and "wide-angle multiplexing" in which several analyzer arms are placed around the sample. By making use of linear position-sensitive detectors, MANTA will be able to associate which analyzer a neutron scattered from. This allows for a measurement process that is 64 times more effective than a traditional triple axis, allowing for rapid data sample measurement. Additionally, by making use of the prismatic concept, MANTA will be able to detect several different energies of neutrons from the same analyzer. An optimal way to study these processes for implementation on a neutron scattering instrument is to use Monto-Carlo simulation programs, such as McStas. The poster will showcase the simulated results of MANTA's design as well as describe the mechanisms of the positionally calibrated prismatic analysis technique.

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[3] J. O. Birk, M. Marḱo, P. G. Freeman et al. "Prismatic analyser concept for neutron spectrometers," Review of Scientific Instruments (2014)

Can Magnetic and Optical Properties Be Harmonized in a Quantum Material?

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Quantum materials are poised to offer the tunability and precision vital to meeting the requirements of optically addressable magnetic spins for quantum technologies. However, tuning both the crystal and electronic structure of a quantum material that promote the coupled spin, orbital, and phonon degrees of freedom necessary for harmonizing magnetic and optical behaviors, those often do not coexist, presents a significant challenge. To address this, we proposed an approach to integrate spin frustration and nonlinear optical properties into a single material by placing spins in a noncentrosymmetric (NCS) extended framework. It is worth noting that NCS magnets are rare compared to their centrosymmetric counterparts. With this idea in mind, we explored magnets $AMTeO_6$ (A = Sr, La, Bi, Pb; M = Cr, Mn, Fe), in which the transition-metal ion M site forms a 2-D triangular lattice separated by the A site. Density functional theory calculations of these reported materials resulted in the M site mainly determines the frontier electronic states while the A site can tune the orbital overlap not only between the magnetic M layers but also around the Fermi level (with or without lone-pair electrons). However, a hurdle remains in terms of either the narrow bandwidth of the HOMO and thus poor orbital overlap, or the inappropriate centrosymmetric structure. To increase the bandwidth of the HOMO while maintaining the NCS framework, we created a new NCS magnet, $CaMnTeO_6$, that features simultaneously incommensurate magnetic structure and nonlinear optical responses. The refined static moment from neutron experiments at T = 1.6 K is consistent with the fitted moment from nuclei Schottky analysis down to T = 100 mK, but only 46% of the expected value for S = 3/2, possibly indicating some low-lying magnetic excitations and potential entanglement between spins. The 2-D NCS magnet also exhibits type-1 phase-matching behavior through the second-harmonic generation process, highlighting its capability of generating coherent photons. The NCS magnet $CaMnTeO_6$ completes the picture of how the A site can modify the bandwidth and desired structure while enabling a new design consideration for coupling magnetic and optical properties.

Correlating Structure to Performance of Nanoparticle Organic Hybrid Materials (NOHMs) Using Neutron Scattering

Author:

Md Ashraful Haque

Co-authors:

Sara Hamilton, Tony Feric, Alissa Park, Mark Dadmun

This abstract focuses on investigations that developed a fundamental understanding of the structure and performance of novel nanoparticle organic hybrid materials (NOHMs) in aqueous solutions. NOHMs consist of organic polymer grafted to inorganic nanoparticles. They have shown great promise in capturing CO2 and interacting with ionic species, which is beneficial for energy storage systems. However, their performance is limited due to their highly viscous nature. Hence, NOHMs have been proposed as additives that can increase the solubility of ionic species and, consequently, improve the performance of energy storage systems. Using neutron scattering techniques as a characterization tool allowed the investigation of the structure and the dispersion of NOHMs.

Initial results using small-angle neutron scattering focus on the increasing concentration of NOHMs additives in the aqueous solution, showing that a significant amount of polymer is not attached to the surface and remains free in the solution. The free polymer interacts with grafted polymer creating a unique NOHMs structure that contains three different polymer regions; grafted polymer, interacting polymer, and free polymer. Now, in the presence of salt, the structural feature of NOHMs alters so that the excess polymer is less interacting with grafted polymer. This structural change drastically reduces the viscosity of NOHMs in solution, indicating a direct relationship between the structure to the performance of NOHMs. In order to better understand the assembly of NOHMs, the next set of experiments focused on the change of bond type of NOHMs. In this case, the polymer is either bonded to the nanoparticle through ionic (similar to the previous experiment) or covalent interaction. Careful analysis indicates that the polymers ionically attached to the nanoparticle surface are loose and, therefore, can detach themselves from the nanoparticle. In covalent NOHMs, no free polymer is observed. However, changing the bond type created fractal aggregates in covalent NOHMs. Lastly, adding salt/ionic species to the solvent showed that the grafted layer thickness in ionic NOHMs assembly is significantly altered compared to covalent NOHMs. These structural changes are reflected in the viscosity study of ionic and covalent NOHMs- the viscosity of ionic NOHMs is significantly reduced due to the collapse of ionically bonded polymer on the nanoparticle surface. Finally, the last study of this project highlighted the ordering of NOHMs near a gold electrode surface using neutron reflectivity, aiming to understand the applicability of NOHMs in a battery storage system. Consequently, ionic NOHMs are dispersed in an aqueous solvent in salt near a gold surface with and without applied potential. The results show that when no potential is applied, the free polymer adsorbs onto the gold surface, and a single layer of NOHMs assembles next to the free polymer. Applied potential disrupt the ordering of NOHMs and deposits a layer of salt near the surface.

High Temperature Program SNS/HFIR

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A general review of the high temperature program at the SNS and HFIR. Overview of the available sample environments, temperature measurement options, and sample containers. Discussion on the process/approval for high temperature experiments and the services/support offered by the High Temperature Sample Environment Group.

Process-Structure Relationships of Lithium-Ion Battery Cathodes

Qingsong ‘Borges’ Liu[1], Gergely Nagy[2], Mathieu Doucet[2], Jeffrey J. Richards[1]

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Energy-dense storage systems such as lithium-ion batteries promise to bridge our current fossil fuel-based economy to a future that relies on renewable, low-carbon electricity [1]. While relatively mature and deployed at the gigawatt scale, there remains a fundamental lack of knowledge and experimental data that links the way that the battery electrodes are manufactured to their performance. Lithium-ion batteries utilize porous electrodes which are a composite of micron-sized electrochemically active particles, nanometer-scale conductive additive carbon black (CB), and polymer binder that must be engineered to balance electronic and ionic transport. This balance is only achieved when there is careful control over the formulation and manufacturing conditions. [2] Further, the structures that yield optimal performance exist far from equilibrium, as the porous electrode’s structural features form in a highly arrested state during the late stages of coating. In order to understand the factors that influence the structure of porous electrodes, we seek to combine rheo-electric measurements of electrode slurries with *in situ* neutron scattering measurements of slurries subjected to coating flows.

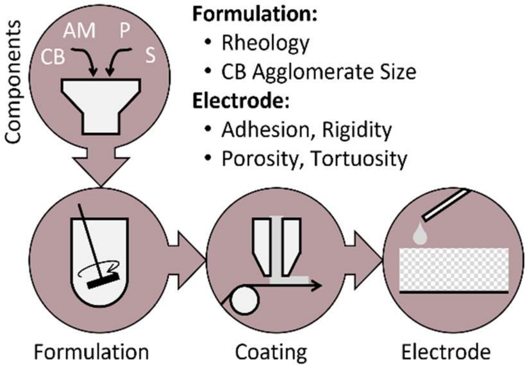

FIG 1: Manufacturing porous electrodes requires understanding the formulation and processing steps that determine the microstructure of porous electrodes. The electrode is a composite manufactured through the combination of carbon black (CB), active material (AM), and polymer binder (PB) dispersed in a solvent (S). These components are mixed and then coated into a thin film that is post-processed to yield a porous electrode.

Our initial work has focused on rheo-electric measurements [3] to probe the structure of CB in suspensions containing polyvinylidene difluoride (PVDF), a commonly used polymer binder in lithium-ion batteries. By combining previous insights from USANS measurements performed by Hipp et al [4], we successfully showed that the rheology of CB/PVDF suspensions can be predicted based on the viscosity of PVDF alone without accounting for PVDF/CB interactions. We anticipate that this will be true for electrode slurries containing active material as well. We will also show our recent efforts to develop a sample environment that enable slot coating with simultaneous microstructural measurements at the SNS EQ-SANS beamline. This sample environment mimics the roll-to-roll coating of liquid-like soft materials, which is ubiquitous in the manufacturing of multiple technologies including high-performance paints, fuel cell electrodes, organic electronics, and electrochemical systems. This sample environment will highlight the unique ability of neutron scattering in providing time-resolved and *in situ* non-destructive measurements that are valuable for optimizing the performance of coated materials.

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THF Effects on Solution of Structured Ionic Co-Polymers: SANS Insight

John Bracewell, Rosita Sivaraj, Jailyn Johnson, Supun Mohottalage, Dvora Perahia, Clemson University

Lilin He, Oak Ridge National Laboratory

Tuning of solvent-polymer interactions is an effective means to control the structure of block co-polymers in solutions, affecting their membrane structure and properties. Among those are ionic block co-polymers whose structure is largely driven by the association of the ionic groups. Controlling ionic clustering through solvent adaptation presents a path to achieve control over their structure in solutions and membranes. This study focuses on the solvent effects of an aprotic solvent, THF, on the structure of micelles formed in ABCBA pentablock co-polymers. Specifically, A, B, and C correspond to poly(t-butyl-styrene), poly(ethylene-r-propylene), poly(styrene-r-styrenesulfonate) respectively. This polymer was designed with the intention of encapsulating ion transport ability (through block C) and mechanical stability (through blocks A and B). This polymer forms well-defined micelles in hydrophobic solvents. With the overall goal to control the cohesion of the ionic clusters, we studied the structure evolution of this pentablock co-polymer as THF was added to cyclohexane across the ionomer to polyelectrolyte transition. THF is an aprotic polar solvent with a dielectric constant of 7.58. We show that even though THF partitions across all blocks, it resides predominantly in the core, which swells, though the micelles remain stable. The structure evolution with THF at the different regime will be reported.

SANS studies of Hierarchical Systems of Biological and Environmental Relevance

Authors:

Hugh O'Neill, Sai Venkatesh Pingali, Manju Senanayake Mudiyanselage, Volker Urban

Complex systems exhibit hierarchical structure and morphology spanning multiple length scales, ranging from 1 nm to microns, making their characterization highly challenging. Here, we present examples of research in biofuels, carbon capture, and plastics, that integrates contrast variation small-angle neutron scattering with complementary X-ray techniques to obtain structural details about different biological and environmental systems.

Development of the NScD Levitation Program

Dante Quirinale
Oak Ridge National Laboratory

Containerless processing is an avenue for the precise in situ exploration of reactive materials at extreme temperatures as well as the development and properties of metastable phases. NScD has developed a diverse suite of levitation instrumentation in order to support the growing needs of the high temperature user community. These systems include the neutron aerodynamic levitator (NAL) and complementary controlled-atmosphere offline aerodynamic levitator; the neutron electrostatic levitator (NESL); the creep electrostatic levitator (CrESL); and the neutron aero-acoustic levitator (NAAL). In addition, we are collaborating with researchers from Iowa State University to demonstrate an ambient condition electrostatic levitator designed for in situ studies of electrolytic solutions (SESL). We have begun developing a suite of next generation levitation systems; a hyperbaric electromagnetic levitation system for high-throughput studies of conductive materials up to 4000 C; and a pressurized levitator intended for the study of molten salts. Finally, we have taken steps to establish a program for the use of these systems for offline measurements. This will enable complementary thermophysical measurement data as well as preparation for beamtime in order to maximize efficiency.

