Applications of Neutron Sources

XIII School of Neutron Scattering (SoNS)

International School of Neutron Science and Instrumentation

Erice, Sicily, 28 July-4 August 2015

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Argonne National Laboratory and

Oak Ridge National Laboratory

Neutron Scattering

1942-1945

Manhattan Project reactors: aimed to produce bomb fuel, ^{239}Pu, and to develop the relevant nuclear data.

The involved scientists, Walter Zinn, Enrico Fermi, Ernest Wollan, Clifford Shull, and others were interested also to apply their neutron beams “on the side,” for scientific purposes: Fundamental physics experiments and materials science measurements revealed the uses of neutrons in science.

These revelations led eventually to reactors designed to produce neutron beams for thermal-neutron scattering applications.

Advantages of Neutrons

- Neutrons penetrate centimeters of most materials; they see in depth, penetrate containers, and are nondestructive of samples.

- Neutrons are sensitive to light elements, especially hydrogen, in the presence of heavy ones.

- Isotopic cross sections (e.g., H/D and $^6Li/^7Li$) enable isotope substitution, index matching; facilitate study of light atoms in materials.

- The range of momentum transfers available allows examining structures on a broad range of length scales (0.1 to 10^5 Å).

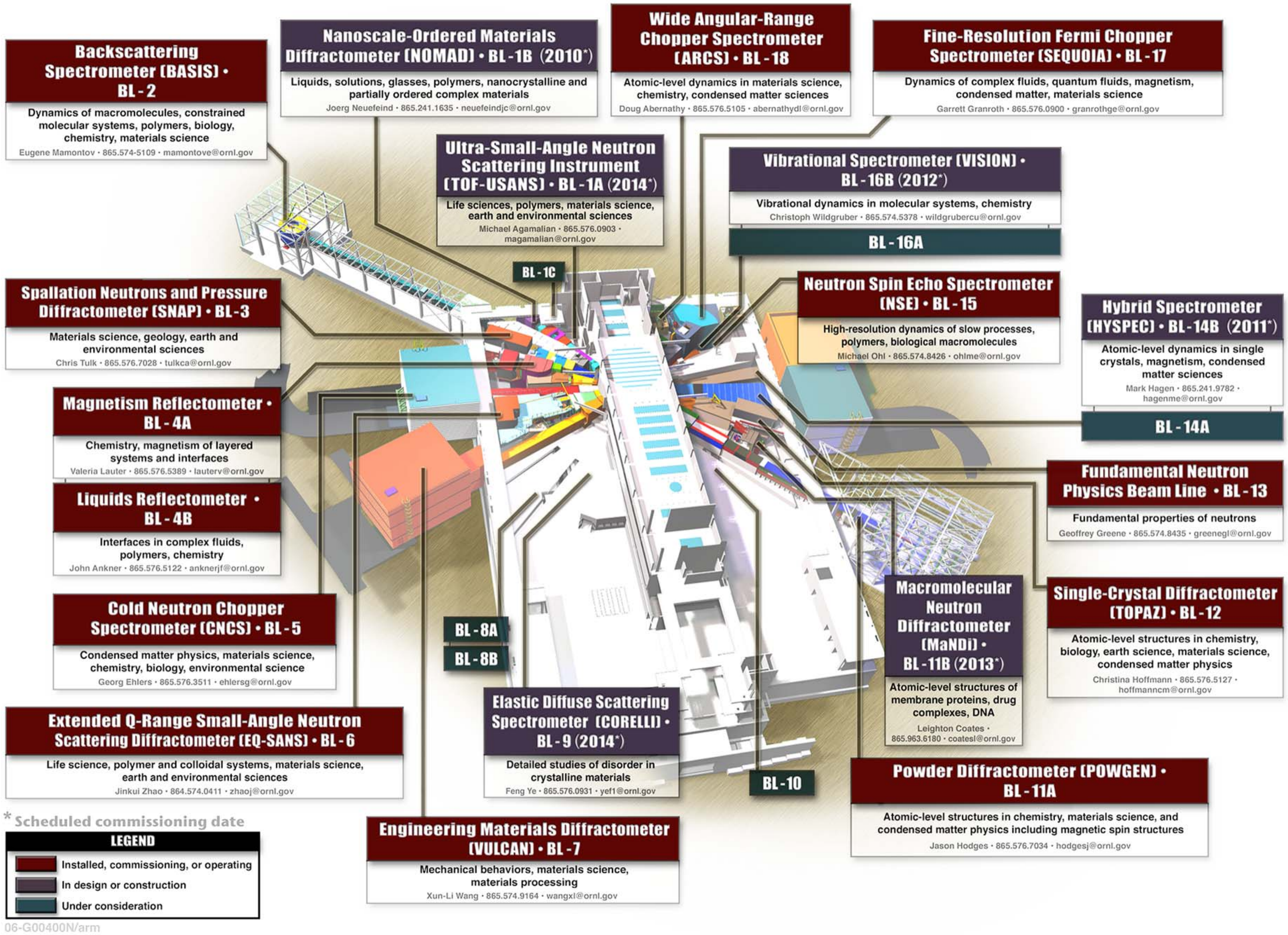
Advantages of Neutrons (Cont'd)

- Neutrons have magnetic moments; are sensitive probes of magnetic ordering and excitations.

- Neutrons can be polarized; allow separation of the nuclear and magnetic cross sections. Enable Larmor precession spectroscopy.

- The simplicity of the magnetic and nuclear interactions facilitates straightforward theoretical interpretation of measurements.

SNS INSTRUMENTS



Facility Developments

Reactors have reached their maximum practical power and neutron flux, ~ 100 MW, ~10^{15} n/cm^2-s. Now optimizing cold & hot sources, instruments, and detectors.

