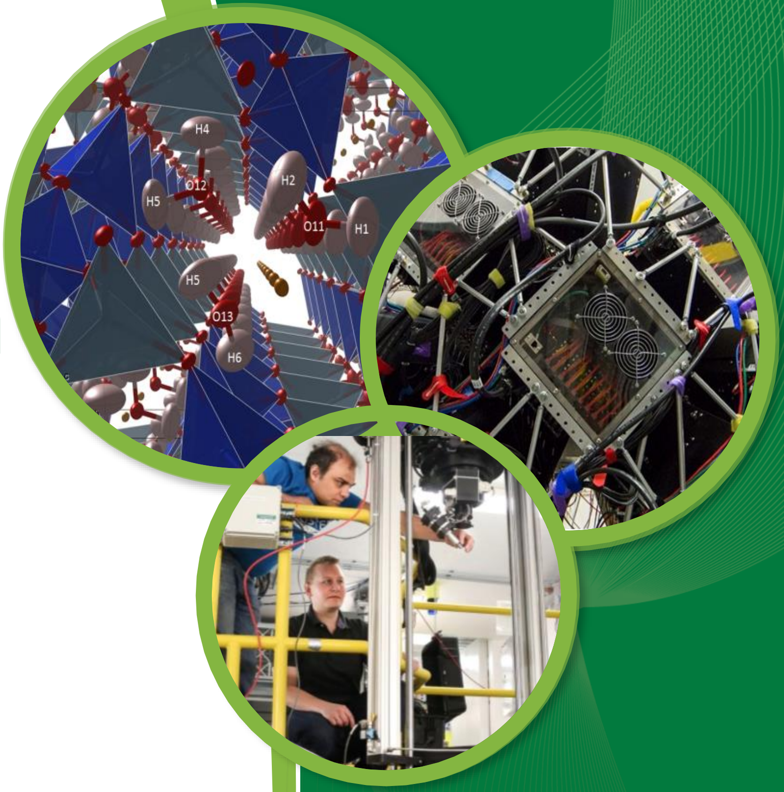
BASIS
Time-of-Flight Backscattering Neutron Spectrometer



Eugene Mamontov

Spectroscopy Group

Neutron Scattering Division

Neutron Sciences Directorate

Oak Ridge National Laboratory

ORNL is managed by UT-Battelle
for the US Department of Energy

Beamline Review Checklist

1. BASIS overview
2. Scientific Mission and Impact
3. Beamline Productivity
4. General user program and beam time usage
5. Adequacy and reliability of software, sample environment and ancillary equipment
6. Science Highlights
7. Future instrument science and development plan
8. Risks
9. Summary

BASIS Overview

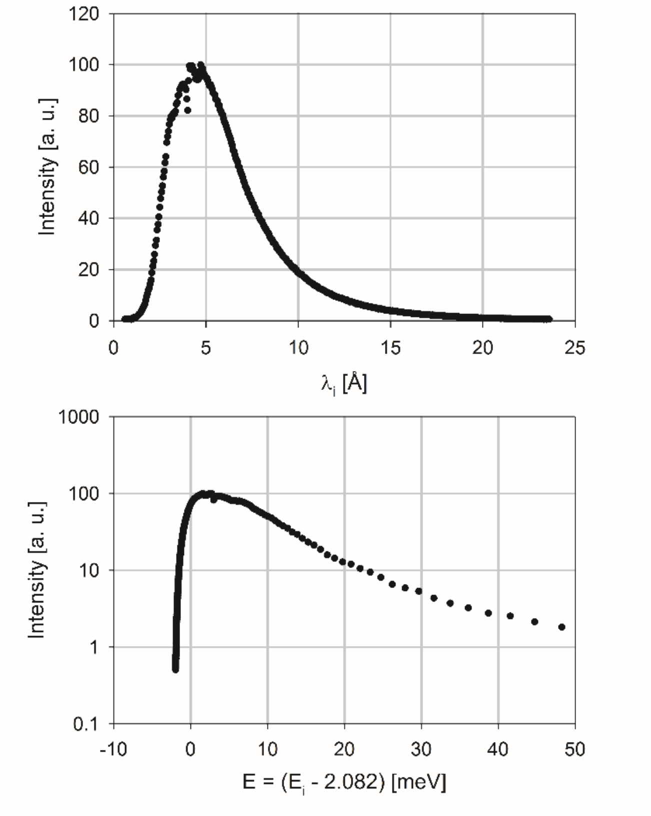
- The SNS BASIS is a Neutron Time-of-Flight Backscattering Spectrometer optimized for high energy resolution (ca. 0.0037 meV, FWHM, in the typically used configuration with Si(111) analyzer crystals, and ca. 0.015 meV, FWHM, with Si(311) analyzer crystals.
- BASIS probes microscopic dynamics in various systems from a multitude of research areas, including very broadly defined soft matter, energy materials, catalysis, hydrogen bonding, magnetism, minerals and earth and environmental sciences, etc.
- BASIS advantages is due to a combination of high counting statistics with a fine energy resolution and a broad (for a backscattering spectrometer) range of accessible energy transfers.

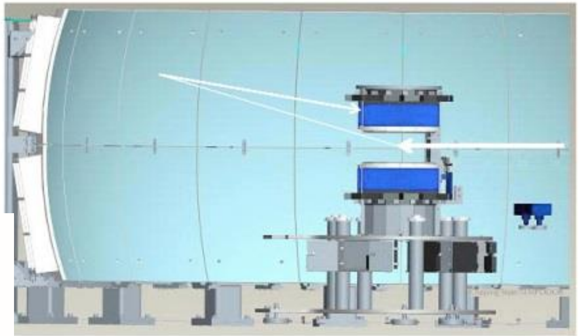
Instrument Specifications

Moderator	Decoupled poisoned hydrogen
Source to sample distance	84 m
Sample to analyzer to detector distance	4.710-4.729 m
Analyzers	3 sets of Si111 at 88° Bragg angle, (11.5-161.2)° in plane, (1-18)° out of plane
Analyzers	1 set of Si311 at 88° Bragg angle, (11.5-161.2)° in plane, (1-18)° out of plane
Q coverage	Si111: 0.2-2.0 Å^{-1}, Si311: 0.4-3.8 Å^{-1}
Incident wavelength bandwidth	0.5 Å at 60 Hz, 1.0 Å at 30 Hz
Energy transfer	Variable, -0.1 meV to +0.1 meV and -0.1 meV to +0.5 meV are used most often for Si111
Energy resolution (FWHM, Q-averaged)	Si111: 0.0037 meV, Si311: 0.015 meV
Sample size	3 cm by 3 cm
Neutron beam divergence on the sample	± 30 mrad horizontally and vertically
Sample environment	variable