SNS and HFIR Low Temperature and Magnets Current Capabilities, Projects, and Developments

Matt Collins, Saad Elorfi, Victor Fanelli; Cory Fletcher, Ryan Morgan, Kostya Nasyedkin, Josh Pierce, Todd Sherline, and Tyler White

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We present the sample environment capabilities currently requiring the largest fraction of effort from the Low Temperatures and Magnets groups at both HFIR and SNS. This effort is invested in the deployment, operation, oversight, and support of equipment in low- and ultra-low temperatures and applied magnetic field.

Ongoing efforts in combining experimental capabilities for multimodal characterization of materials (laser excitation, high pressure, ultra-low temperatures, etc...), developments involving pulsed magnets and elastic properties probes as well as projects to optimize supporting the neutron scattering scientific user facilities at ORNL NScD are included.

Segmental Dynamics of Networks Formed by Ionomers: Neutron Spin Echo and Simulations Insight

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Understanding the dynamics of ionizable polymers, which overall control their mechanical stability and often their ability to transport ions, is critical to their current and potential uses ranging from clean energy to biotechnology. A small number of ionizable groups tethered to the polymer backbone is sufficient to significantly hinder their macroscopic motion. Using Neutron Spin Echo (NSE) and molecular dynamics simulations, we probe the dynamics of polystyrene sulfonate (PSS) in toluene solutions.

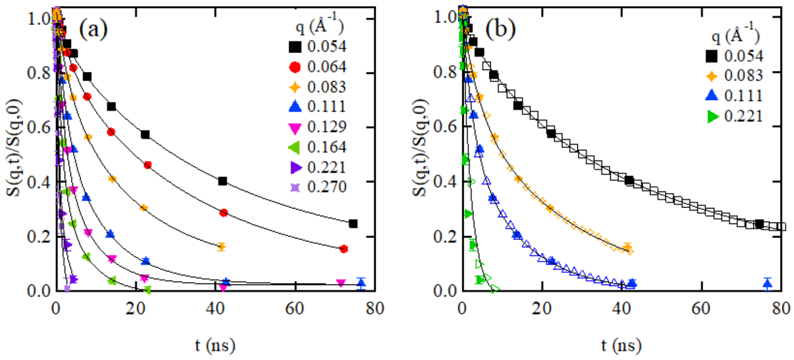

Figure 1: PSS 0.03 in Toluene at 30 °C (a) NSE data (b) NSE data (bold) overlay with computational (open) S(q,t) extracted from MD simulations, at the indicated q values

With NSE measurements coupled with molecular dynamics simulations, we were able to see that clustering constrains the motion of the polymer, and two types of motion are observed for PSS in toluene in the length scales measured. Increasing the temperature of the system releases constraints and increases the motion of the polymer, while increasing the sulfonation fraction decreases the motion.

Time-of-flight Neutron Grating Interferometry for Dark-field Contrast Imaging at SNS

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The dark-field contrast modality[1] of neutron imaging with grating interferometers[2] provides access to spatially resolved small angle scattering information and thus to measure variations of the microstructure in a bulk material or in a process. The probed correlation length range is defined by instrumental parameters including the wavelength, sample to modulation analyser distance and the beam modulation period.[3] Utilizing a pulsed source and thus a time-of-flight approach provides an intrinsic wavelength scan and thus an instantaneous probe of a certain correlation length range. While this bears the potential for future time resolved studies, we here present a first attempt and investigation of time-of-flight grating interferometric dark-field contrast neutron imaging at the Spallation Neutron Source SNAP beamline. A conventional Talbot Lau neutron interferometer consists of three gratings. A source grating consisting of absorption lines creates sufficient coherence for the phase grating. The interference pattern, i.e. a transversal beam modulation, is typically smaller than the detector resolution and is thus resolved by an analyser grating with a period matching to modulation and a corresponding phase stepping approach of one of the gratings. The interferometer is optimized for a single wavelength by the phase shift capability of the phase grating and the set Talbot distance at which the modulation is measured. However, it provides useful signal over a certain range of wavelengths. The dark-field signal refers to the dampening of the modulation visibility through small angle neutron scatter redistributing the intensity between modulation maxima and minima. It can be shown that the relative visibility measured against the probed correlation length provides a direct measure of the projected real space correlation function G of the system's microstructure.[3] Here we report a first test with an ad-hoc grating set-up optimized for the peak wavelength at SNAP and some initial results on the formation of filter cakes, phase transformation in tensile test TRIP steel samples and structural information revealed on multi-material selective laser melting additively manufactured test specimen.

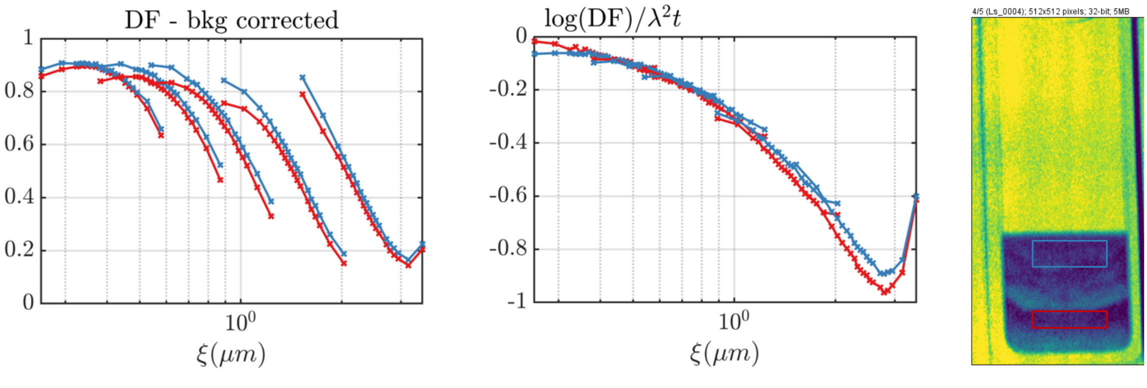

Figure 1 (left) Background corrected relative visibility signal measured in the two regions of interest marked in the right hand side image recorded for different sample to analyser grating distances; (mid) reduced dark-field contrast signal representing the product of the wavelength corrected total small angle scattering cross section and (G-1); (right) individual dark-field contrast image at a specific probed correlation length displaying the inhomogeneity of the sedimented filter cake in a standard cuvette;

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Development of laser-pump-neutron-probe measurements of Yb qubit candidates at SNS

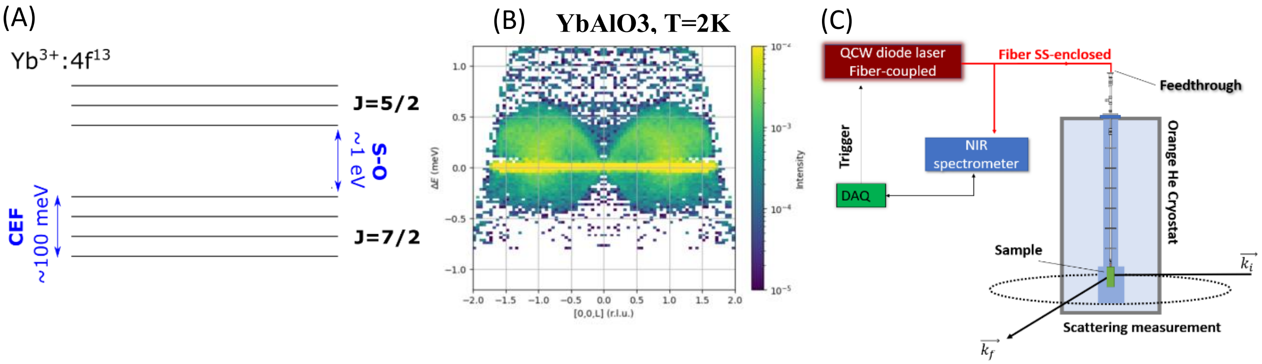
L. L. Kish[1], M. Piannasola[2], O. V. Garlea[3], A. A. Podlesnyak[3], A. A. Sirenko[4], B. Winn[3], I. A. Zaliznyak[3]

(1) Brookhaven National Laboratory (2) University of Tennessee, Knoxville (3) Oak Ridge National Laboratory (4) New Jersey Institute of Technology[4]

Rare earth ions in materials have emerged recently as promising candidate qubits for quantum information systems applications [1,2]. The strong spin-orbit coupling intrinsic to rare earths combined with screening of *4f* electronic shells by outer electrons leads to sharply defined optical excitations with extremely long coherence times up to several milliseconds. At low temperatures, the magnetic properties of such ions with odd numbers of electrons arise from the lowest energy Kramers doublets and can exhibit effective $S = \frac{1}{2}$ physics [5] (Figure (A) shows a schematic of energy levels of Yb^{3+} in a material while (B) shows the resulting two-spinon continuum). Such systems therefore open new possibilities for the optical control of states with long-range quantum entanglement.

The millisecond timescales of these spin-orbit excitations are in a range accessible to time-resolved neutron studies. Here we present ongoing efforts to explore magnetic dynamics of optically pumped Yb ions in oxide insulators ($Yb_xY_{1-x}AlO_3$ and $Yb_{3x}Y_{3-3x}Al_5O_{12}$) using time-resolved neutron spectroscopy at HYSPEC and CNCS. These laser materials are known for highly efficient conversion of incoming NIR photons (940 nm-980 nm) into single-ion excited states and back into outgoing photons.

In our design (Fig. C), laser excitation is achieved by feeding the output of a near-infrared diode laser through an optical fiber cable mounted in a standard Orange Helium cryostat. The laser is square-wave modulated, with falling edges synchronized with incoming neutron pulses. With no free-space laser involved, our setup is designed to be portable between beamlines accepting Orange cryostats and various other low-temperature sample environments, opening new possibilities for such studies at SNS and HFIR.



(A) Schematic of electronic levels in Yb^{3+}, showing spin-orbit and crystal field splittings (B) Our recent measurement of two-spinon continuum in YbAlO3 (C) Simplified schematic of LPNP setup

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Recent Developments at the Biological Small-Angle Neutron Scattering Instrument (Bio-SANS) at Oak Ridge National Laboratory

Authors:

Luke Heroux, Wellington Leite, Hugh O'Neill, Sai Venkatesh Pingali, Volker Urban, Kevin Weiss, Honghai Zhang, Qiu Zhang

The Center for Structural Molecular Biology (CSMB) at Oak Ridge National Laboratory (ORNL) is a national user facility funded to support and develop the user access and science research program of the Biological Small-Angle Neutron Scattering (Bio-SANS) instrument at the High Flux Isotope Reactor (HFIR). The Bio-SANS instrument is ideally suited for studies of biomacromolecules including proteins, DNA/RNA, lipid membranes and other hierarchical complexes. Bio-SANS has a diverse range of sample environment capabilities for the studies of biological systems. 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 to multiple phases (e.g. microemulsions) with additional capability of flowing one or two phases during measurement. We have developed a series of new sample environment capabilities that open new opportunities for the studies of biological systems. A robotic sample changer sample environment has been installed that supports measurement of a range of sample types including solutions, suspensions, powders, and solid materials. It can maintain samples during storage (up to 58) in a desired temperature range between 10 – 70 oC. A Peltier heating block at the sample position allows rapid temperature change between 10 – 100 oC for in operando measurements. Another example is combined size-exclusion chromatography – SANS for fractionation of biomacromolecules in beam. A novel aspect of this capability is the ability to perform continuous flow measurements as well as fractionation of complex mixtures of biomacromolecules. Other improvements to Bio-SANS include a new data acquisition system and a data reduction program that allows wedge-reduction for anisotropic systems such as biomass, and the ability to time-slice data files for analysis of time-resolved SANS measurements. In addition, the Bio-SANS detector system is currently being upgraded to include an additional mid-range detector bank that will greatly benefit time-resolved measurements of a variety of biological systems.