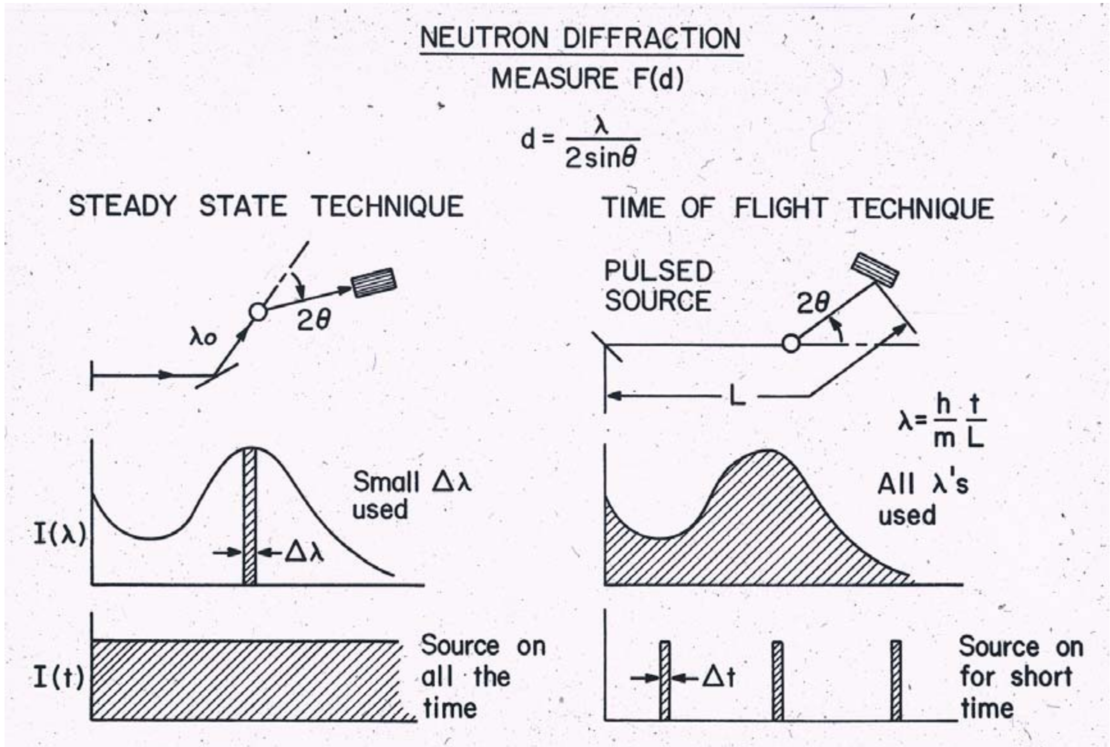
Accelerator-based sources are nearing practical limits on target and accelerator power, 2-5 MW, and peak flux,
~10^{17} n/cm^2-s. Target problems remain. Opportunities abound for target, moderator, instrument, detector, and techniques innovation, which need testing. All of the larger accelerator-based sources are designing or already have second target stations driven by their existing accelerators. These aim to serve needs for more instruments, low-frequency operation, and copious cold neutron fluxes.

Steady vs. Pulsed Operation

Pulsed sources—Accelerator delivers energy to the target in short (~ microsecond) bursts: heat is removed during the interval between pulses.

Steady sources use
some of the neutrons
all of the time.

Pulsed sources use
all of the neutrons
some of the time.



Why Pulsed Spallation Sources?

• Spallation process—efficient: ~ 30 MeV heat per neutron vs. ~ 200 MeV heat per useful neutron from fission.

• Pulsed operation—high instantaneous power; long times between pulses for heat removal; favors cold moderators.

• Pulsed sources—well suited to time-of-flight instrumentation; define the time origin.

• Pulsed-source moderators—short neutron pulses; ~ constant $\Delta t/t$; high fluxes of epithermal neutrons.

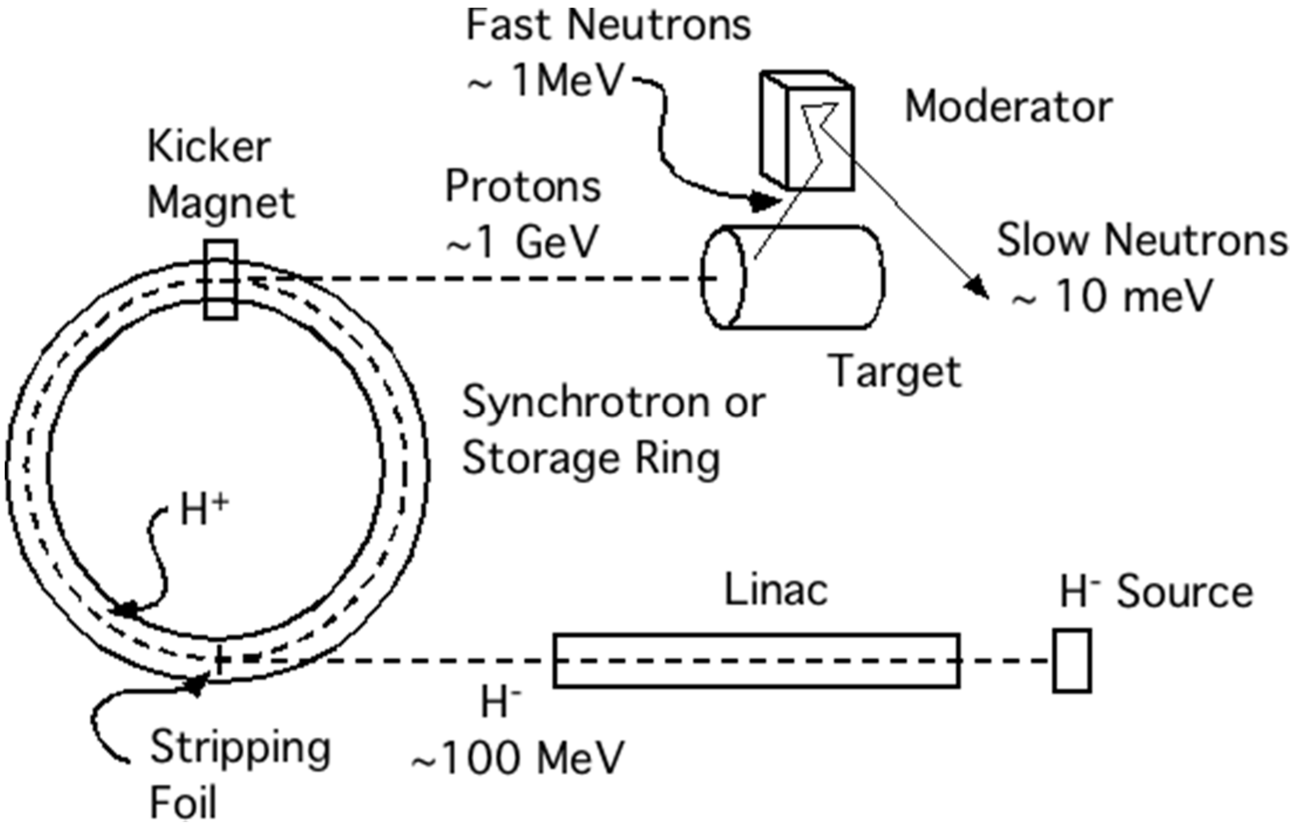
Accelerator Developments

Listing the steps in particle accelerators that led to the modern powerful spallation neutron sources would be too much.

Starting with Lawrence's 1930 cyclotron, up to the 1940s' 37-inch machine, cyclotrons produced the most neutrons. Reactors took over as sources for neutron scattering research.

In the 1960s, efforts concentrated on higher energies and higher power. Linacs were favored for both but deliver long pulses. H- stripping injection enabled high currents. High-power, high-frequency klystrons for TV and radar helped. Short pulses demanded storage rings and synchrotrons. Radio-frequency quadrupoles replaced Cockroft-Walton injectors. Now long-pulse sources contend with short-pulse sources depending on scientific applications. Accelerator-based sources now complement and exceed reactor sources for many uses.