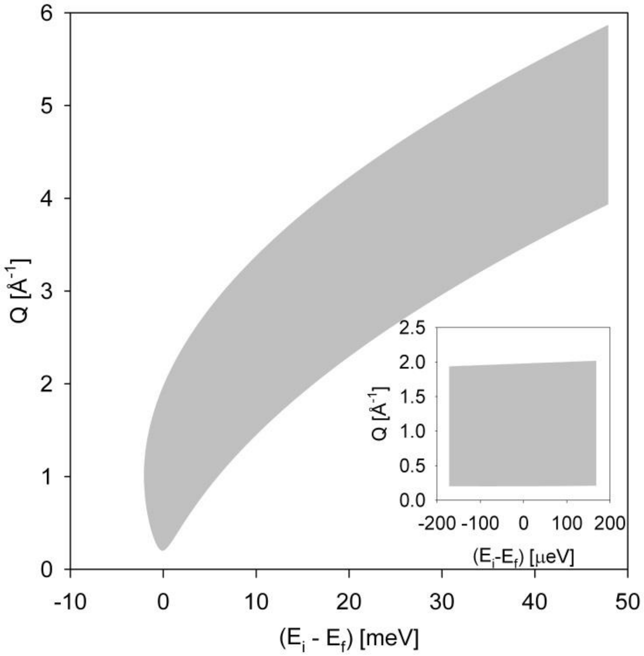
A few illustrative figures for BASIS

Incident spectrum (bandwidth to choose from, using choppers)

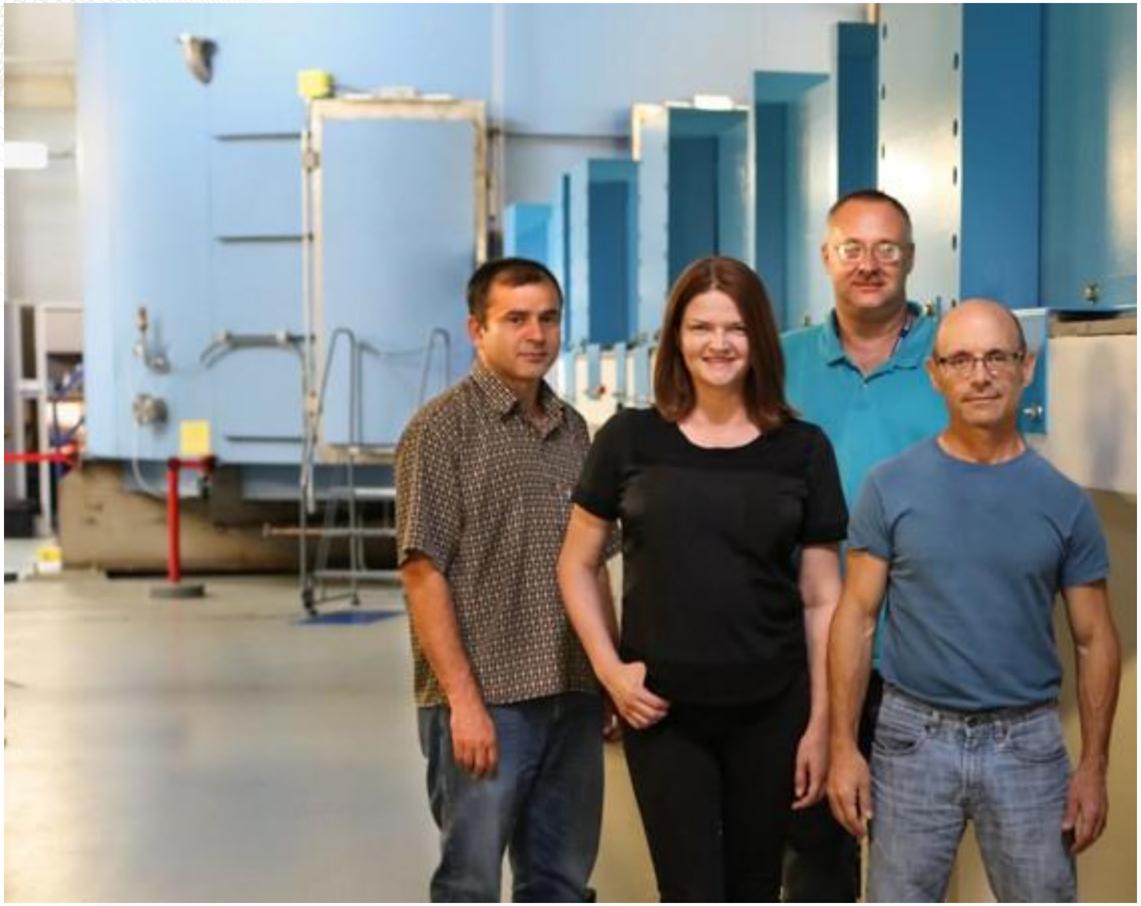




Accessible (in principle) Q-E coverage (for a given analyzer reflection and a set of scattering angles)



BASIS Instrument Team



Instrument team (left to right):

- Naresh Osti
- Niina Jalarvo
- Eugene Mamontov
- Christopher Schmitt (photo below) has replaced Richard Goyette

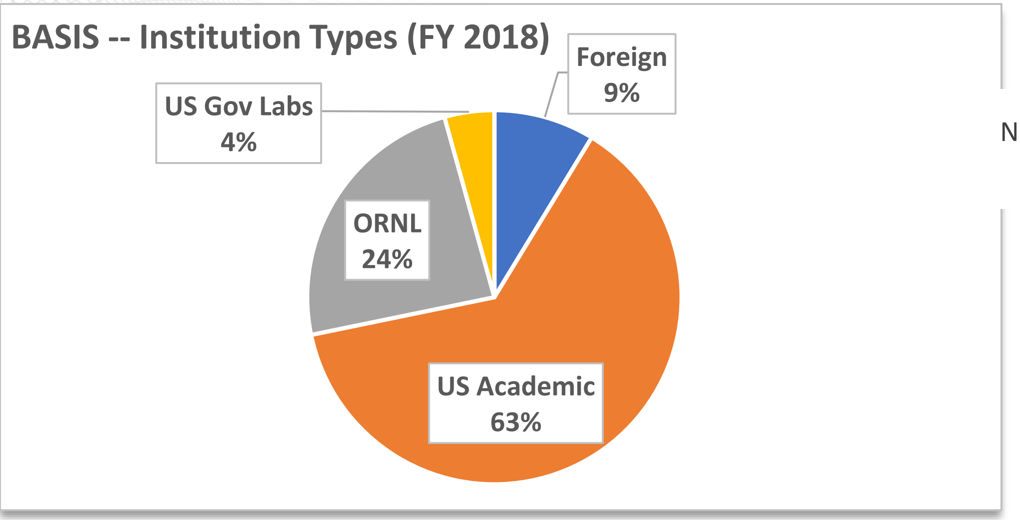
Scientific Mission and Impact

BASIS provides time-of-flight backscattering data for a broad and diverse user community.