Website URL: https://www.ornl.gov/facility/csmb

In Situ Neutron Scattering Study of the Structure Dynamics of the Ru/$Ca_2N:e^-$ Catalyst in Ammonia Synthesis

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Ammonia (NH_3) synthesis is one of the most critical industrial processes. Compared to commercial iron catalysts, Ru catalysts show high intrinsic activity in this reaction but suffer from hydrogen poisoning. By loading Ru onto supports such as electrides and hydrides, the hydrogen poisoning problem can be significantly alleviated. For Ru/$Ca_2N:e^-$ catalysts, a reaction between the anionic electron of the support and adsorbed hydrogen species produces a hydrogen-deficient Ca_2NH hydride under the NH_3 synthesis condition. However, relevant studies on the structural dynamics of the Ru/electride catalysts under reaction conditions are very scarce. Taking advantage of the high sensitivity to hydrogen species, *in situ* neutron scattering (INS) techniques may provide insights into the structural changes during the reaction.

First, we synthesized $Ca_2N:e^-$ support by a solid-state method followed by loading Ru particles *via* a chemical vapor deposition (CVD) method. We studied the structure dynamics of the Ru/$Ca_2N:e^-$ catalyst in NH_3 synthesis at 350 °C *via in situ* INS experiment. After the initial NH_3 synthesis, peaks at 562, 711, and 762 cm^{-1} suggested that hydrogen-containing species were formed in the sample, most likely Ca_2NH *via* the reaction of the electride with hydrogen.[1] When we flowed H_2 over the catalyst, the intensity of most peaks became stronger, while the profile of the spectrum remained largely the same, indicating that more of the same H-containing species had formed (**Figure 1 a, b, black**). Then we introduced N_2 stream into the cell and the intensity of the peaks at ~550 and ~760 cm^{-1} decreased, while that of the peak at ~710 cm^{-1} increased. These differences suggested that the environment of hydrogen in the catalyst structure had changed, possibly due to the formation of a new phase(s).[2]

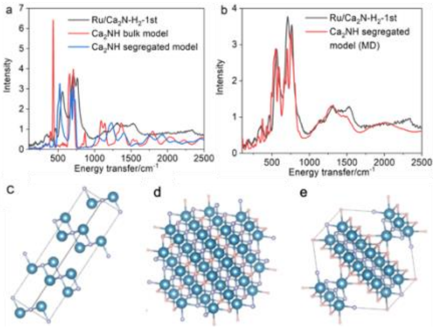

Figure 1. (a, b) INS spectra of Ru/Ca_2N in H_2 at 350 °C in the first cycle (black) and the comparison with simulated spectra from different models (blue and red). (c) Structure of the original Ca_2N, (d) Ca_2NH segregated model, (e) Ca_2NH segregated model with MD approach.

To understand these observations, simulated INS spectra were obtained based on various structural models of Ca_2NH. In Ca_2NH bulk model, N and H atoms were mixed between Ca layers (**Figure 1 c**). However, the peak at ~400 cm^{-1} in the simulation, presumably corresponding to the peak at 550 cm^{-1} in the experiment, was significantly underestimated in frequency and too sharp (**Figure 1 a, red**). We then adopted a model in which N and H were segregated (**Figure 1 d**). Phonon calculation produced a VISION spectrum much closer to that observed in the experiment, but the peak positions still had a systematic red shift (**Figure 1 a, blue**). Finally, the effects of phonon anharmonicity were examined by running a molecular dynamics (MD) simulation (**Figure 1 e**). The MD-directed VISION spectrum from the Ca_2NH segregated model showed an excellent agreement in all major peak positions (**Figure 1 b, red**). Thus, according to the neutron scattering data, we hypothesized that the H and N atoms were in different layers separated by the Ca layer, *i.e.*, a segregated structure, drastically different from the traditional mixed structure.

1. M. Kitano, *et al*. Essential Role of Hydride Ion in Ruthenium-based Ammonia Synthesis Catalysts. *Chem. Sci.* **7**, 4036-4043 (2016).
2. X. Yu, *et al*. In Situ Neutron Scattering Study of the Structure Dynamics of the Ru/$Ca_2N:e^-$ Catalyst in Ammonia Synthesis. *Chem. Mater.* **35**, 6, 2456–2462 (2023).

Recent development of operando neutron diffraction for studying energy storage materials

Authors:

Zhijia Du, Michelle Everett, Jue Liu

Neutron scattering has unique advantages for battery research. Neutron scattering is very sensitive to light elements (e.g., H, Li, C, and O), which are the most important ingredients for rechargeable Li/Na-ion batteries. It can also distinguish adjacent transition metal (TM) cations (e.g., Mn, Fe, and Ni) in battery cathodes, especially when conducting isotope substitution experiments. This capability allows accurate investigation of how cation arrangements affect the electrochemistry performance of various rechargeable battery cathodes. Neutron scattering can also be used to probe dynamics, particularly ligand anion vibration/lattice dynamic and ionic diffusions, in both electrode and electrolyte materials. Moreover, the strong penetration and nondestructive nature of neutron scattering makes it an ideal tool to characterize battery materials without damaging the sample or disturbing the electrochemical reactions, as often occurs with high-energy x-ray diffraction. Despite all these advantages, the use of neutron scattering (e.g., diffraction, quasi-elastic and inelastic scattering) for battery research has often been confined to ex situ studies of pristine or postmortem samples recovered from charged/discharged batteries. Although they may provide useful information about the functionality of individual components (e.g., cathode or anode), they often fail to provide key insights about what governs the battery performance. Furthermore, many charged or cycled materials are metastable, and recovered ex situ samples often differ from those under real operational conditions. Thus, developing operando neutron scattering capability, with the needed spatial/temporal resolution, is highly desired to fully unleash the unique advantages of neutron scattering for battery research. In this talk, I will present our recent efforts on developing neutron diffraction friendly in situ electrochemical cells, sample environments and related data reduction and analysis routines. Particularly, I will present the first high throughput and fast operando neutron diffraction study of the conventional Li-ion batteries, and the recent breakthrough of realizing the first operando neutron diffraction study of all solid-state batteries at NOMAD.

Correlated spin-orbital excitations from complex orbital order in MgV_2O_4

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MgV_2O_4 is a spinel based on magnetic V^{3+} ions which host both spin ($S = 1$) and orbital ($l_{eff} = 1$) moments. Owing to the underlying pyrochlore coordination of the magnetic sites, the spins in MgV_2O_4 only antiferromagnetically order once the frustrating interactions imposed by the $Fd\bar{3}m$ lattice are broken through an orbitally-driven Jahn-Teller structural distortion at $T_s \simeq 60$ K. Consequentially, a Néel transition occurs at $T_N \simeq 40$ K. We apply neutron and x-ray diffraction to probe the low-temperature spin-orbital ground state and hysteretic critical fluctuations near the transition temperatures. We apply neutron spectroscopy to observe multiple excitation bands and parameterize these in terms of a multi-level (or excitonic) theory based on the orbitally degenerate ground state. In particular, we observe an "optical-like" mode at high energies that we model as a spin-orbit exciton from the spin-orbital j_{eff}=2 ground state manifold to excited j_{eff}=1 energy level. This parameterization incorporates a magnetic Hamiltonian with spin-orbit coupling and local crystalline electric field distortions resulting from deviations from a perfect octahedra surrounding the V^{3+} ions. We use diffraction and spectroscopic results to discuss the excitation spectrum including weak optical-like excitations resulting from spin-orbital degeneracy. We suggest that this provides evidence for complex orbital order in MgV_2O_4. We then apply the consequences of this model to understand hysteretic effects in the magnetic diffuse scattering where we suggest that MgV_2O_4 displays a high temperature orbital memory of the low temperature spin order.

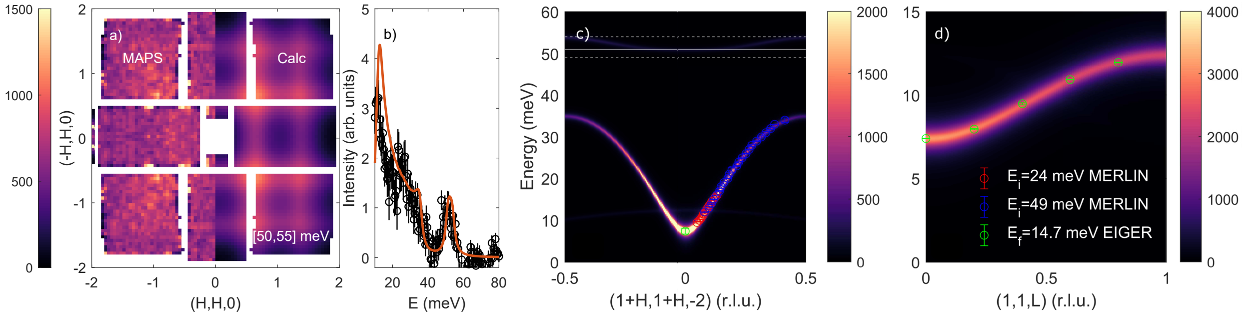

FIG. 1. *a*) Two-dimensional slice through the spin-orbital excitation comparing the neutron scattering data (left) and multi-level theory (right). *b*) One dimensional cut through $\vec{Q} = (2,0,0)$ showing the spin-orbital mode at ~ 50 meV, overlaid is the calculated intensity from the multi-level spin-orbital model. Calculated dynamical structure factor along the *c*) chain and *d*) inter-chain direction with extracted neutron scattering peaks overlaid.

Automatic Sample Alignment at TOPAZ using Machine Learning

Authors:

Jonathan Edelen, Morgan Henderson, Matthew Kilpatrick

This poster will present on recent work to apply machine learning for automation of sample alignment at the TOPAZ beamline. We have developed a neural network model for sample identification and contouring that computes the sample center of mass. This information is then integrated with the motor controller to automate the alignment of the sample. Here we present a summary of our efforts and our resent experimental results.

Update on the Extended Q-Range Small-Angle Scattering Diffractometer at the SNS

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Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830, USA

The status of the EQ-SANS diffractometer at the Spallation Neutron Source of the Oak Ridge National Laboratory will be presented. Recent upgrades in the sample environment area, in the available sample environment options, in the instrument control software and the data reduction protocol renders this instrument more versatile and more accessible to the user community. A redesign of the sample environment area enabled a wider range of sample environment equipment to be deployed. Many of the new ones are primarily of interest to the soft matter and biological sciences user community, the instrument can now accommodate sample environments for studies of magnetic materials and alloys. New equipment developed for the EQ-SANS instrument include a tensile stage combined with a designated oven – allowing the study of deformation of soft materials over a wide temperature range; a rotatable sliding plate shear cell – allowing the time-resolved characterization of deformed polymeric materials in different planes relative to the neutron beam; a Peltier-block system – allowing sample temperature control in the -10 C ~ 130 C range with improved precision. The instrument can also host Rheo-SANS experiments in conventional bob-cup geometries. A stopped-flow system is also under commissioning. The instrument control software was upgraded to the EPICS platform, which resulted in improved instrument stability, ease of sample equipment control and remote access. This change, coupled with the recently implemented drtsans data reduction package, largely improves the user experience especially for new users.