Accelerator-Based Pulsed Neutron Source

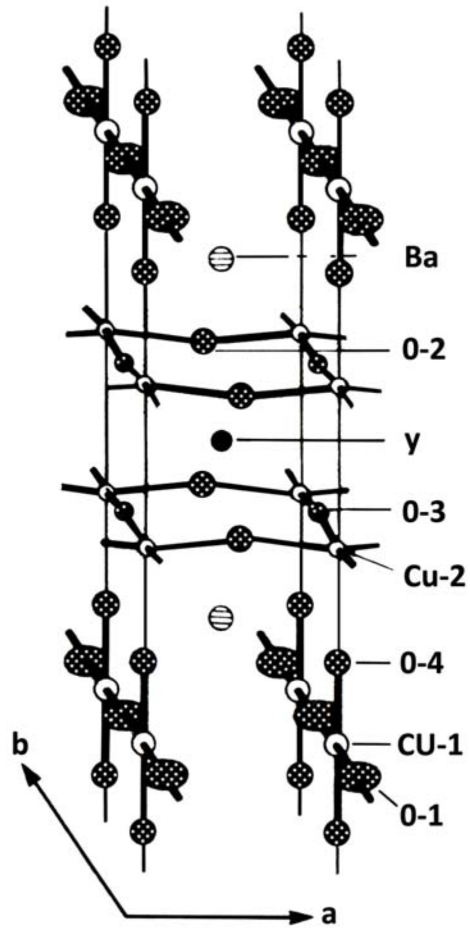


Moderator(s) close to the target slow down fast neutrons to energies useful for applications. Typically, 3 or 4 differently optimized moderators serve about 25 neutron scattering instruments.

Structures of high-temperature superconductors

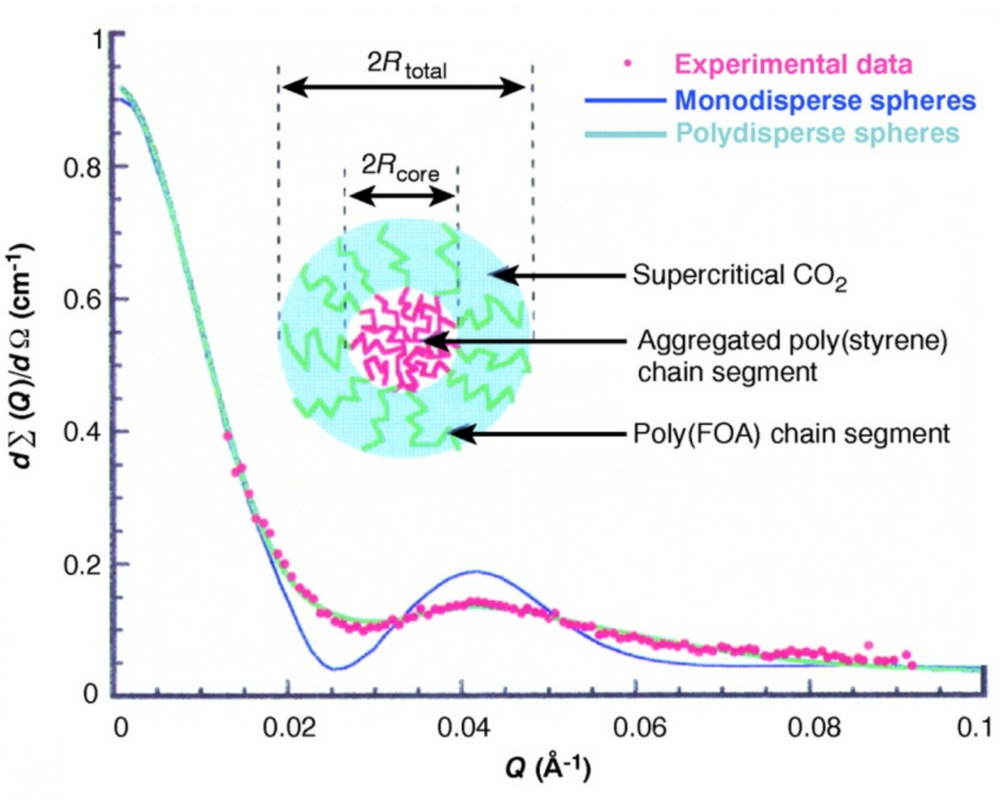
1989—At IPNS, Rietveldt refinement of the data on YBCO produced the first view of what is now the well-known structure. Within days workers at KENS and ISIS obtained identical results.

Pulsed-source powder diffractometers remain the method of choice for determining the structures of newly developed hi-T_c materials.



SANS research team wins Presidential Green Chemistry award for a CO_2 surfactant

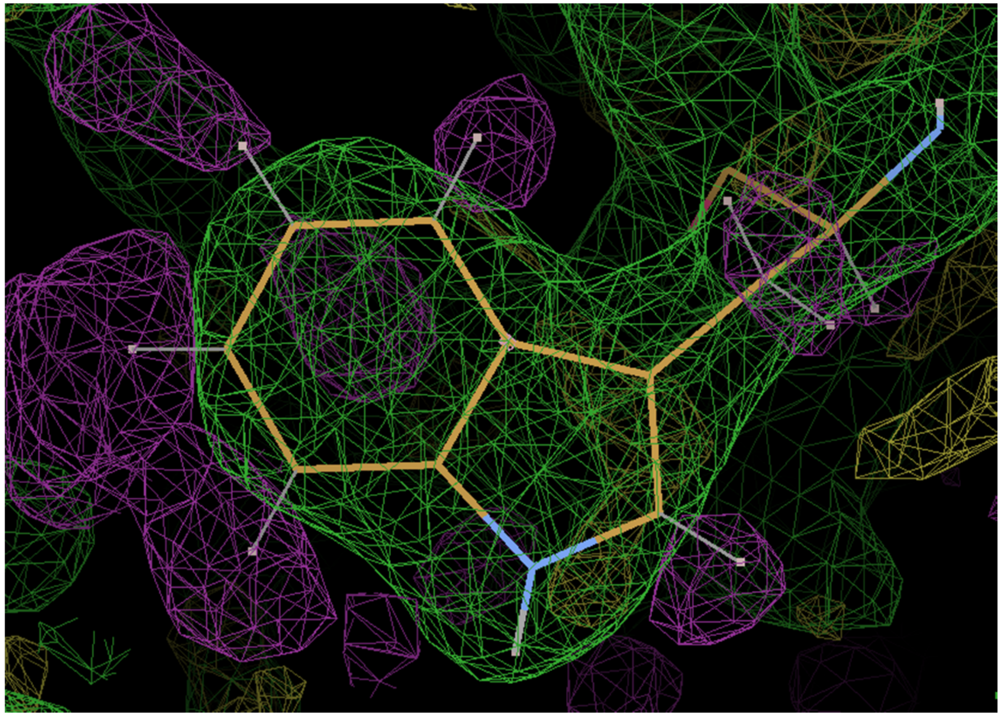
Scattering function of surfactant on polymer droplet in CO_2



Surfactants (long molecules, one end of which likes CO_2 and the other end of which likes hydrocarbon) would dissolve in supercritical CO_2 and form micelles. Scientists showed that their surfactant can suspend up to 20 wt% of hydrocarbon in CO_2. The figure shows the results of SANS measurements.