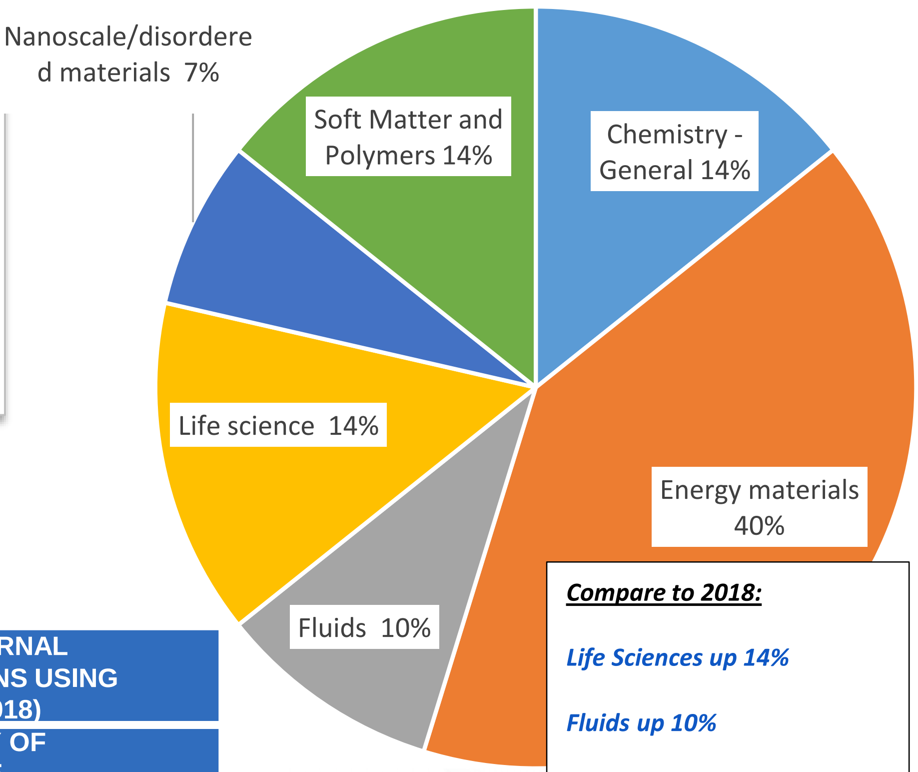
The User program on BASIS serves researchers who are interested in systems exhibiting dynamics (usually of diffusion/relaxation type) on pico-to-nano-second time scale and Angstrom to nano-meter length scale

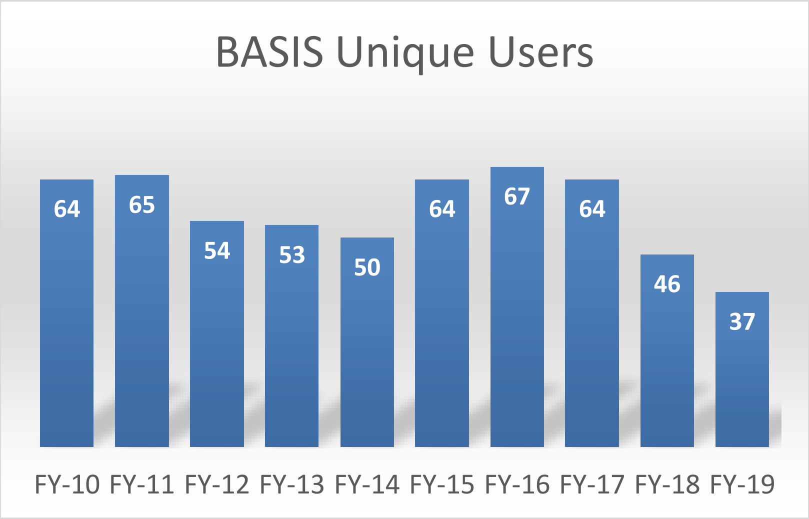
- **Soft Matter (very broadly defined)**
    - Water, solutions, complex fluids, polymers, biological systems (proteins, membranes, cells, etc.)
- **Hard Matter**
    - Energy materials, catalysis, hydrogen bonding, magnetism, minerals and earth and environmental sciences, etc.

The BASIS User Community FY-2018/2019


BASIS -- Institution Types (FY 2018)

BASIS Research Areas (2019)




BASIS Unique Users

TOP 5 EXTERNAL INSTITUTIONS USING BASIS (FY2018)
UNIVERSITY OF TENNESSEE
CLEMSON UNIVERSITY
DREXEL UNIVERSITY
UNIVERSITY OF CINCINNATI
NATIONAL CENTRAL UNIVERSITY