This research used resources at the Spallation Neutron Source, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory.

Interactive Automated Bragg Peak Identification with 3D Neutron Scattering Data at the TOPAZ Experiment

Authors:

David Bruhwiler, Evan Carlin, Matthew Kilpatrick

Neutron scattering experiments have undergone significant technological development through large area detectors with concurrent enhancements in neutron transport and electronic functionality. Data collected for neutron events include detector pixel location in 3D, time and associated metadata, such as, sample orientation, neutron wavelength, and environmental conditions. RadiaSoft and Oak Ridge National Laboratory personnel are considering single-crystal diffraction data from the TOPAZ instrument. We are leveraging a new method for rapid, interactive analysis of neutron data using NVIDIA's IndeX 3D volumetric visualization framework and data streaming. We have implemented machine learning techniques to automatically identify Bragg peaks and separate them from diffuse backgrounds and analyze the crystalline lattice parameters for further analysis. The implementation of automatic peak identification into IndeX allows scientists to visualize and analyze data in real-time. Our methods include a robust comparison with current analysis techniques which show improvement in a variety of aspects along with EPICS integration to automatically suggest new test parameters for user analysis. These improvements will be incorporated into IndeX for visualization to allow scientists an interactive tool for crystal analysis.

SNAPRed: A tool for data reduction and instrument calibration for the SNAP high-pressure diffractometer.

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The SNAP diffractometer is perhaps one of the most re-configurable instruments at the SNS, possessing movable detectors, bandwidth shifting choppers and an optional focusing optic. It has a wide angular coverage and highly pixilated detectors introducing multiple possibilities for grouping pixels to balance counting statistics and angular resolution. Furthermore, complex sample-environments are almost always present. Taken together, these instrumental realities introduce significant challenges for data reduction. As a consequence, it is often impossible to access the full information content of the diffraction pattern until days or weeks after the experiment ends.

In this poster, we will present the SNAPRed project that will support data reduction on SNAP. We will focus on key features of the conceptual design, illustrated with some prototype code using mantid algorithms [1]. A central feature of the approach is the definition of unique Instrument States, defined by the instrumental configuration (e.g. detector positions) and the ability to locate corresponding calibration folder with sample run number as input. A workflow for rapid, standardized calibration along with metrics to quantify the quality of calibration will be implemented.

The impact of the pressure cell (generically "container") manifests primarily in complex wavelength dependent backgrounds and attenuation effects. Since the pressures are sufficient to displace the nuclei in the containers, both background and attenuation change during the experiment and traditional "empty container" measurements are impossible. Existing approaches to managing these, along with their integration into the SNAPRed reduction flow will be presented.

Considerations relating to the UX of the software design will be discussed. These include accessibility to novice users, coupled with advanced controls for more experienced users and instrument scientists. An important aspect of the UX is performance and there are strict requirements on total time to complete reduction. This latter stems from a central requirement to real-time enable analysis via Rietveld in order to facilitate informed decision-making during the experiment. An important development has been the implementation of a method to re-label events, so called "lite" mode, that reduces the effective number of pixels without losing diffraction resolution while significantly speeding up data processing. A final important goal of the software is to standardize the reduction workflow and to capture all parameters, metadata and process ensuring full provenance of the reduced data is retained.

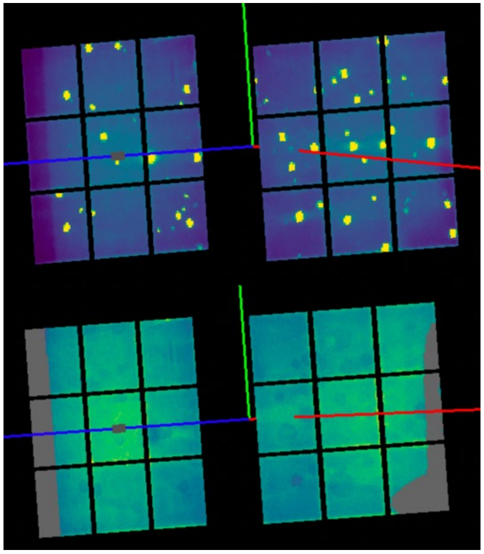

Figure 1 (top) a diffraction dataset collected from a diamond-anvil cell which creates a complex single-crystal background. (bottom) The same data after application of three separate masks via the SNAPRed prototype

This research used resources at the High Flux Isotope Reactor and the Spallation Neutron Source, both DOE Office of Science User Facilities operated by the Oak Ridge National Laboratory.

[1] Mantid 6.6.0: Manipulation and Analysis Toolkit for Instrument Data.; Mantid Project. doi: 10.5286/SOFTWARE/MANTID6.6, Arnold, O. et al. Mantid-Data Analysis and Visualization Package for Neutron Scattering and mu-SR Experiments. Nuclear Instruments and Methods in Physics Research

Section A: Accelerators, Spectrometers, Detectors and Associated Equipment 764 (2014): 156-166 doi: 10.1016/j.nima.2014.07.029

High Pressure Magnetometry and Neutron Scattering of the Frustrated Spinel $MgCr_2O_4$

Lila Nassar

Georgia Institute of Technology

Magnesium Chromite ($MgCr_2O_4$) is an example of a cubic AB_2O_4 spinel in which magnetic Cr^{3+} ions occupy a pyrochlore lattice that hosts highly frustrated antiferromagnetic spin interactions. Its proximity to two distinct highly degenerate phases, the coulomb and spiral-spin-liquid, results in unique behavior prior to the onset of magnetic ordering at around 13K. The application of pressure may permit the tuning of exchange interaction terms in the Hamiltonian enabling one of these nearly degenerate phases to dominate.

This presentation reports high pressure magnetometry of phase-pure polycrystalline $MgCr_2O_4$ conducted using a piston-cylinder pressure cell attachment for the MPMS3 SQUID magnetometer. Additionally, neutron scattering data collected on the HYSPEC beamline at Oak Ridge National Laboratory under ambient conditions and 1.7 GPa of pressure is presented. The magnetometry data shows an increase in the Néel temperature of the material with applied pressure. Inelastic neutron scattering spectra illustrate an energetic redistribution of excitations in the system. Elastic scattering spectra reveal a shift in spectral weight consistent with a change in the magnetic ground state of the system.

Controling trajectories of individual electrons: thermodynamics, kinetics, conformational gate, or all of the above?

Sharique A. Khan[&,%], Wellington Leite[%], Debarati Das[&], María Gonzaléz-Viegas[†], Ahmadullah Ansari[%], Maria-Andrea Mroginski[#], Hugh O'Neill[%,*], Anne-Frances Miller[&,*]

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Electron transfer bifurcation ('bifurcation') enables enzymes to produce a more potent reductant at the expense of a weaker one, in apparent deffiance of thermodynamics. However no rules are broken, because only one super-reducing electron is produced from each pair of electrons consumed. In-effect, exergonic transfer of one electron pays for endergonic transfer of the other, to yield an increased-potency reduced electron carrier. The resulting reduced ferredoxin or flavodoxin drives fixation of N_2 or CO_2. Both reactions are critical to life on our planet but not readily acheivable based on the more abundant biological reductant NADH. Thus, bifurcation enables otherwise impossible reactions, while conserving excess energy from exergonic transfers. Efforts are underway to confer these properties on man-made materials and devices. However to do so, it is important to understand the mechanisms that underlie nature's deft redistribution of energy among electrons.

An exergonic path is required for transfer of one electron, for thermodynamic feasibility. However its existence creates the challenge that this path must not be accessible to the second electron, which is endowed with most of the energy. Working with bifurcating electron transfer flavoprotein (BfETF), we are assessing the applicability of several possible mechanisms that could bar the high-energy electron from exploiting the exergonic path and dissipating energy. Via a combination of mutagenesis, spectroelectrochemistry, NMR spectroscopy, presteady-state kinetics and small angle neutron scattering (SANS), we are addressing three complementary hypotheses. Our presentation will address (1) possible thermodynamic restrictions on accessibility to the endergonic path, (2) a possible role for kinetics in transfer of the high-energy electron to the high-energy destination, and (3) the catalytic significance of an enormous domain-scale conformational change that is documented in structural studies and proposed to gate electron transfer.

Our studies of the redox tuning applied by the BfETF protein demonstrate that the flavin on the exergonic path is tuned to function as a one-electron carrier. This is in contrast to the behaviour of free flavins, which function primarily in pairwise electron transfer (hydride transfer). Meanwhile, nuclear magnetic resonance (NMR) and SANS data collection is already underway to test for rapid binding/dissociation events and domain-scale motions. These two methods are uniquely well suited to this problem, because they do not perturb the oxidation state of the flavins that are the electron carriers in ETFs (wherein the 'F' stands for flavin). Indeed, the more common SAXS and FRET-related methods, as well as X-ray crystallography, employ electromagnetic radiation that causes photoreduction of flavins and therefore could inadvertently trigger the conformational change we seek to control and characterize. However the neutrons employed by SANS are non-perturbative. Thus, we are pleased to demonstrate the applicability of SANS to BfETF, with data showing resolution of difficult behaviour attributable to spontaneous complex formation. Our new data moreover reveal subtle but consistent changes in response to substrate analog binding and reduction of the BfETF. Thus, longer distances appear populated in the states that would transfer electrons to partner proteins. Accelerated MD trajectories and molecular modelling are underway to understand these observations, and NMR will provide complementary residue-specific information.

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Frustration, dipolar, and quadrupolar physics on the square lattice oxyhalides DyOX (X=Cl,Br,I)

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2. Department of Physics and Astronomy, Louisiana State University, Baton Rouge LA

3. Oak Ridge National Laboratory, Oak Ridge TN

Rare-earth ions are an important ingredient in frustrated magnetism due to their propensity for anisotropic magnetization distributions. Due to this and their crystal field splitting allowing for an effective spin-½ degrees of freedom, they are commonly investigated in the search for exotic magnetic phases of matter. The Dysprosium Oxy-halides (DyOX, X=Cl,Br,I) have come under recent investigation as both layered Van der Waals materials [1] and a realization of a frustrated J1-J2 model (this work), with interplanar spacing being a function of the halide's ionic radius. This, paired with Dysprosium's high magnetic moment and single-ion quadrupolar behavior, leads DyOX to be an exciting platform to study specific aspects of quantum magnetism that are generally difficult to probe. This poster will present several forms of data: neutron diffraction and scattering, thermomagnetic measurements, and simulation results to elucidate their magnetic properties. Firstly, the results systematically show two ordering transitions. Integrated heat capacity data (Fig. 1c) will show that the second ordering gives a total of Rln4 entropy, implying four released degrees of freedom. This, combined with Dysprosium's known quadrupolar moment, implies a separated dipolar and quadrupolar ordering.