Neutron coherent scattering length density contour map

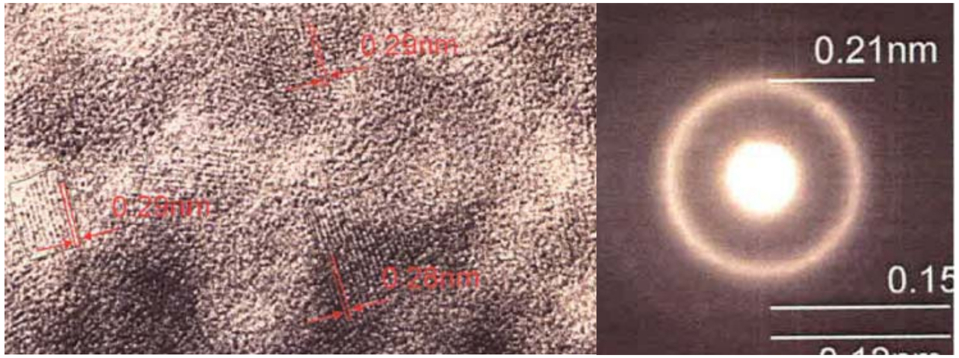
lysozyme and rubridoxin

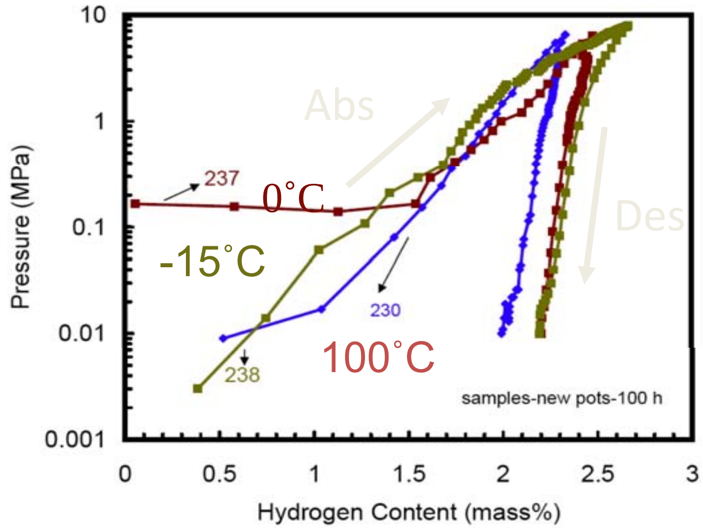


Purple, hydrogen (negative scattering length)
Green, carbon, oxygen, etc. (positive scattering lengths)

Local structure of MgCoH

New Mg-Co based hydrogen storage material.
Amorphous substance synthesized by ball milling.





5 nm crystals & amorphous part.

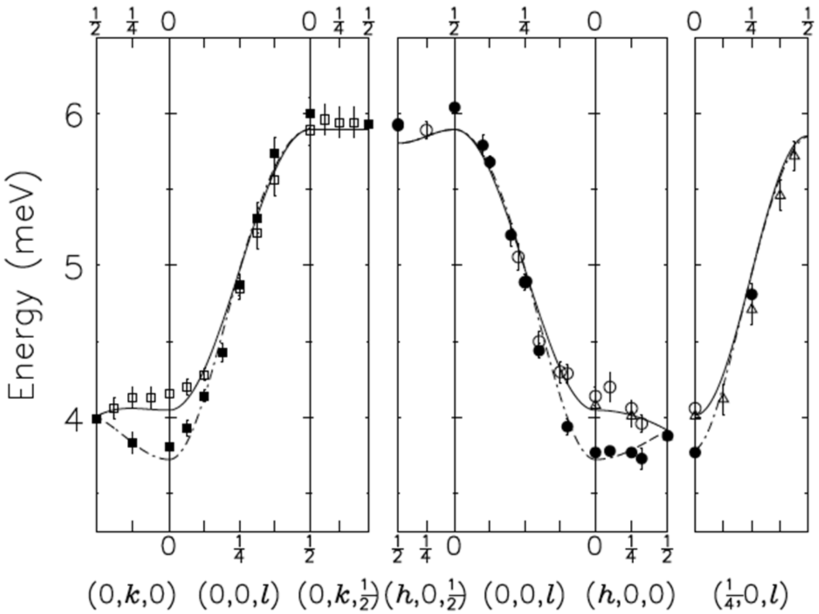
Conventional methods cannot analyze this *complicated* structure. No total scattering structure solution tools exist.

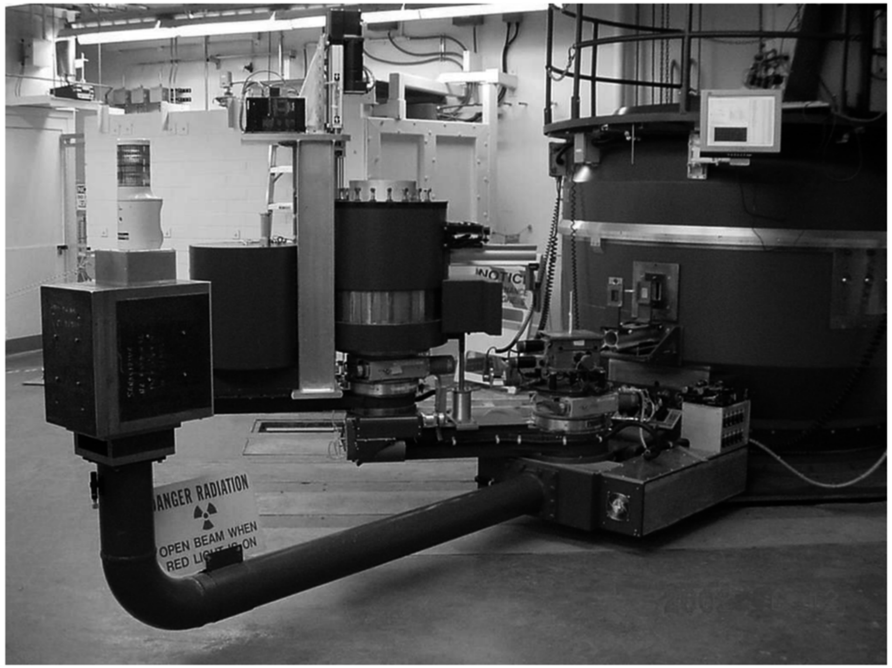
~ 2.5 wt% of hydrogen absorbed at low temp.

PDF method based on both x-ray and neutron diffraction necessary to understand the structure.

Triple-axis spectrometer

The magnon dispersion relations of $CoCl_2 \cdot 2D_2O$ at 7 K.