__Compare to 2018:__

Life Sciences up 14%

Fluids up 10%

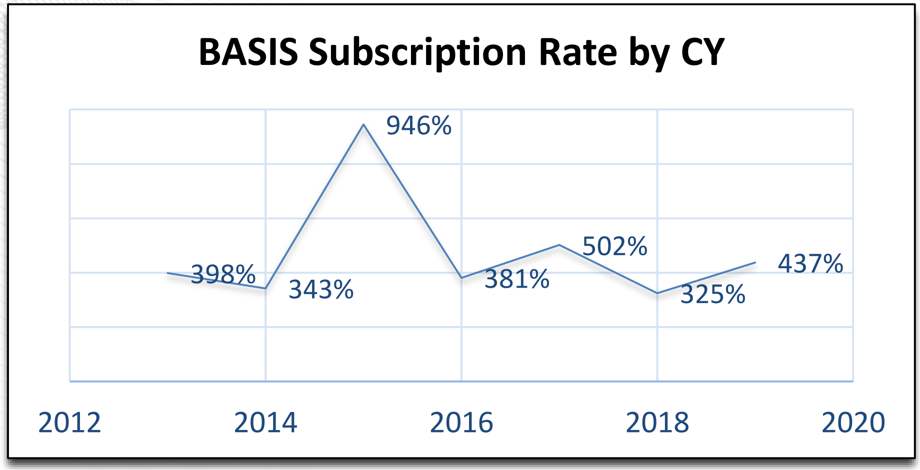
Nanoscale Materials up 7%

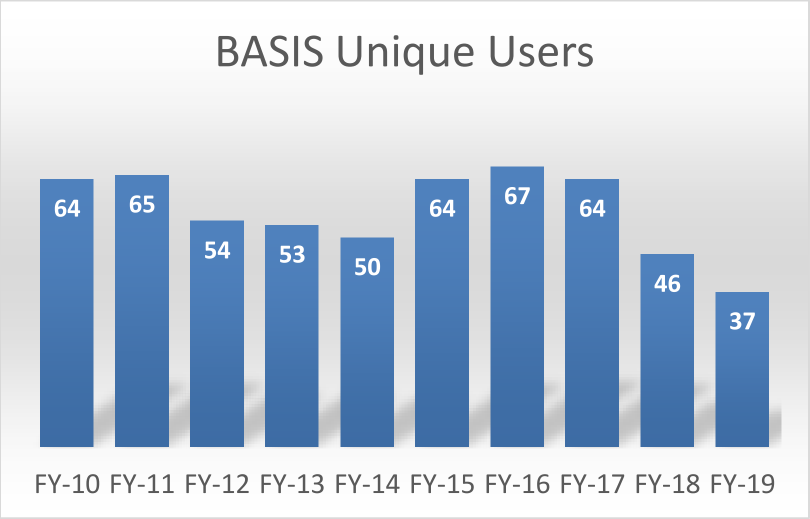
Soft Matter and Polymers down 21%

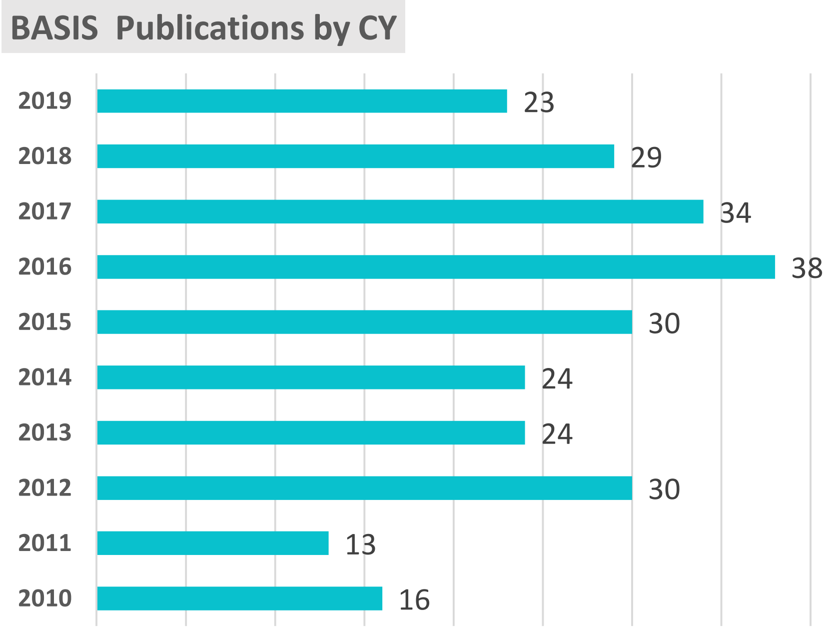
Energy Materials down 8%

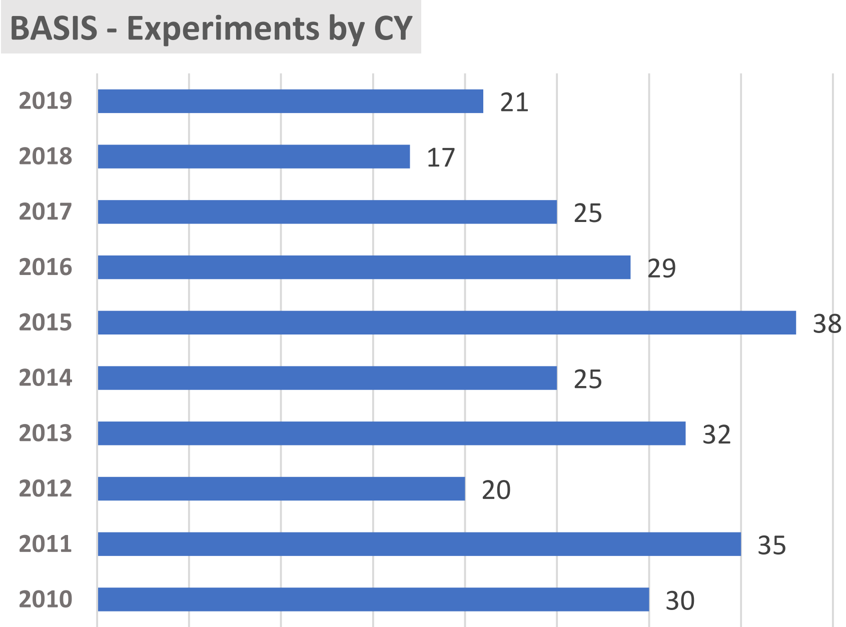
- BASIS partner agreement with *Forschungszentrum Juelich* has expired

Beamline Productivity


BASIS Subscription Rate by CY


BASIS Unique Users


BASIS Publications by CY


BASIS - Experiments by CY

Beamline Productivity - Publication Output

	2017	2018	2019
BASIS (SNS)	34	29	23
DNA (J-PARC) https://mlfinfo.jp/en/publications.html	10	10	8

- *In attempt to account for the operation time offset, how was BASIS doing in the Year 3, Year 4, and Year 5 since the first "regular" publication (taken as 2008 for the BASIS and 2015 for the DNA)?*

	2010	2011	2012
BASIS (SNS)	16	13	30

Software

Data Acquisition

- **A major transition to EPICS-based DAS completed in 2019**

  No legacy software anymore

Experiment Planning

- **Utilities in DAVE**

  (E.g., sample transmission calculations)

Data Reduction/Analysis

- **Mantid**

  Always used for reduction, can be used for analysis

- **DAVE**

  Utilized for analysis by may users

- **QClimax**

  Utilized for analysis by many users

Sample Environments

- Currently operating
  - A workhorse: top-loading CCR-018, 4-370 K (with helium exchange gas)
  - A workhorse: top-loading CCR-015, 10-500 K (with helium exchange gas), 50-700 K (under vacuum)
  - A bottom loading CCR (up to 325 K)
  - Orange cryostats (there is now a viable option for a 100 mm bore Orange)
  - Furnaces (up to 1400°C)
  - 5 T magnet
  - Gas pressure cell (4.8 kbar); new pressure capabilities under development
  - Some specialty cells are available (e.g., for low- and high applied voltage measurements)

Research highlights

- **Mixed Ionic Liquid Improves Electrolyte Dynamics in Supercapacitors**
- **Spatial-Temporal Characteristics of Confined Polymer Motion Determine Proton Conduction of Polyoxometalate-Poly(ethylene glycol) Hybrid Nanocomposites**
- **Elucidating the Mobility of H^+ and Li^+ Ions in $(Li_{6.25-x}H_xAl_{0.25})La_3Zr_2O_{12}$ via Correlative Neutron and Electron Spectroscopy**
- **Abnormally Low Activation Energy in Cubic Na_3SbS_4 Superionic Conductors**

Mixed Ionic Liquid Improves Electrolyte Dynamics in Supercapacitors

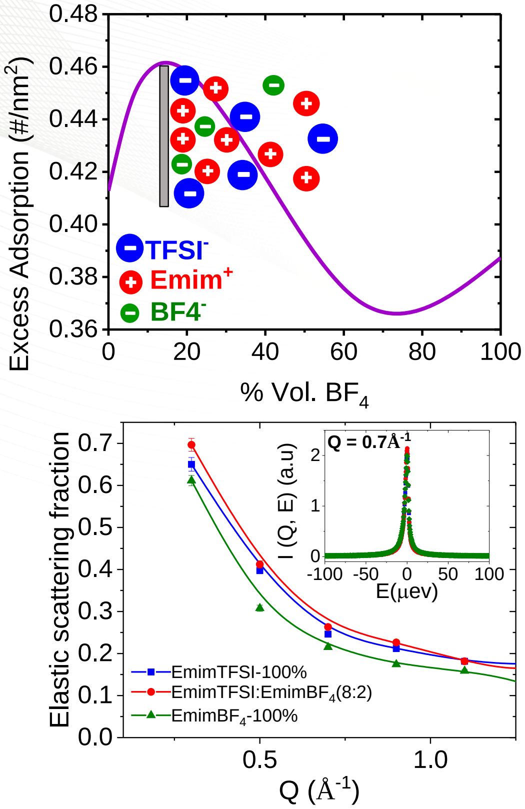


FIG.1. Excess adsorption of [Emim+] near an OLC at zero applied potential with inset showing a schematic of the EDL at 13 % EmimBF4 in EmimTFSI. (b) Elastic scattering fraction obtained from QENS spectra analysis of neat EmimTFSI and EMIMBF4 and their mixture at 4:1 mixing ratio. Inset shows QENS spectra.