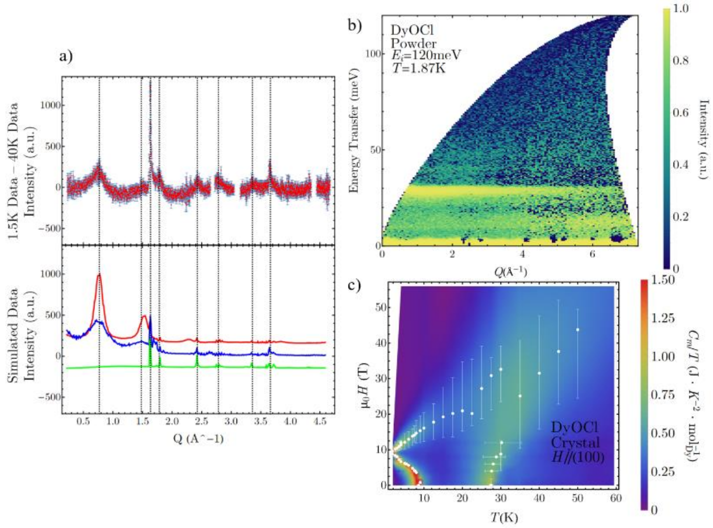

Figure 1: (a) Magnetic portion of neutron diffraction data compared to simulation on DyOBr. Here, the green line allows only c-axis (hard axis) ordering, the red line only allows a-b plane ordering, and the blue line contains both in equal measure. (b) Inelastic neutron scattering on DyOCl showing crystal field excitations. (c) Heat capacity measurements on single crystal DyOCl showing two separated orderings in zero field.

Inelastic neutron scattering data (Fig 1b) allows for the fitting of a crystal field Hamiltonian that predicts: a) a low-lying mode that is not experimentally observed and b) an XY-like anisotropy of the compounds. This anisotropy is reinforced with further bulk magnetic measurements. This then sheds light on the magnetic structure of the family compounds, which is driven primarily by the dipole-dipole forces across the Van-der-Waals gap. For increased c-axis spacing (DyOBr and DyOI), the system does not achieve complete long-range order and instead exhibits shorter range fluctuations as implied by significant magnetic diffuse scattering. Reverse Monte-Carlo simulations confirm c-axis disorder as a possible cause of both sharp and diffuse features in magnetic diffraction data. These results confirm DyOX as an exciting opportunity to study a variety of frustrated physics.

[1] Tian, Congkuan, Feihao Pan, Le Wang, Dehua Ye, Jieming Sheng, Jinchen Wang, Juanjuan Liu, et al. "DyOCl: A Rare-Earth Based Two-Dimensional van Der Waals Material with Strong Magnetic Anisotropy." *Physical Review B* 104, no. 21 (December 7, 2021): 214410. https://doi.org/10.1103/PhysRevB.104.214410.

Neutron scattering studies on Metal Organic Framework for gas storage and separation

Author:

Cheng Li

The current need for basic research to identify and understand the fundamental principles governing gas adsorption and separation processes is as high as ever. The relevance has been highlighted in recent U.S. Department of Energy (DOE), Office of Basic Energy Science Roundtable Reports, including Foundational Science for Carbon Dioxide Removal Technologies and Foundational Science for Carbon-Neutral Hydrogen Technologies. Thanks to its sensitivity to light elements and isotopes, neutron scattering experiments readily provide information on the position, occupancy, and short-range order about the guest-host interactions, providing unparalleled insight into long-range order, local steric hindrance, and dynamic local environments. In this talk, I will present the most recent experimental results from the POWGEN diffractometer, SNS. In particular, two model systems will be discussed:

Investigating the H2 adsorption behavior in MFM-170 and its derivatives. MFM-170 samples have demonstrated favorable H2 adsorption capabilities. Interestingly, introducing an amine group to the pyridine ring linked to the Cu metal in MFM-170 resulted in a different adsorption isotherm, despite the linker size and pore size remaining unchanged. In situ neutron scattering experiment identifying eight adsorbed sites after stoichiometric gas loading at 77 K. Total uptake ~ 0.055 g/g was achieved during the in situ experiment, comparable with the Ni2(m-dobdc)benchmark. I will discuss the effect of the side functional group on the adsorption behavior.

Optimizing pore size in M3(vtz)6 MOFs for H2/D2 separation . The pore size of MOFs plays a crucial role in determining their properties. Indeed, a linear correlation between volumetric absolute hydrogen uptake and volumetric surface area was observed, favoring small pores that could be better tuned chemically. One model system is M3(vtz)6, whose pore size could be tuned by substituting metal ions (M = Mg, Mn and Zn), and prompting drastically different H2/D2 adsorption selectivity, from ~30 to 15. Gas dosing experiment at POWGEN has identified two

adsorption sites in the Zn3(vtz)6: one sitting in a “pocket” surrounded by 3 vtz linker, and the other located in an open position. Although both sites have similar H2 occupancy, they demonstrated varied selectivity: the H2 sitting in the "pocket" site is more likely to be replaced by D2 after exposing the H2-loaded sample under D2. The location of the adsorption and its implication for isotope separation will be discussed.

Biosynthesis of deuterated lipids for structural and biophysical characterization of biomembranes and membrane proteins

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[5] Second Target Station, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

Membrane proteins play crucial roles in many cellular processes, however, studying membrane proteins is challenging because of their complex structure and fragility when isolated from their native environment. One solution is to embed membrane proteins in a membrane-mimic to provide a more native environment to facilitate their characterization. Small-angle neutron scattering (SANS) is an ideal technique to obtain structural information on biomacromolecules under physiologically relevant conditions. With this technique, deuterated phospholipids need be used to suppress their ^{1}H signal in SANS measurements. Currently, there are three ways to obtain deuterated phospholipids; extraction of native lipids from cells produced in deuterated media, chemical synthesis, or semi-synthetic approaches that combine both routes. In this study, we report on producing deuterated phosphatidylethanolamine (PE) by extraction and fractionation from native *Escherichia coli* extracts, and phosphatidylcholine (PC) from an engineered *E. coli* strain. The PC synthase (PCs) pathway was introduced into *E. coli* to produce partially deuterated and perdeuterated PC by feeding deuterated *E. coli* cultures with hydrogenated or deuterated choline chloride. The isolated PC product was confirmed by ^{1}H Nuclear Magnetic Resonance (NMR) and Liquid Chromatography - Mass Spectrometry (LC-MS) was used to determine the deuteration level of PC produced under different growth conditions. These materials can be used for neutron scattering studies with micelles, bicelles, liposomes, styrene-maleic acid lipid particles (SMALPs), and Membrane Scaffold Protein (MSP)-based lipid nanodiscs to produce a membrane-mimicking environment for studying membrane proteins, and can be used for deuterated lipids for NMR studies as well.

Investigating Short-Range Magnetic Correlations in the Dense Spin Glass (Zn,Mn)Te

Sabrina Hatt, Benjamin Frandsen

Department of Physics and Astronomy, Brigham Young University

Spin glasses have occupied a prominent role in condensed matter physics for decades, stimulating extensive experimental investigation and theoretical development in an effort to understand the complexity of the spin glass transition. At the heart of the spin glass transition is the cooperative freezing of individual magnetic moments, resulting in a ground state exhibiting short-range order but no long-range magnetic symmetry breaking. These short-range correlations give rise to diffuse neutron scattering. (Zn,Mn)Te is a representative spin glass compound which belongs to the class of II-VI-based magnetic semiconductors of interest not only for spin glass physics, but also potential applications in spintronics.

The HB-2A instrument at HFIR was used to conduct a temperature-dependent neutron diffraction study of Zn0.5Mn0.5Te. Sharp magnetic peaks and diffuse magnetic scattering were observed to coexist at low temperature, pointing to the development of both short-range and long-range magnetic correlations. At higher temperature, the sharp peaks were destroyed, but strong magnetic diffuse scattering features were present at all temperatures measured (up to 295 K), indicating that the short-range correlations are robust with temperature. This poster details an analysis of these magnetic correlations in reciprocal space and real space, using the magnetic PDF method; the implications of the findings on the nature of the spin glass phase in this compound are examined.

We acknowledge to Stuart Calder at ORNL for assistance with data collection.

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[1] J. A. Mydosh, “Spin glasses: redux: an updated experimental/materials survey”, Rep. Prog. Phys. 78, 052501 (2015).

Local cation order and ferrimagnetism in compositionally complex spinel ferrites

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1. Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee 37996, USA 2. Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

We present an exploration of a family of compositionally complex cubic spinel ferrites featuring combinations of Mg, Fe, Co, Ni, Cu, Mn, and Zn cations, systematically investigating the average and local atomic structures, chemical short-range order, magnetic spin configurations, and magnetic properties. All compositions result in ferrimagnetic average structures with extremely similar local bonding environments; however, the samples display varying degrees of cation inversion and, therefore, differing apparent bulk magnetization. Additionally, first-order reversal curve analysis of the magnetic reversal behavior indicates varying degrees of magnetic ordering and interactions, including potentially local frustration. Finally, reverse Monte Carlo modeling of the spin orientation demonstrates a relationship between the degree of cation inversion and the spin collinearity. Collectively, these observations correlate with differences in synthesis procedures. This work provides a framework for understanding magnetic behavior reported for "high-entropy spinels," revealing many are likely compositionally complex oxides with differing degrees of chemical short-range order—not meeting the community stablished criteria for high or medium entropy compounds. Moreover, this work highlights the importance of reporting complete sample processing histories and investigating local to long-range atomic arrangements when evaluating potential entropic mixing effects and assumed property correlations in high entropy materials.

In-Situ Neutron Total Scattering Studies on the Methane Oxidation and Reduction of CeZrO4 and Pd-CeZrO4

Author:

Sreya Paladugu

Co-authors:

Cheng Li, Katharine Page, Stephen Purdy

Integration of renewable feedstocks into the current energy infrastructure will require the development of catalysts and sorbents that can maintain high surface area and catalytic activity under challenging thermal/hydrothermal environments and acid gas exposure. Studying the time-resolved structural evolution of materials under gas flow conditions is key to understanding catalytic performance under real-world operating conditions with the end goal of extracting design strategies for industrially relevant catalysts. Total scattering, including both Bragg and diffuse scattering signals, enables the study of structural evolution in catalysts and can provide key insights into how long-range, nanoscale, and local atomic structure motifs differ and deliver unique properties. We have designed a new high temperature sample environment capable of hazardous gas flow (HGHS) at the Nanoscale Ordered Materials Diffractometer (NOMAD) at Oak Ridge National Lab, that will result in the capability to study acid gas interactions with sorbents and catalysts in-situ by neutron total scattering. The HGHS will deliver in-situ exposure to industrially relevant acid gas at NOMAD, enabling investigations of acid gas interactions with sorbents and catalysts, which will be a unique capability among neutron sources in the world and will aid in the design of new materials and processes with higher energy efficiency and a smaller emissions footprint. We will discuss the commissioning and proof-of-concept demonstration of the capabilities of the HGHS using Pd-CeZrO4 catalysts. We have developed Pd-CeZrO4 demonstrated to have improved low temperature methane oxidation activity and improved reducibility compared to the pristine support. Overall, this study will offer crucial structural insights into the effects of Pd loading on the structural evolution of CeZrO4 under methane oxidation and reduction conditions.

Recent advances at MARS, the cold neutron imaging instrument at HFIR

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Abstract

Neutron imaging, like X-ray imaging, is a non-destructive technique that investigates the internal features/structures of an object. The neutron’s high penetration through metals and its high sensitivity to light elements (H, Li, etc.) has enabled the development of neutron imaging as a unique tool in many research fields such as energy storage materials, additive manufacturing (AM), geology, nuclear materials, etc. Recently, the spatial resolution at MARS has been improved to resolve ~20 um features over a ~50 mm x ~35 mm field-of-view. In addition to the spatial resolution improvement, neutron grating interferometry (nGI) has been developed at MARS to utilize phase contrast to probe the existence of nanometer-sized features within a pixel or voxel. This poster will present both new capabilities along with some results from demonstration experiments.