The HB1 spectrometer at HFIR, ORNL

High-resolution spectroscopy

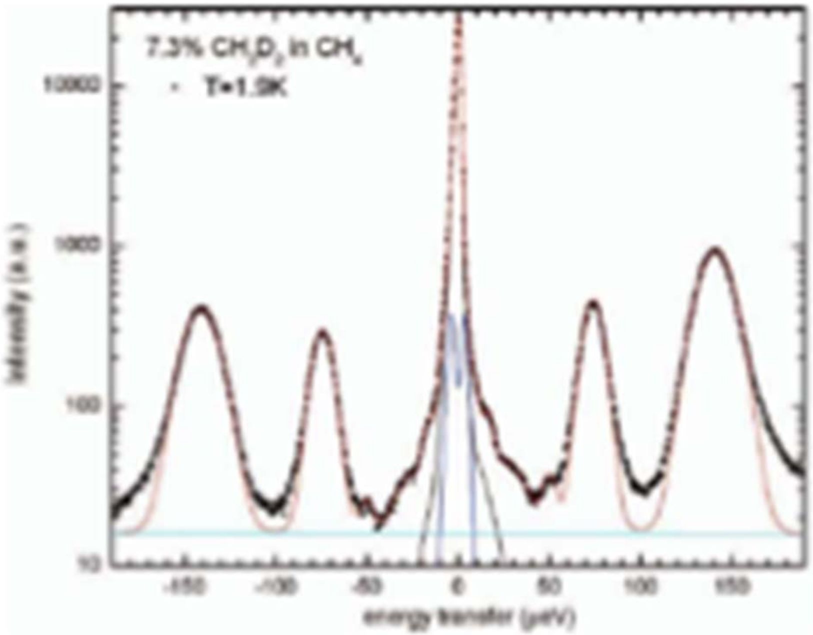
Disorder effects in rotational tunneling in CH_4:CH_2D_2(7.3%)

Backscattering spectrometer BASIS at SNS:

E-Resolution ~ 3 micro-eV

$$\Delta\lambda / \lambda = cot\left(\theta_s/2\right)\Delta\theta_s/2$$

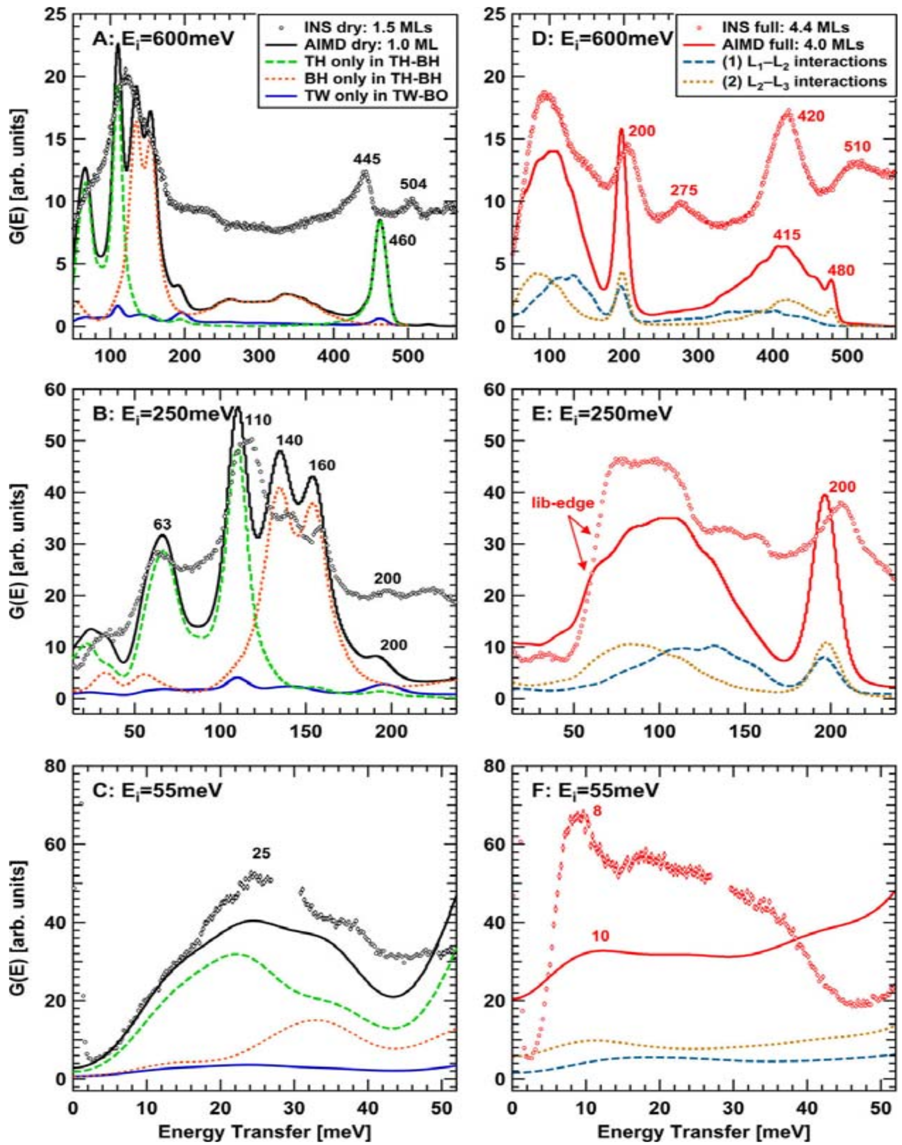
W. Press, I. Krasnow, et al.