Naresh C. Osti, Alejandro Gallegos, Boris Dyatkin, Jianzhong Wu, Yury Gogotsi, Eugene Mamontov, “Mixed Ionic Liquid Improves Electrolyte Dynamics in Supercapacitors,” *J. Phys. Chem. C, DOI:* 10.1021/acs.jpcc.8b02521

Work performed at ORNL SNS’s BL-2 BASIS, sponsored by DOE Office of Science, Scientific User Facilities Division.

Scientific Achievement

We investigated two room-temperature ionic liquids, 1-ethyl-3-Methylimidazolium bis(trifluoromethylsulfonyl)imide (EmimTFSI) and 1-ethyl-3-methylimidazolium tetrafluoroborate (EmimBF4). We studied their electric double-layer (EDL) behavior in the neat state and as binary mixtures on the external surfaces of onion-like carbon (OLC) electrodes using quasi-elastic neutron scattering (QENS) and classical density functional theory (cDFT) techniques. Computational results reveal that a mixture with 4:1 EmimTFSI/EmimBF4 volume ratio displaces the larger [TFSI$^-$] anions with smaller [BF4$^-$] ions, leading to an excess adsorption of [Emim$^+$] cations near the electrode surface providing a nonuniform ion diffusivity change of [Emim$^+$] ions with changing composition from QENS measurements.

Significance and Impact

Molecular-level understanding of ion packing near OLC electrodes provides insight for design of ionic liquid formulations that enhance the performance of electrochemical energy storage devices.

Research Details

- Structural details of ions at ions-electrode interfaces were obtained from cDFT.
- The microscopic dynamics of the structural modifications in the adsorbed ions with changing composition were studied from QENS measurements using the BASIS spectrometer.

Spatial-Temporal Characteristics of Confined Polymer Motion Determine Proton Conduction of Polyoxometalate-Poly(ethylene glycol) Hybrid Nanocomposites

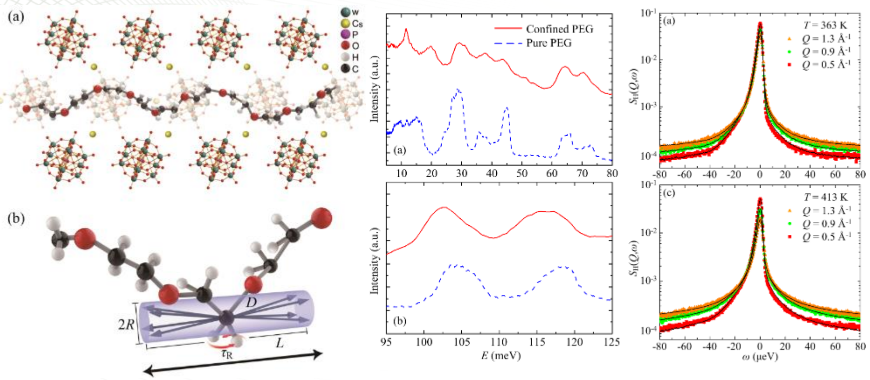


FIG.1 Left panel, top: conformation of the PEG inside the 1D nano-channel defined by the framework of POMs**. Left panel, bottom**: some characteristic length scales of the molecular motions investigated - a cylinder with a length of L and a radius of R denotes the space that a carbon atom can explore, D is the diffusivity of a C atom, and τ_R is the characteristic time of the two-side jump of an H atom in a methylene group. The double-headed arrow denotes the direction of the 1D nano-channel. **Middle panel**: INS spectrum (VISION) of the PEG confined in the framework defined by POMs (solid line) and that of a pure PEG (dashed line). Panels (a) and (b) display the intensities in the energy range of 5 to 80 meV and of 95 to 125 meV, respectively. The intensities of the confined PEG are shifted up for clarity. **Right panel**: QENS spectra (BASIS) at selected temperatures and wave vector transfers, data (symbols)and fits (lines).

H. Wu, L. Li, M. Tsuboi, Y. Cheng, W. Wang, E. Mamontov, S. Uchida, Z. Wang, and P. Yin, "**Spatial-Temporal Characteristics of Confined Polymer Motion Determine Proton Conduction of Polyoxometalate- Poly(ethylene glycol) Hybrid Nanocomposites**," *Journal of Physical Chemistry Letters (**2018**)*
DOI: 10.1021/acs.jpclett.8b02113

Work performed at ORNL SNS's BL-2 BASIS and BL-16B VISION, sponsored by DOE Office of Science, Scientific User Facilities Division.

Scientific Achievement

We find that a single PEG chain stays as a distorted helix in a POM nano-channel. Furthermore, the PEG segments perform a localized longitudinal random walk, and there is a strong correlation between the local motion of PEG and the macroscopic proton conduction of the hybrid material. Based on these spatial-temporal characteristics, we propose a comprehensive microscopic picture for the proton conduction process in POM-PEG hybrid materials.

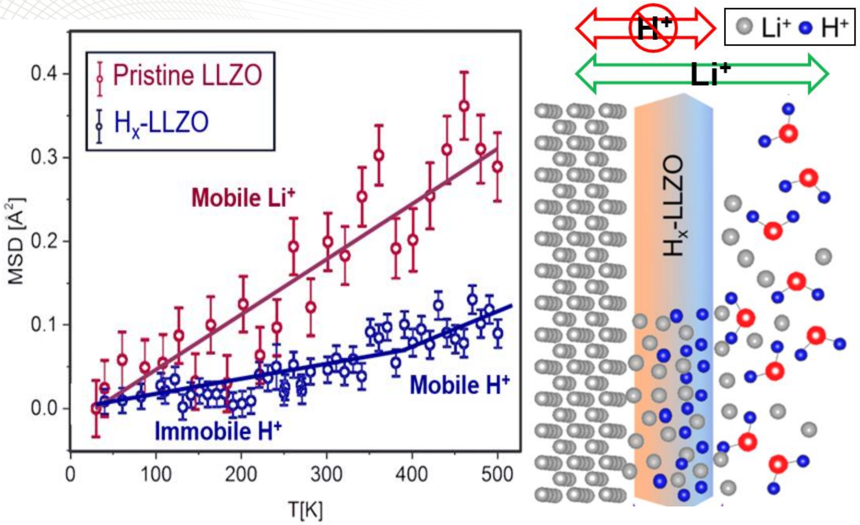
Significance and Impact

As the key elements in fuel cell devices, proton conductive materials are actively researched to meet urgent need for improving their conductivity and stability performances. As a group of highly charged metal oxide clusters at nanoscale, polyoxometalates (POMs) possess appreciable stability against high temperature and promising proton conductivity in ambient environment. We have prepared and studied the POM-poly(ethylene glycol) (PEG) hybrid nanocomposites with PEG molecules encapsulated inside the nano-channels defined by POMs. To understand the proton conduction mechanism and balance the high conductivity with desirable mechanical properties, delineating the structure-property relation of POM-polymer hybrids at the molecular level is of fundamental importance.