Incommensurate magnetic order in Topological Antiferromagnet $ErMn_6Sn_6$

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RMn_6Sn_6 (R166) compounds (R = Gd-Lu, Y) with kagome Mn bilayers separated by triangular R layers have the possibility to tune topological states within the kagome layer via the magnetism of the R layers. In particular, competition between uniaxial R and easy-plane Mn anisotropies leads to a temperature-dependent spin-reorientation transition which can switch topological electronic phases. Here we present detailed single-crystal neutron diffraction data for Er166 as a function of temperature showing complex incommensurate antiferromagnetic (AFM) order between temperatures of $T_{ER} \approx 88$ and $T_N \approx 350$ K. The easy-plane ferrimagnetic order involving both Mn and Er sublattices below T_{ER} is in agreement with previous reports. Above T_{ER}, the Er and Mn lattices potentially decouple, and we find the Bragg peaks corresponding to incommensurate spiral-like magnetic order. Unlike Y166, we report even and odd higher-order harmonics of the AFM propagation vector. The second-order peaks, if nonmagnetic, could indicate a structural transition induced by magnetoelastic coupling. The triple-helix magnetic structure is applied on the mean-field calculation. Minimizing the free energy shows a good agreement with the change of propagation vector and magnetization results.

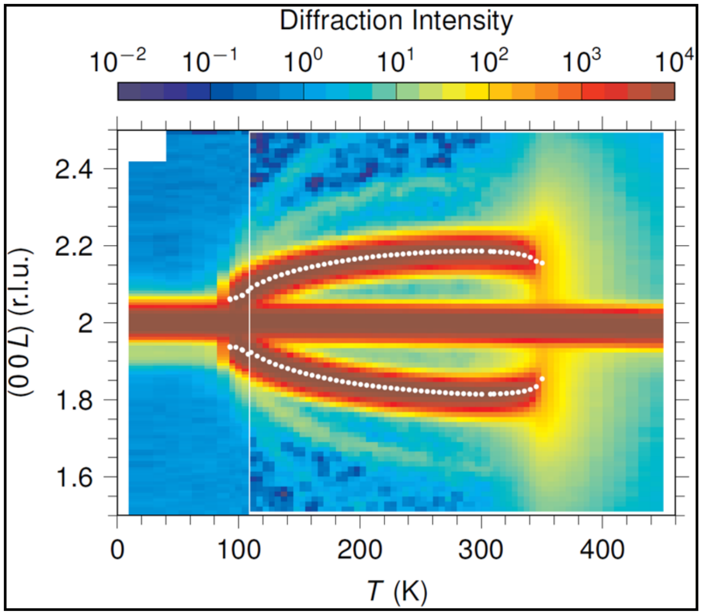

*Figure 1.*Temperature evolution of elastic neutron scattering intensity on $ErMn_6Sn_6$.

This research was supported by the Center for Advancement of Topological Semimetals, an Energy Frontier Research Center funded by the U.S. Department of Energy Office of Science, Office of Basic Energy Sciences, through the Ames Laboratory under Contract No. DE-AC02-07CH11358. Measurements at the High Flux Isotope Reactor at ORNL are sponsored by the User Facilities division of DOE BES.

Effect of chemical evolution on mechanical properties of dual-phase quaternary AlCoCrNi high-entropy alloy with high specific strength

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Keywords: High-entropy alloys, Chemical evolution, Mechanical properties, Specific strength.

Abstract. Quaternary AlCoCrNi alloy was fabricated by removing the heavy constituent of Fe from the dual-phase quinary AlCoCrFeNi high-entropy alloy to reduce the density and achive excellent mechanical properties. The AlCoCrNi alloy exhibited a nano-scale dual-phase structure consisting of Cr-rich A2 and Ni(Co)-Al-rich B2 phases with a high degree of coherence in both dendritic and interdendritic regions. In particular, the Ni(Co)-Al-rich B2 phase revealed non-stoichiometric composition between the Ni and the Al, which deviated with the Ni-Al-rich B2 phase with a stoichiometric composition in the previous AlCoCrFeNi high-entropy alloy. It was found that chemical evolution in the constituent phases strongly enhanced the mechanical properties of the dual-phase high-entropy alloy. Based on these microstructural features of the AlCoCrNi alloy, the mechanical properties were systematically investigated at wide temperature ranges.

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Intriguing magnetism in the chiral lattice antiferromagnet CoNb3S6

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Peter Siegfried, Andrew Balk, Hari Bhandari, John Freeland, Scott Crooker, Albert Davydov, Filip Ronning, Lekhanath Poudel, John Mitchell, Igor Mazin, Huibo Cao, Jeffrey Lynn, Nirmal Ghimire

CoNb3S6 is a chiral lattice antiferromagnet which belongs to a class of intercalated transition metal dichalcogenides known for complex magnetic textures, nontrivial band topology, and superconductivity. Previous neutron diffraction measurements below the Néel temperature (TN=27K) pointed to a collinear spin arrangement in this material. However, a more recent discovery of a large anomalous Hall effect (AHE), three orders of magnitude large than that explained by its weak field-induced magnetism, raises questions about the true nature of its magnetic ordering. Here, we present results on high resolution magnetic neutron diffraction and magnetic circular dichroism (MCD) measurements to unravel the details of its magnetic structure. We identify a long wavelength incommensurate magnetic structure with moments lying in the ab plane. Higher harmonic peaks are absent down to 2 K, consistent with a helical ground state. The results are complemented by MCD data suggesting changes in the underlying magnetic structure in an applied field, which may help explain the origin of the large AHE.

High pressure neutron diffraction at ultra-low temperature

Author:

Yan Wu

Co-authors:

Bianca Haberl, Todd Sherline, Jamie Molaison, Antonio dos Santos, Josh Pierce

In the physics of quantum materials, pressure is regarded as a clean ‘tunning’ parameter for manipulating material properties and probing emergent phenomena. Neutron studies are an essential tool to explore the magnetic order evolution and provide the information necessary for understanding the underlying mechanisms in materials. The development of ORNL large-volume diamond anvil cells (DAC) suitable for neutron diffraction now coupled with ultra-low temperature experiments provides the needed tools to allow access to many previously unreachable regions of the phase-space in material studies. In our ultra-low T DAC neutron experiment, refinable magnetic and nuclear single-crystal diffraction data were obtained on SNS’s SNAP beamline at 6 GPa down to 170 mK. This was achieved using a clamped diamond anvil cell equipped with polycrystalline diamond anvils and inside a large bore dilution refrigerator with modified tails for low background at the SNAP beamline.

VERITAS: a VERsatile Intense Triple Axis Spectrometer at HFIR

Wei Tian, Adam Aczel

Neutron Scattering Division

The **F**ixed **I**ncident **E**nergy **T**riple-**Ax**is **S**pectrometer (FIE-TAX, HB-1A) at HFIR has been renamed to the **VER**satile **I**ntense **T**riple **A**xis **S**pectrometer (VERITAS) after the recent completion of an entire instrument rebuild. VERITAS utilizes a double bounce monochromator system and a pyrolytic graphite analyzer array to produce a clean beam at $\lambda = 2.37$ Å with low background and an excellent signal-to-noise ratio. This instrument is optimized and well-suited for diffraction and spectroscopy studies of weak magnetic signals coming from single crystal and thin film samples. In this poster presentation, the VERITAS instrument team will give an update on the upgrade project, discuss the new capabilities, and provide an outlook for the science program.

Machine learning assisted reverse Monte Carlo modeling for neutron total scattering data

Author:

Yuanpeng Zhang

In the area of atomic-level structure modeling, there are two well known parallel problems. The theory driven modeling usually cannot fully account for the disorder of practical system and therefore may fail to reproduce the complete picture of structure model as observed experimentally. The data driven approach tries to derive the structural model from the experimental data in a reverse manner (i.e., data to model) and therefore naturally is able to catch features observed experimentally. But quite often it lacks the accurate coverage of energetic landscape from the theoretical perspective. In this contribution, we aim at bringing in a novel approach combining the theoretical and experimental considerations. To realize this, the LAMMPS module for energy calculation is implemented into the reverse Monte Carlo routine (here, the RMCProfile package was used) for modeling total scattering data. Through such a combined approach, atomic positions would be adjusted according to the agreement with experimental scattering data and the energy landscape simultaneously. Specifically concerning the energy calculation, the Gaussian processing based machine learning routine for potential field construction is employed here. Such an approach, at the same time providing density functional theory level of accuracy, guarantees a reasonably short computational time which is required for the metropolis algorithm for structure modeling. The LAMMPS implemented RMCProfile package for conducting the combined modeling is generally applicable to utilize neutron and X-ray total scattering data, X-ray absorption spectroscopy data, electron scattering data, etc. for structure modeling to provide insights into structure-property link of general condensed matter systems.

Artificial Intelligence-driven Hyperspectral Neutron Computed Tomography (HSnCT) Systems

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Hyperspectral neutron computed tomography (HSnCT) is an advanced neutron CT technique that can not only provide complementary information to X-ray computed tomography (CT), but also measure Bragg edge and resonance spectra. ORNL is constructing the new wavelength-dependent imaging beamline (VENUS) at spallation neutron sources. The traditional approach of reconstruction involves acquiring projection data by rotating the object over a pre-defined set of angles about a single axis. Once all the data has been collected (typically over the span of a few days at a pulsed source) the volume is reconstructed using an analytical reconstruction algorithm such as the filtered back projection (FBP). However, this method is not efficient for pulsed sources because : 1) each projection is time-consuming, i.e. usually requiring several hours of acquisition time to reach a reasonable signal-to-noise ratio (SNR); 2) the projection directions are not adapted to the sample features, and 3) the reconstruction is always done at the end of the experiment which might yield low SNR and artifact-ridden reconstructions at which point several days' worth of measurement time has been spent.

In this poster, we will present an autonomous HSnCT system that can acquire projection in a sample-shape adaptive manner and assess the quality of scans in real-time during the measurement. Once the system is running, an edge-alignment scanning angle selection algorithm utilized after a few projections have been measured to dynamically decide the next projection direction. Simultaneously, an AI-based evaluation of the reconstruction quality after each scan is completed for the decision making (if continue the measurement). Our proposed method can lead to dramatic decreases in acquisition time for HSnCT scans while acquiring data from the most informative orientations that are adaptive to the object being measured.

Key words: Hyperspectral neutron computed tomography, Deep learning, Image processing, Autonomous system, Neutron imaging, Spallation Neutron Source

A portion of this research used resources at the Spallation Neutron Source, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory.

Effect of chemical evolution on mechanical properties of dual-phase quaternary AlCoCrNi high-entropy alloy with high specific strength

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Quaternary AlCoCrNi alloy was fabricated by removing the heavy constituent of Fe from the dual-phase quinary AlCoCrFeNi high-entropy alloy to reduce the density and achive excellent mechanical properties. The AlCoCrNi alloy exhibited a nano-scale dual-phase structure consisting of Cr-rich A2 and Ni(Co)-Al-rich B2 phases with a high degree of coherence in both dendritic and interdendritic regions. In particular, the Ni(Co)-Al-rich B2 phase revealed non-stoichiometric composition between the Ni and the Al, which deviated with the Ni-Al-rich B2 phase with a stoichiometric composition in the previous AlCoCrFeNi high-entropy alloy. It was found that chemical evolution in the constituent phases strongly enhanced the mechanical properties of the dual-phase high-entropy alloy. Based on these microstructural features of the AlCoCrNi alloy, the mechanical properties were systematically investigated at wide temperature ranges.