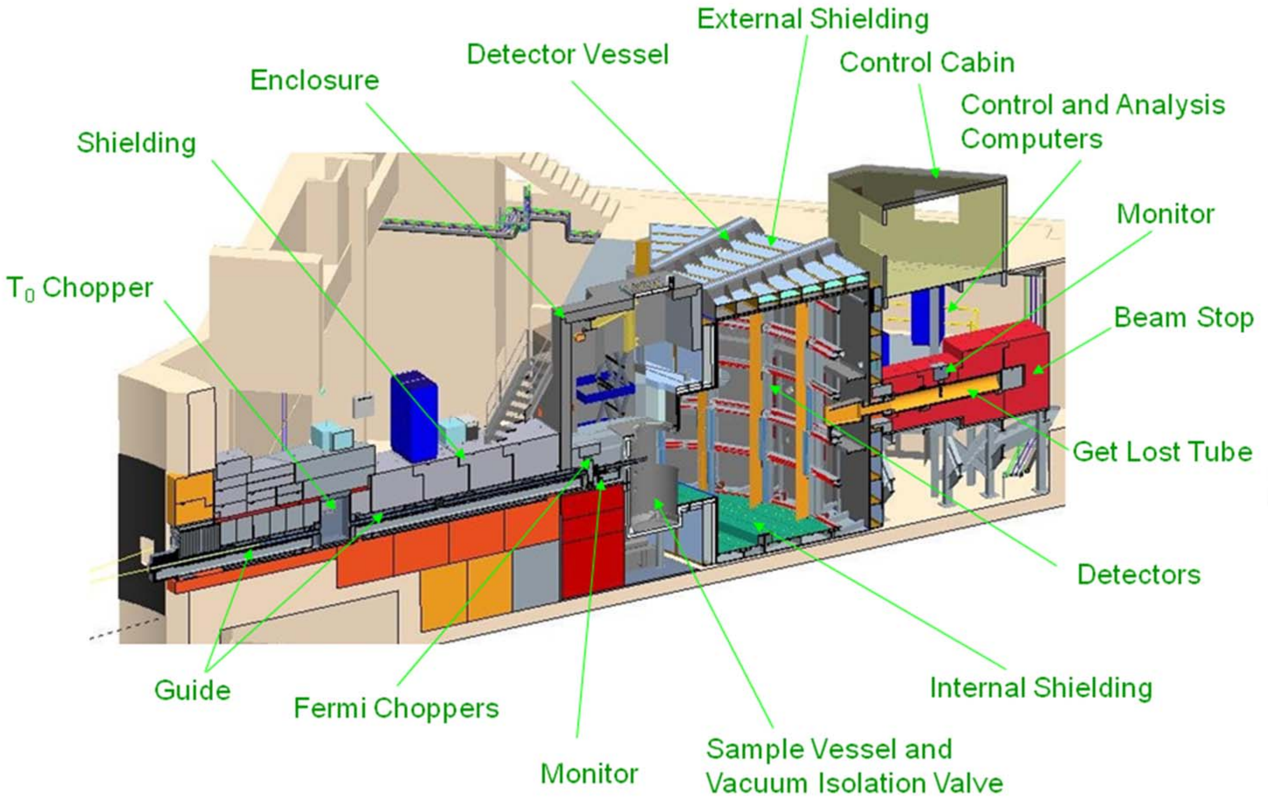
Catalysis:
Water on SnO_2

Alexander (Sasha) Kolesnikov (ORNL), James Kubicki (Penn State), and others studied the vibrational density of states (VDOS) of water strongly bonded at the surface of nanophase SnO_2 using the SEQOUIA inelastic neutron scattering spectrometer at the SNS of ORNL. Ab initio molecular dynamics (AIMD) simulations carried out in parallel supported the interpretation of the measurements.

Inelastic neutron scattering spectra of dynamics of H_2O on nano-SnO_2



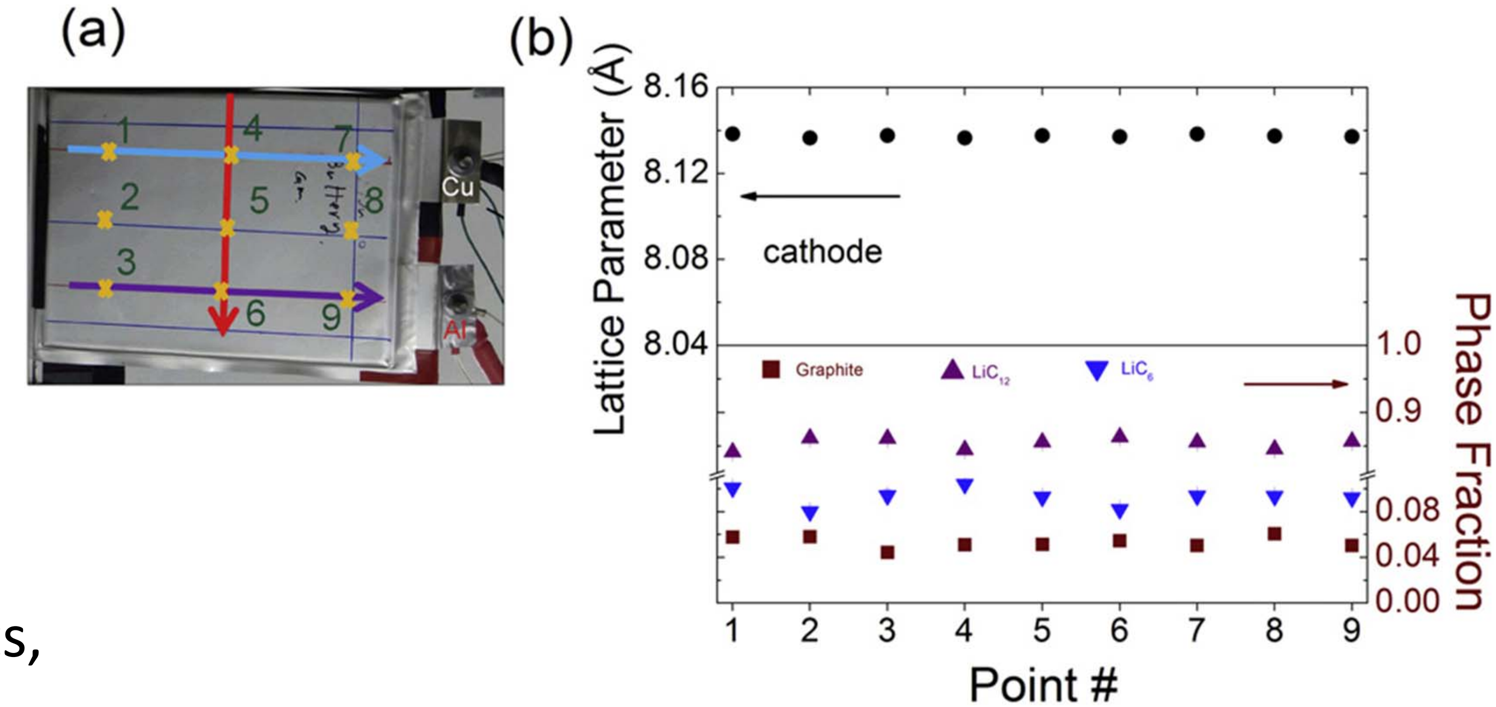
The SEQUOIA Chopper Inelastic Scattering Spectrometer at SNS