Research Details

- BASIS and VISION spectrometers at the SNS were used to study the microscopic dynamics of PEG in POMs.

Elucidating the Mobility of H^+ and Li^+ Ions in $(Li_{6.25-x}H_xAl_{0.25})La_3Zr_2O_{12}$ via Correlative Neutron and Electron Spectroscopy



By correlating neutron and electron spectroscopy, H^+ ions were found to be immobile while Li^+ ion maintained a desired mobility in the solid electrolyte $(Li_{6.25-x}H_xAl_{0.25})La_3Zr_2O_{12}$.

Neutron scattering experiment was performed at the BASIS, VISION, and VULCAN beamlines of ORNL's Spallation Neutron Source, which is a DOE Office of Science user facility.

Scientific Achievement

A correlative neutron and electron spectroscopy method was used to identify cubic $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ (H-LLZO) as a potential separation layer to enable the use of lithium metal anode towards high-performance aqueous lithium metal batteries.

Significance and Impact

A major challenge toward achieving high-performance aqueous lithium batteries (ALBs) is to find a solid electrolyte "enabler" that can protect metallic lithium from reacting with aqueous solutions while maintaining a high lithium ion conduction. The novel approach used in this research, which can probe the diffusion behavior of individual ion species in dual-ion solids, is demonstrated to be a powerful tool in identifying such an enabler.

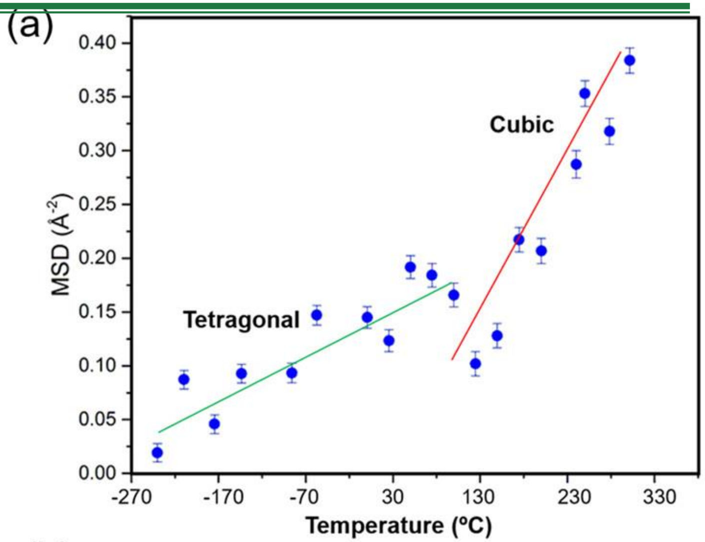
Research Details

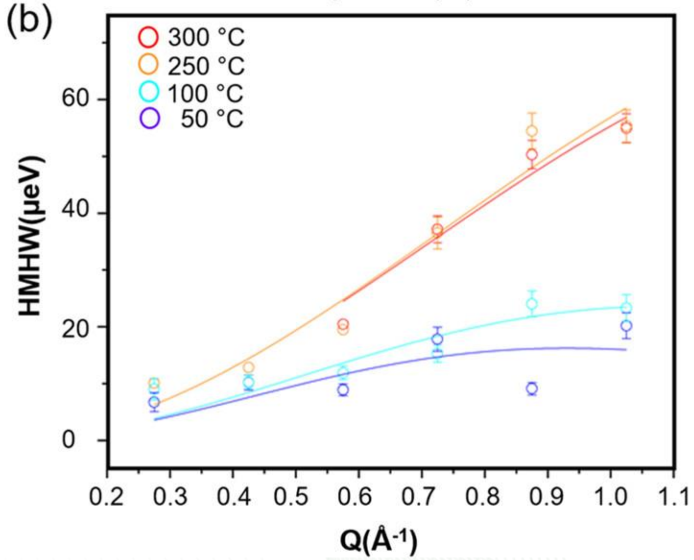
- For the first time, the conduction behavior of Li^+ and H^+ in H-LLZO is unambiguously differentiated using neutron spectroscopy. EELS in STEM and neutron diffraction were used to quantify the lattice occupancy.
- H^+ ions are found to be immobile while Li^+ ions maintain a desired mobility in H-LLZO at the operating temperature range of ALBs, highlighting its potential to be used as a protection layer in ALBs.

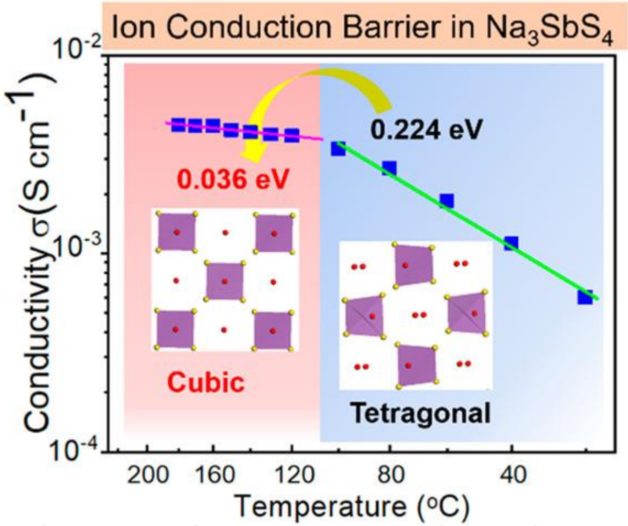
Xiaoming Liu, Yan Chen, Zachary D. Hood, Cheng Ma, Seungho Yu, Asma Sharafi, Hui Wang, Ke An, Jeff Sakamoto, Donald J. Siegel, Yongqiang Cheng, Niina H. Jalarvo, and Miaofang Chi, "Elucidating the mobility of H^+ and Li^+ ions in $(Li_{6.25-x}H_xAl_{0.25})La_3Zr_2O_{12}$ *via* correlative neutron and electron spectroscopy" *Energy Environ. Sci.*, DOI: 10.1039/c8ee02981d

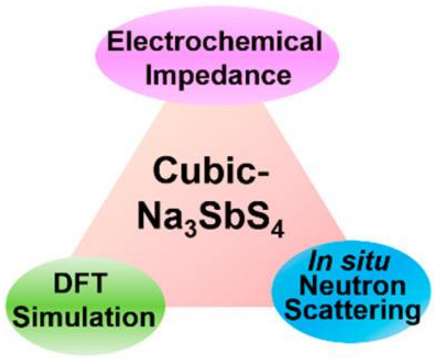
Abnormally Low Activation Energy in Cubic Na_3SbS_4 Superionic Conductors

- Inorganic Na-ion superionic conductors play a vital role in all-solid-state Na batteries that operate at RT
- fundamental understanding of the Na-ion diffusion mechanisms in Na_3SbS_4 with different crystal structures (e.g., tetragonal and cubic) from QENS
- The high degree of symmetry in cubic Na_3SbS_4 leads to less interatomic correlations between Na and S(Sb) atoms, a shorter jump distance (2.85 Å), and a larger diffusion coefficient.