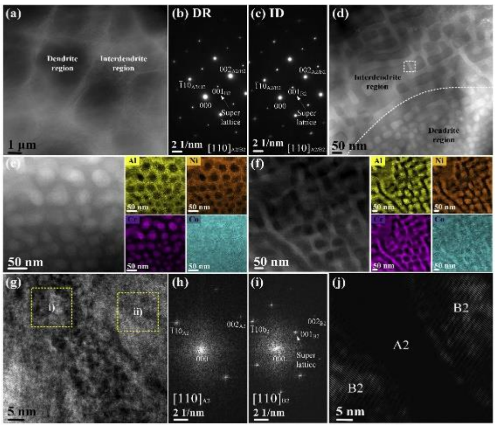

Figure 1. [(a) and (d)] STEM HAADF images and [(b) and (c)] SAED patterns correspond dendritic and interdendritic regions, [(e) and (f)] STEM HAADF images with corresponding EDS elemental maps, (g) HRTEM image obtained from the white dotted rectangle in (d), [(h) and (i)] FFT patterns taken from i) and ii) areas in (g) and (j) corresponding DF image of as-cast AlCoCrNi alloy.

Firstly, the microstructural features and the related mechanical properties of the AlCoCrNi HEA designed by modulating the alloy component from the AlCoCrFeNi HEA were systematically investigated. The detailed investigation on the microstructural features of the alloy revealed that the nano-scale Cr-rich A2 and Ni(Co)-Al-rich B2 dual-phase structure with a high degree of coherence were formed in both the micro-scaled DR and ID regions. The Ni(Co)-Al-rich B2 phase in both regions revealed the non-stoichiometric atomic ratio between the Ni and Al elements, which deviated with that of the Ni-Al-rich B2 phase in the previous AlCoCrFeNi HEA.

Secondly, from the modest change in the chemical composition of the Ni(Co)-Al-rich B2 phase and the high degree of coherence between the constituent phases[1], the AlCoCrNi HEA with a lower density compared with the AlCoCrFeNi HEA exhibited a highly improved yield strength and the remarkable SYS without a trade-off between the strength and the ductility at room temperature. Moreover, The AlCoCrNi HEA also represented superior strength at high temperatures up to 873 K, which was much higher than that of the commercial Ni-based superalloys.

Finally, based on these results, it is believed that tailoring the chemical composition or the atomic ratio on the constituent phases through the alloy designing can act as an effective way to improve the mechanical properties of the dual-phase HEAs. Furthermore, the development of the AlCoCrNi HEA with remarkable mechanical properties at wide temperature ranges can contribute to extending the potential of dual-phase HEAs for structural applications.

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Development of a scintillator-based neutron detector using a Timepix3 camera for Larmor labeling techniques

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Larmor labeling techniques are methods to investigate material properties using polarized neutrons by taking advantage of the additional spin freedom of neutron. Since the Larmor precession phase of neutron spin carries the static or dynamic structure information of the sample, the achievable spatial or energy resolutions are decoupled with the neutron wavelength spread, which allows us to extend the resolution beyond the conventional scattering techniques. Some of these Larmor labeling techniques require the modulation of neutron beam in the space or time domain, such as spin-echo modulated small angle scattering (SEMSANS)[1] and modulated intensity with zero effort (MIEZE)[2] techniques, which imposes great challenges to the spatial and temporal resolution of current detectors. Recently, a detector with a Timepix3 chip in combination with an image intensifier, optical lens, and scintillator has been developed.[3] This detector offers high spatial and temporal resolution with the center of mass calculation in time and space dimensions. Furthermore, the field of view and scintillator can be tailored relatively easily for each experiment. Neutron and gamma events can be distinguished using each scintillation light property, which enables us to conduct experiments with a high signal-to-noise ratio. These features make this detection system promising for experiments with Larmor labeling techniques.

Figure 1 shows a picture of the developed detector in ORNL. Neutrons that pass through the silicon window (30×30 mm^2) interact with a ^{6}LiF:ZnS(Ag) scintillator. The scintillation light is reflected by a mirror towards the optical lens. The reflected light is multiplied with the image intensifier and detected with the Timepix3 chip. The clustering and centroiding analyses are conducted using *Sophiread*, which is a toolkit for reading and processing raw data from Timepix3, developed in ORNL.[4] Using this code, we have succeeded to discriminate gamma events and construct a neutron image. In this presentation, the details of the detector setup and data analysis flow will be presented. An analysis method to increase the spatial resolution of neutron images will also be discussed.

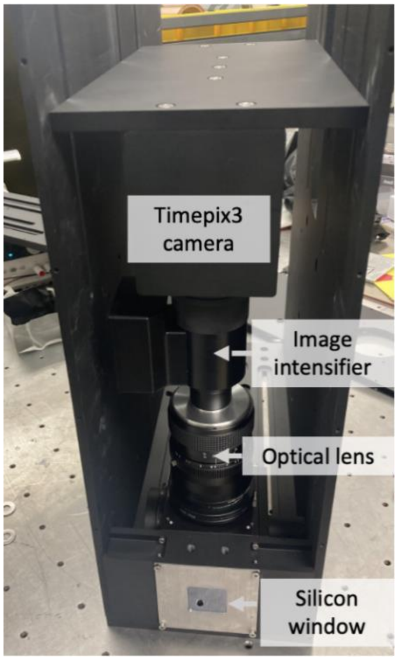

Figure 1. A scintillator - based neutron detector using a Timepix3 camera

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Anharmonic Stabilization of Rutile TiO_2

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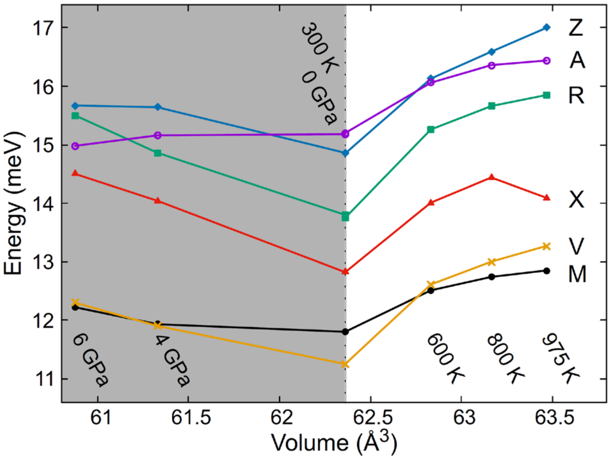

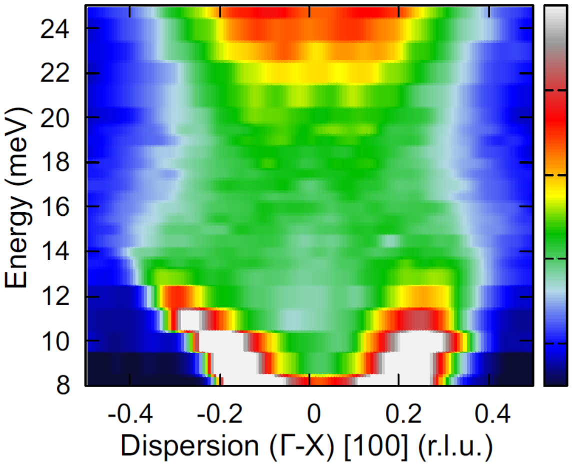

Abstract

Rutile is the stable phase of TiO_2, despite not being the commonly synthesized product, which is metastable anatase. It also exhibits unusual behavior in the phonon branches, specifically low-lying transverse acoustic modes that harden with increasing temperature instead of the typical softening behavior. Here, we have studied the phonon dispersion of rutile TiO_2 using a combination of temperature- and pressure-dependent inelastic neutron scattering (with the direct geometry spectrometer ARCS) and inelastic x-ray scattering. Our work reveals unusual behavior of phonons with temperature and pressure for a large fraction of modes. Many modes, including low-energy TA modes and higher-energy transverse optic (TO) modes, exhibit significant softening with decreasing temperature at the zone boundaries (ZB). Near the zone center, more conventional phonon softening with increasing temperature is observed. The same ZB phonons that soften upon cooling with a thermally induced volume contraction harden with a pressure-induced volume contraction, indicating essential departure from the quasiharmonic approximation. Another unusual feature we discovered is the formation of a "waterfall effect" at the Γ-point, where the intensity of a TO mode couples strongly with the neighboring TA mode. This effect becomes notably stronger with increasing temperature as the two phonon branches shift away from each other. Such effects may have significant implications for the unusual stability of the rutile phase over many other metastable phases, such as anatase, which is a commonly synthesized phase at ambient pressure.

The story of moving Indium: Tracking structural peculiarities of Indium Tin Oxide nanoparticles multilayer films

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Transparent conducting indium tin oxide (ITO) films are prevalent as top electrode material in photovoltaic devices, LEDs, TV and computer screens. While operating with solid state semiconductors, ITO electrodes have proven their exceptional performance, even against state-of-the-art nanomaterials-based transparent conducting electrodes [1]. However, in the configuration needed for organic semiconductors, ITO was found to degrade under applied bias. While the complete mechanism of device degradation is not known, researchers have speculated on possible diffusion of indium into the polymer, leading to polymer doping [2]. Relatively stiff ITO electrodes may not be suitable for flexible/stretchable electronics. This problem can be mitigated by replacing sputtering with multilayer, solution based (e.g., LBL, sol-gel) deposition of ITO [3] Will indium be mobile in multilayer ITO? Here we present pilot results on investigation of indium diffusion in sol-gel ITO films composed of several layers of ITO nanolayers.

In our previous NR study of sol-gel ITO films deposited on quartz substrates [4], it was concluded that the non-ideal interfaces in between individually spin coated layers was a result of lower NSLD in that region due to the presence of voids or delamination at the interfaces. This was further supported by a higher sheet resistance than expected and the presence of very small elongated voids that could be seen on AFM images. Because we had earlier deposited ITO films on sodium silicate glass substrates [5] which had shown spherical voids that we labeled as volcano shaped, we hypothesized that the effect was due to surface properties of the substrates. As a result, we conducted a more detailed study using borosilicate, sodium silicate and quartz glass substrates. Films with 1, 2, 3 and 5 layers were deposited using a 0.5M ink concentration at a very low humidity of 18.9% and processed in the same manner as the earlier studies [4,5] as we believed that the humidity during film deposition might have caused the formation of the voids observed in both cases which was proven to be correct [6].

Figure 1 demonstrates that the films analyzed in this study do not contain either of the two types of voids described above and are quite smooth with an rms of <2.5 nm for all three substrates which can be seen on the 10 x 10 μm^2 images and < 1nm on 2 x 2 μm^2 AFM images (not shown). The sheet resistance of all three films was comparable and less than ~ 400Ω/square with excellent transmittance.

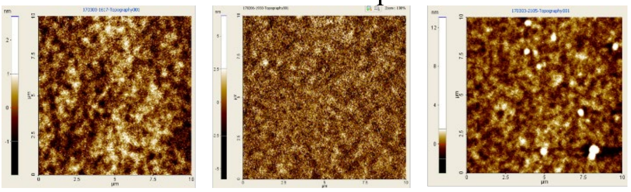

Figure 1. AFM Topography images of 5-layer ITO thin films deposited onto fused quartz, sodium silicate and borosilicate glass showing no obvious voids as in previous studies.

Neutron reflectometry (NR) experiments were conducted first, and the analysis resulted in similar cross sections for all three films with NSLD showing a lower NLSD density at the interfaces between layers. The complementary XRR results confirmed NR data and suggested that films were inhomogeneous across the layer and therefore required us to conduct SIMS analysis to determine elements variations. SIMS results revealed that interfaces are enriched with indium and showed lower In content in the bulk of each layer. The results are quite similar for the multilayer films deposited onto borosilicate as well as sodium silicate glass substrates.