Lithium-ion batteries

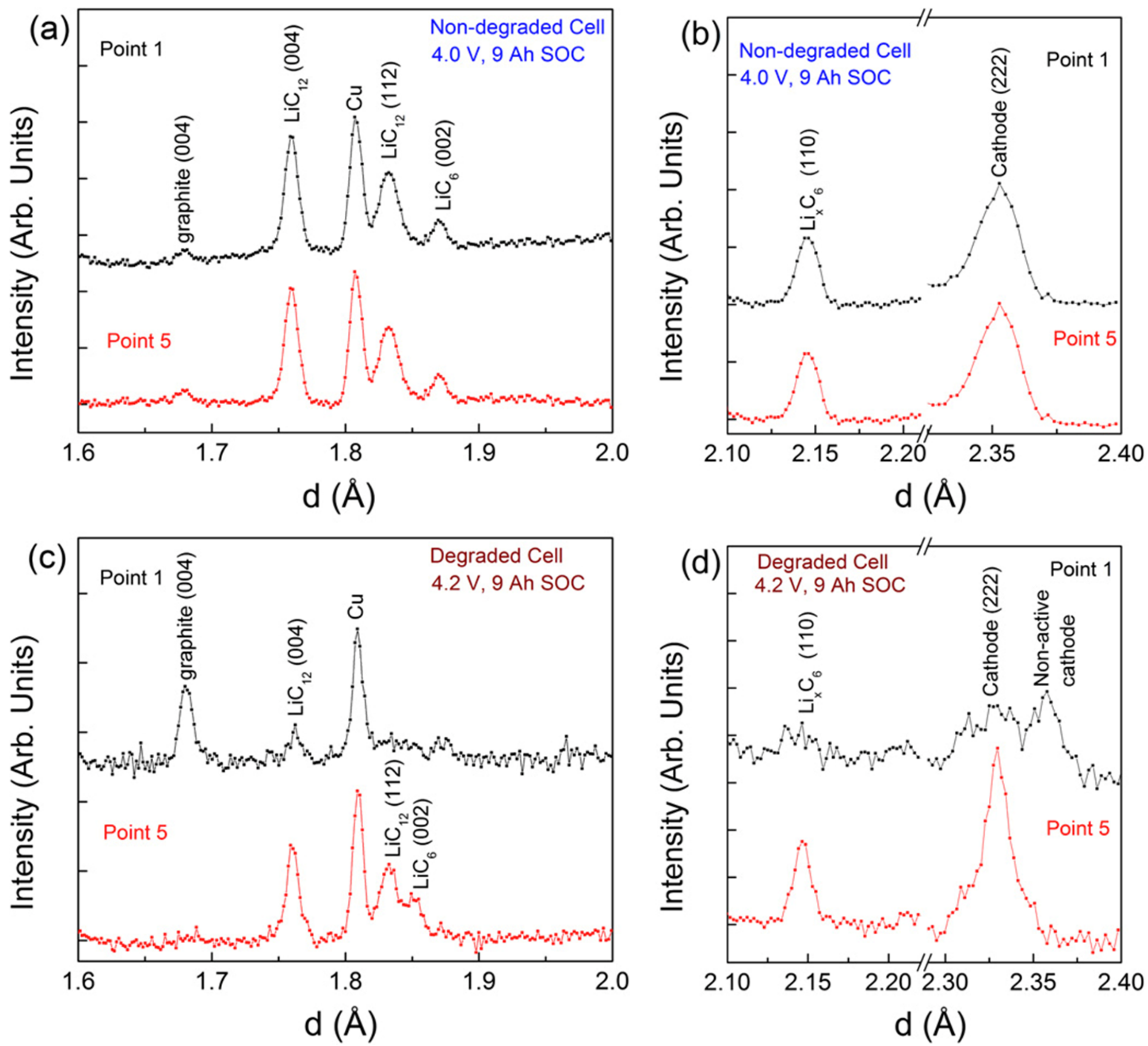
Ke An (ORNL), Stephen Harris (Lawrence Berkeley Lab), and others examined a production-version battery intended for GM vehicles at the VULCAN diffractometer at SNS. They tested a cell in two states of charge: in the fresh state (15 A-hr) and after cycling 400 times until its capacity was 9 A-hr.

The figure shows the battery and the phase fractions of components of the fresh cell at 4 volts, 9 A-hrs SOC.

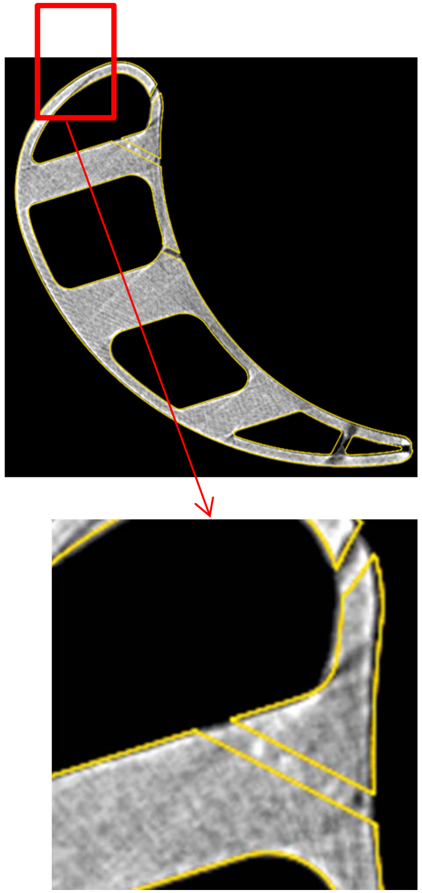


Lithium-ion batteries

The figures show diffraction patterns of the fresh cell and the degraded cell.



Microstructures of Advanced Materials: Neutron Radiography



Access to Neutron Facilities

You can apply for time on SNS and HFIR neutron scattering instruments.

For example, this Spring's call for proposals

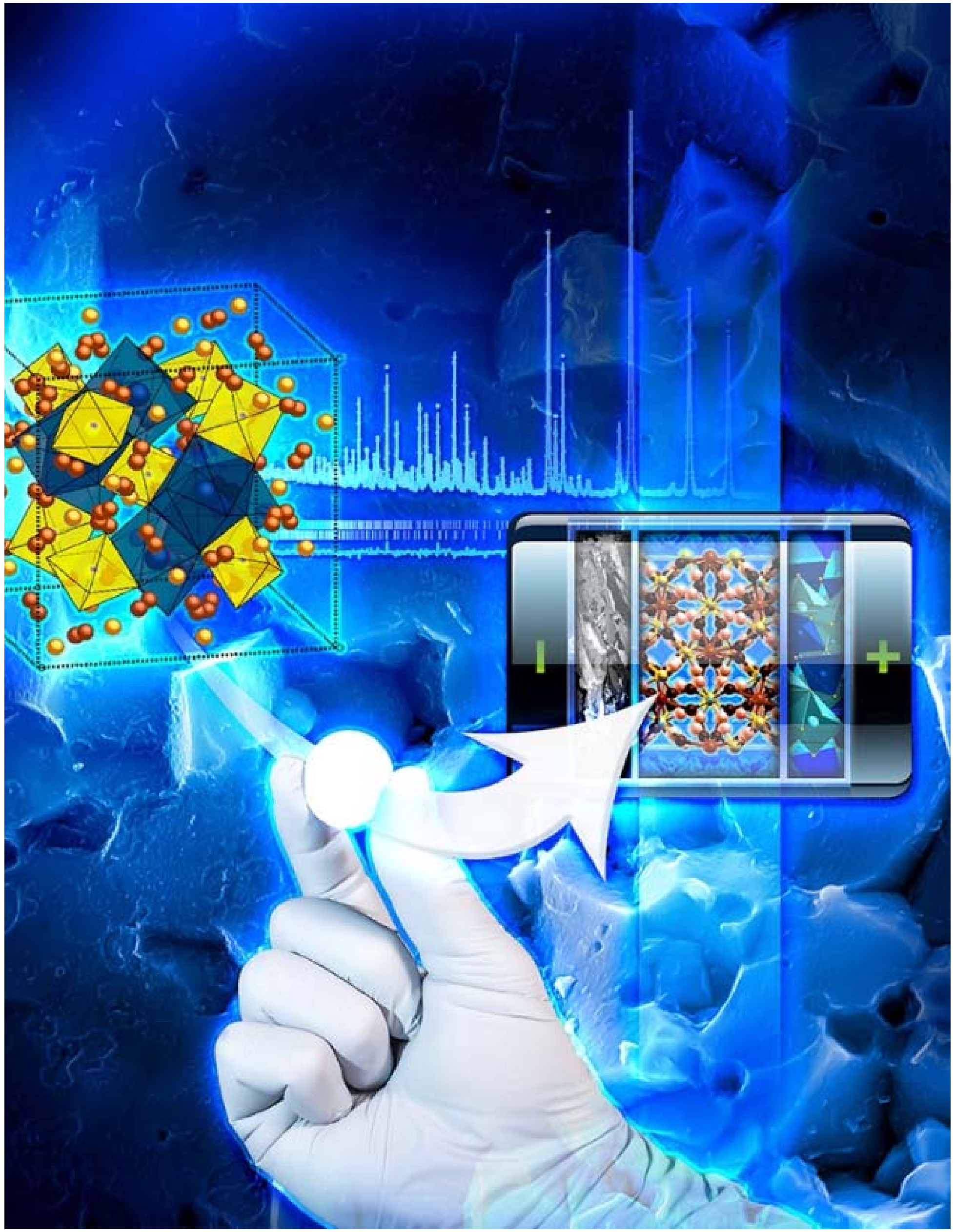
Neutron Sciences Call for Proposals

Proposals for beam time at Oak Ridge National Laboratory's High Flux Isotope Reactor (HFIR) and Spallation Neutron Source (SNS) will be accepted via the web-based proposal system until **NOON EASTERN TIME**, **Wednesday, April 8, 2015**. This call is for experiments anticipated to run July through December 2015.