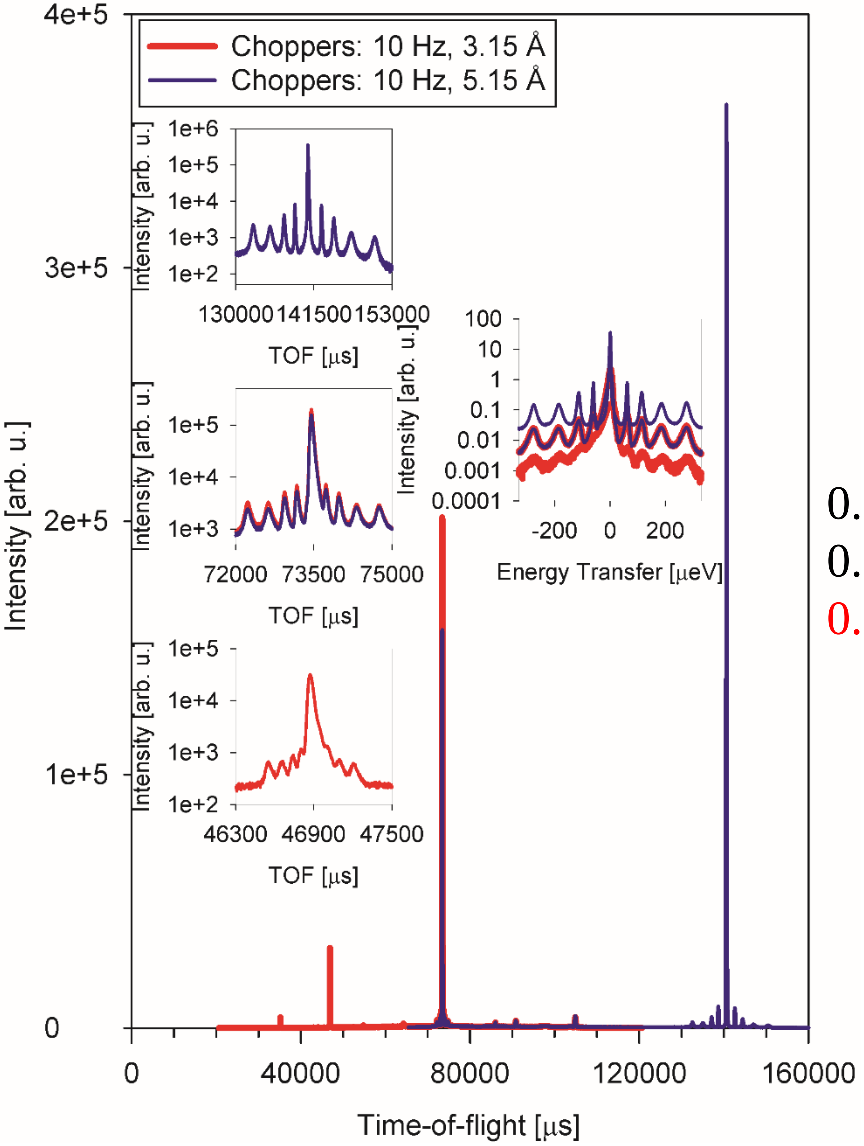






Q. Zhang, C. Zhang, Z. D. Hood, M. Chi, C. Liang, N. H. Jalarvo, M. Yu, and H. Wang, “Abnormally Low Activation Energy in Cubic Na_3SbS_4 Superionic Conductors”, Chemistry of Materials 32, 2264-2271 (2020); doi: 10.1021/acs.chemmater.9b03879

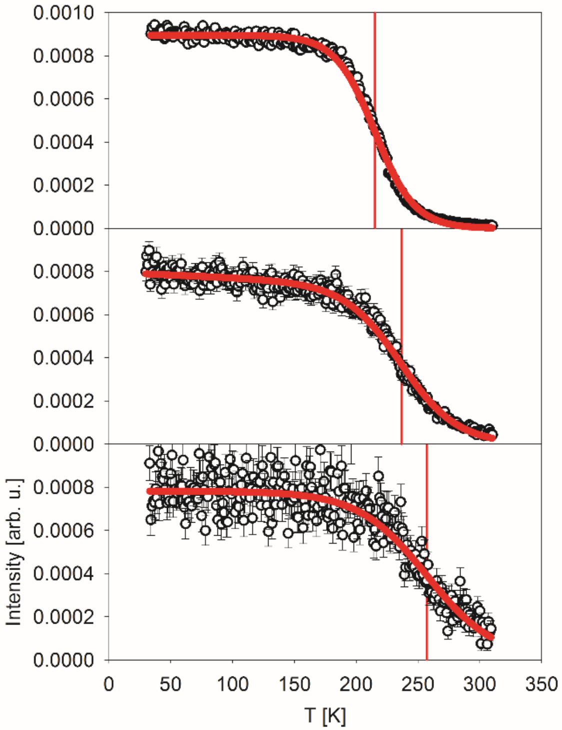
Future Upgrades: in hardware, or “virtual”?