Thus, we present evidence that sol-gel ITO coatings are non-uniform with heavily In-doped interfaces and under-doped layers of TiO_2. The questions of the mechanism of electron/hole conductivity in these coatings and whether interfacial trapping indium may prevent its diffusion into organic electronic device will need to be answered through follow-on experiments.

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A Graph Theory Approach to High Throughput Crystal Motif Identification

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Department of Physics, Massachusetts Institute of Technology

Often in the search for novel electronic, magnetic, and structural phases in bulk single crystals, it is useful to search for materials with certain structural motifs. For example, in the search for quantum spin liquid candidates, much attention is given to certain lattice motifs such as the triangular, honeycomb, kagome, hyperkagome, etc. With the broad availability of large materials databases, high throughput methods for identification and classification of the crystal motifs present in a material are a powerful tool for identifying new growth candidates. Here, we describe the application of a graph theory algorithm, Systre [1], to identify and classify motifs in elemental sublattices of materials (general workflow depicted in Figure 1). For example, in the Materials Project, 5853 kagome, 36,475 triangle, and 17,419 honeycomb lattices are identified. This graph theory driven approach has several distinct advantages, including its invariance to distortions from the maximally symmetric form of a motif, and its generality to quickly search for any motif of interest in a large database. Additionally, parsing through results can provide insight into which crystal families and space groups support certain motifs, as well as overall statistics on how common a certain motif is. We believe this approach is useful to the materials design of a wide range of desired states such as electronic flat band materials [2], spin liquids, topological materials, and exotic magnets.

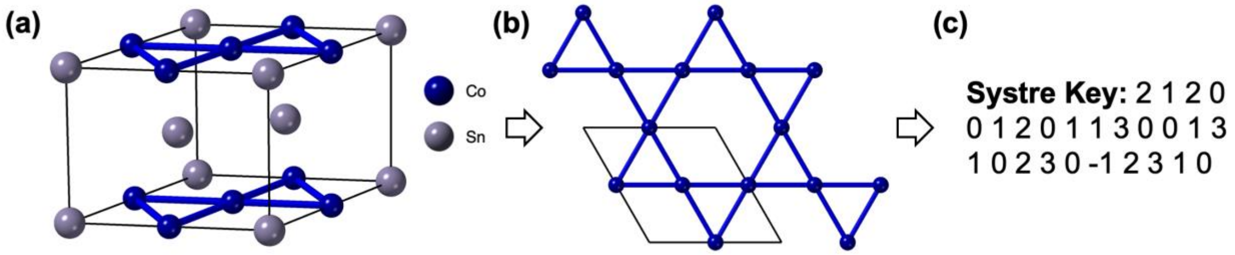

Figure 1. (a) The kagome flat band material CoSn with kagome motif on the cobalt sublattice. (b) The isolated kagome elemental sublattice. (c) a unique identifying code generated by Systre for the kagome lattice, allowing rapid search and identification of motifs in large materials databases.

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Magnon Softening in Y-doped TbSb

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Understanding the behavior of magnetic systems in the presence of disorder is a challenging yet important area of research, as it has implications for the design and development of novel magnetic materials. In this context, dilute magnetic systems with a cubic crystal structure, such as Y-doped TbSb, have attracted significant attention as they offer a simple yet effective platform for studying disordered magnetism. TbSb is an interesting system for studying disordered magnetism due to its cubic crystal structure, and large magnetic scattering ($S = 7/2$, 9.7 μB). Doping with non-magnetic Y gradually lowers the Neel temperature, consequently increasing the disorder within the system. This allows us to study the effects of increasing disorder in the magnetic structure as a function of doping concentration. Consequently, Y-doped TbSb can serve as an effective testbed to investigate the interplay of disorder and magnetic excitations. Additionally, the cubic crystal structure of TbSb makes it an ideal and simple material for studying the effects of disorder on magnetic properties, as it lacks the anisotropy that is often present in other magnetic materials. In this aspect, a recent work on a high entropy oxide $(MgCoNiCuZn)_{0.2}O$ showed the existence of magnons above the Neel temperature, which exemplifies entropy-based stabilization of magnetic order.[1] However, the chemical complexity of such oxides prohibits further investigation of the role of disorder in its magnetic properties, as they cannot be grown as single crystals. In this regard, Y-doped TbSb is a perfect candidate material to study the role of disorder in such entropy-based stabilization of magnetic order.

In this work, we investigate the effect of disorder on the magnetic properties of dilute magnetic system based on Y-doped TbSb. Furthermore, we used inelastic neutron scattering at the HYSPEC spectrometer at SNS to investigate the change in the magnetic excitation spectrum of Y-doped TbSb as a function of doping concentration. The softening of magnons with increasing Y concentration is dramatic, gradually softening and broadening until we reach the percolation threshold of 40% Y, where the system no longer remains antiferromagnetic. Our study provides new insights into the behavior of magnons in disordered magnetic materials and highlights the potential for further research in this field.

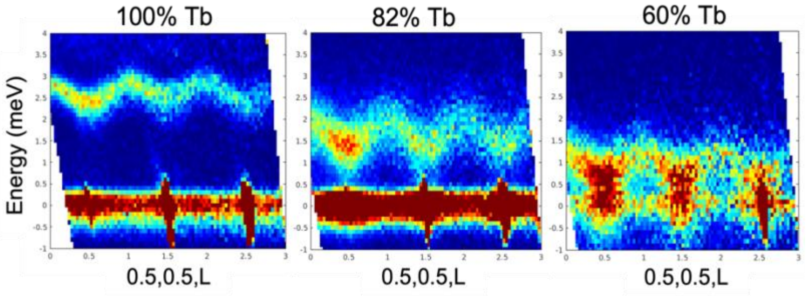

Figure 1. Magnon softening as a function of Y-doping in TbSb.

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1. Zhang, J. et al., "Long-Range Antiferromagnetic Order in a Rocksalt High Entropy Oxide" Chem. Mater. **31**, 3705 (2019)

Spin Switchable 2D-Superlattice Perovskite Film via Multiferroic Interface Design

Bogdan Dryzhakov, Valeria Lauter, and Bin Hu

Abstract:

Spin-switchable phenomena, which enable the control of electron spins in materials to directly influence their magnetic and electronic properties, are essential in the development of emerging properties and functionalities in semiconductors and advanced optoelectronic applications. This presentation reports spin-switchable circularly photoluminescence (CPL) between right-hand σ+ and left-hand σ- polarizations in 2D-superlattice perovskite (4,4-DFPD$_2$PbI$_4$) films through a multiferroic perovskite/Co interface design. By altering the ferromagnetic spins on the Co surface between positive and negative magnetic field directions (+B and -B), we demonstrate that the CPL in the 2D-superlattice perovskite can be switched between σ+ and σ- polarizations at room temperature due to selective interactions between the ferromagnetic spins on the Co surface and the circularly polarized σ+ and σ- orbitals within Rashba band structures. Polarized neutron reflectometry (PNR) measurements reveal tunable interfacial coupling of the Co magnetism to the perovskite's spin-polarized excitons, with chemical (NSLD) and magnetization (MSLD) depth profiles showing optically induced magnetization within the perovskite's surface due to coupling between photoexcited orbital magnetic dipoles and spins of the ferromagnetic atoms at the interface. When the Co is removed, switching the magnetic field between positive and negative directions (+B and -B) consistently changes the CPL from the excited σ+ band to the unexcited σ- band, indicating a non-directional spin-scattering-induced intersystem crossing within Rashba structures. This understanding highlights the key parameters of spin ordering and scattering in order to develop switchable phenomena in functional perovskite superlattices through their Rashba band structures and advancing a path towards spin-tunable opto-electronics.

Coupling of magnetism and Dirac fermions in $YbMnSb_2$

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Dirac semimetals remain at the forefront of research on topological materials because of the fascinating quantum electronic phenomena they show and of their potential technological applications in spin-polarized transport. Among different types of Dirac semimetals, the family of 112 ternary pnictogens $A/R\text{Mn}X_2$ (A = Ca, Sr; R = Yb, Eu; X = Bi, Sb) have attracted extensive attention due to their common layered structure in which the X layers hosting itinerant Dirac charge carriers are separated by strongly correlated insulating Mn-X layers. Both inter-layer charge transport and the magnetic correlations between Mn layers require that Dirac carriers are coupled to strongly-correlated Mn electrons. Therefore, these materials have become a fertile playground for investigating the interaction of the conduction Dirac electrons with the local-spin magnetic Mn-X sublattice, *i.e.* spin-fermion coupling.

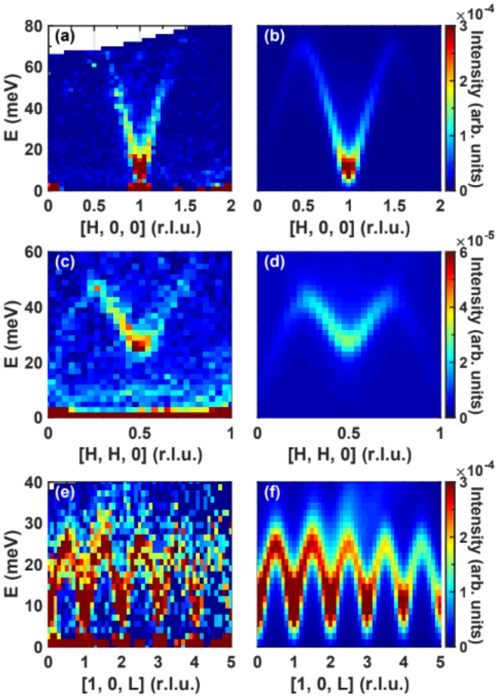

Figure. 1 Measured (a)(c)(e) and fitted (b)(d)(f) spin wave spectra of $YbMnSb_2$ at 5.5 K.

To establish the systematics of spin-fermion coupling in the 112 family of Dirac semimetals and elucidate its properties, we performed inelastic neutron scattering measurements of magnetic excitations in $YbMnSb_2$, a typical 112 family material. Fig. 1 (a)(c)(e) present inelastic neutron scattering spectra for $YbMnSb_2$ in the antiferromagnetic (AFM) phase at 5.5 K, which reveal the spin-wave dispersion along [H, 0, 0], [H, H, 0], and [1, 0, L] directions, respectively. Fig. 1 (e) clearly demonstrates the presence of a spin-gap, resulting from uniaxial anisotropy. The spectra are also slightly blurred along the energy axis, indicating the presence of damping. To quantify the magnetic interactions and the spin-wave damping (parameterized as γ), we performed quantitative analysis using the effective spin Hamiltonian, $H = \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + D \sum_i (S_i^z)^2$, where J_{ij} represent the in-plane nearest, next-nearest, and out-of-plane nearest neighbor interactions. D quantifies the uniaxial anisotropy for Mn^{2+} spins. We use a damped-harmonic-oscillator representation of the dynamical spin correlation function $S(\boldsymbol{Q}, E)$[1], with which we extracted the damping parameter $\gamma = 6.9(4)$ meV that is directly related to the spin-fermion coupling according to the theoretical description [1]. The spin wave damping in $YbMnSb_2$ is roughly twice as large as that in $YbMnBi_2$ and the inter-layer interaction is also much stronger, indicating that the interaction mechanism is rooted in the spin-fermion coupling. Comparison of these model parameters in 112 family materials allows establishing systematic phenomenology of spin-fermion coupling in these systems.

[1] A. Sapkota *et al.*, Physical Review B **101**, 041111 (2020)