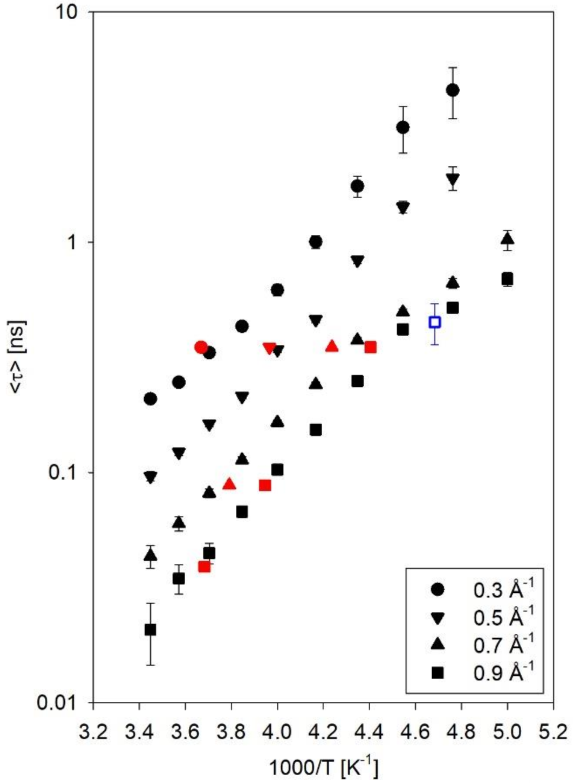


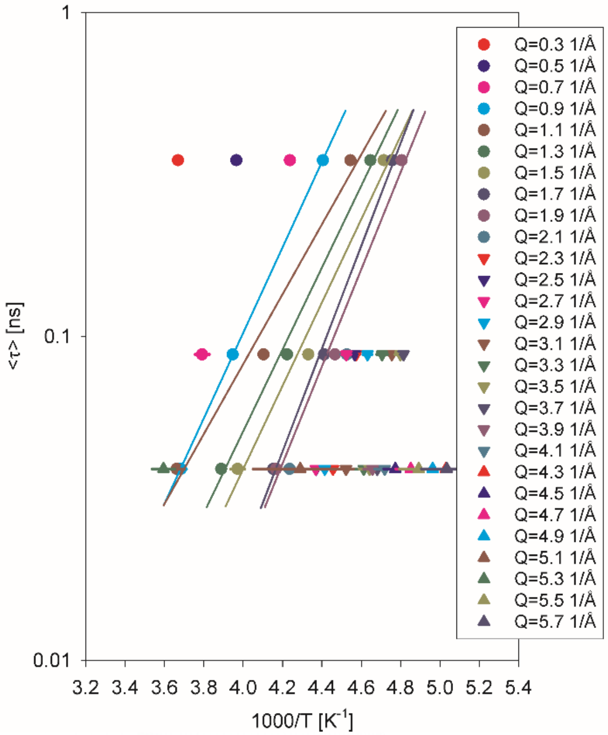
“Implementation and assessment of resolution-dependent elastic incoherent neutron scattering measurements at a backscattering spectrometer for probing relaxations in complex systems”. E. Mamontov, *Nuclear Instruments and Methods in Physics Research A* **949**, 162534 (2020).

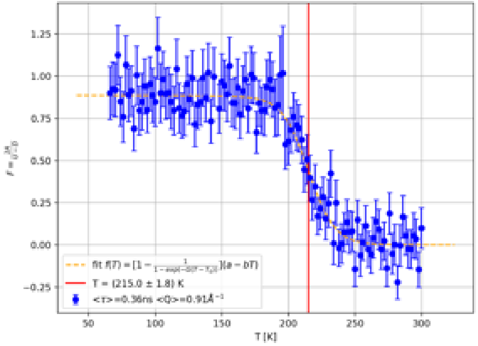
0.3 Å^{-1} < Q < 1.9 Å for Si(111), FWHM=0.0037 meV
0.7 Å^{-1} < Q < 3.7 Å for Si(311), FWHM=0.0150 meV
0.9 Å^{-1} < Q < 5.7 Å for Si(333), FWHM=0.0336 meV

Original idea: “elastic intensity scans” for small or weakly scattering samples





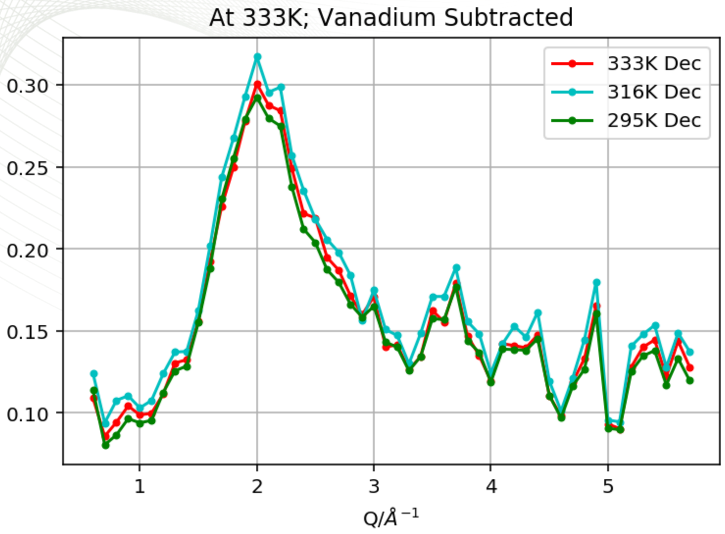


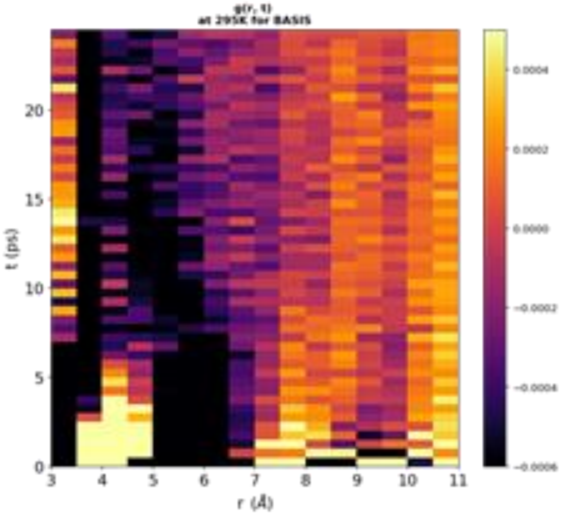


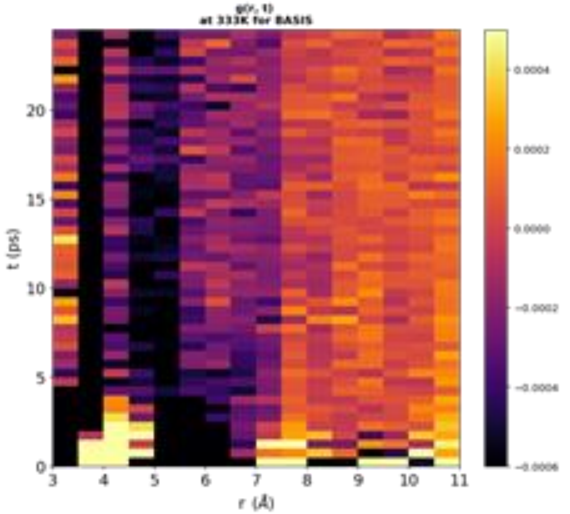
We propose to extend the same approach to NSE; no need to measure the full echo!! (paper to be published)

OAK RIDGE National Laboratory | HIGH FLUX ISOTOPE REACTOR | SPALLATION NEUTRON SOURCE

However, Si(333) can also be used for full dynamic measurements







Dynamic PDF (van Hove function measurements) of water, T. Egami's group, 2019

Risks

- ~~Short-term: Epics conversion of data acquisition~~ Resolved

- Intermediate term: Increasing competition with the DNA (J-PARC) We are holding, for now

- Long-term: Competition from the MIRACLES spectrometer at ESS

Papers profile could potentially be enhanced by (1) consistent and (2) rapid application of simulations

Overall Summary

- One of the two best in class neutron backscattering spectrometers in the world
- Adequate sample environment options and actively developing software options
- Active, diverse, and growing user community
- Growth potential: the publication output has reached a plateau, papers profile could be enhanced by (1) consistent and (2) rapid application of simulations
- Clear vision for short-term and long-term future