Proposals will be reviewed for feasibility, safety, and potential for high-impact science. Users for approved projects must complete access and training requirements prior to beginning experiments. Specific information about this call and about each of the instruments available during this experimental period is included on the ORNL Neutron Sciences web site at http://neutrons.ornl.gov/. To learn more about submitting a proposal for beam time, go to http://neutrons.ornl.gov/usersor directly to the proposal system at www.ornl.gov/sci/iums/ipts/.

Proposals are similarly accepted at most other facilities.

Neutrons Help Define the Carrier Concentration in Garnet-based Ionic Conductors for Advanced Li-ion Batteries



Scientific Achievement

Neutron and synchrotron diffraction were used to correlate the partial occupancy of two Li sites with the conductivity of solid garnet type Li-ion superionic conductors, explaining why the maximum in the conductivity is observed for a specific composition.

Significance and Impact

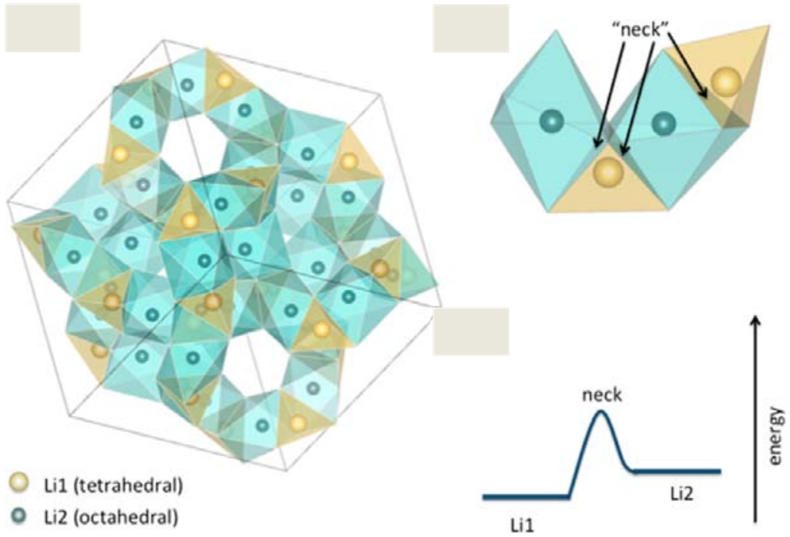
This study demonstrates that the Li site occupancy is an important factor that controls the highly non-linear increase in the ionic conductivity. This work identifies compositions for targeted future optimizations and corroborates previous reports suggesting not all Li-ions participate in conduction.

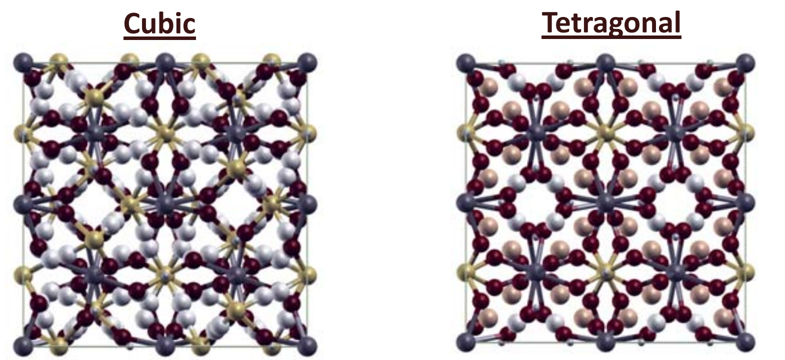
T. Thompson, A. Sharafi, M. D. Johannes, A. Huq, J.L. Allen, J. Wolfenstine, J. Sakamoto. *Advanced Energy Materials*. 2015.

Optimizing the Functional Properties of the Solid Electrolyte $Li_{7-x}La_3Zr_{2-z}Ta_zO_{12}$

Research Details

- Neutron diffraction was used to determine the partial occupancy of two Li sites in a garnet type Li-ion superionic conductor.
- A novel hot-pressing technique was used to minimize microstructural effects.
- The ionic conductivity was measured and modeled with equivalent circuit modeling to isolate and quantify the bulk response.
- It was found that the conductivity maximizes with occupation of the Li2 site, which also corresponds to the shortest Li1-Li2 separation distances.
- The short Li-Li separation distances are believed to destabilize the Li sublattice, giving rise to the superionic behavior, and exclusion of some fraction of the ions in participation during conduction.





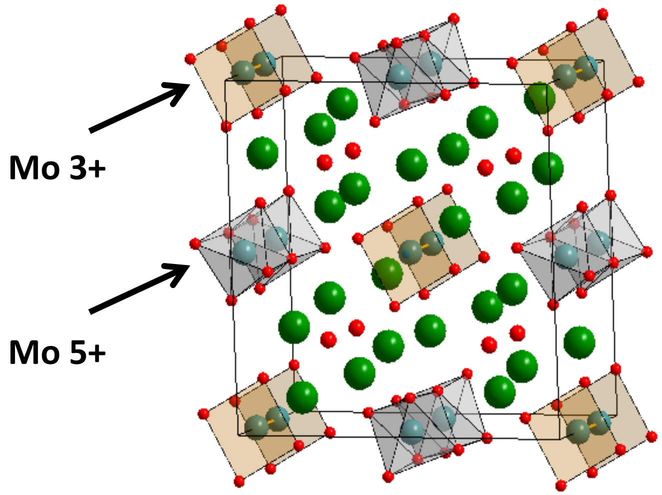
Li_1 = tetrahedral (3)
Li_2 = octahedral (12)

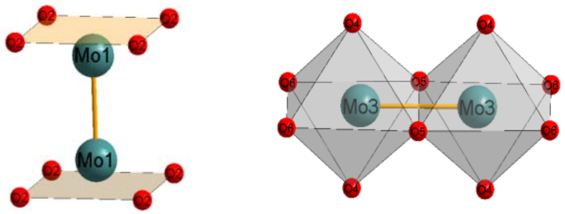
$\sigma = 10^{-3}$ S/cm

Li_1 = tetrahedral (1)
Li_2 = octahedral (2)
Li_3 = octahedral (4)

$\sigma = 10^{-6}$ S/cm

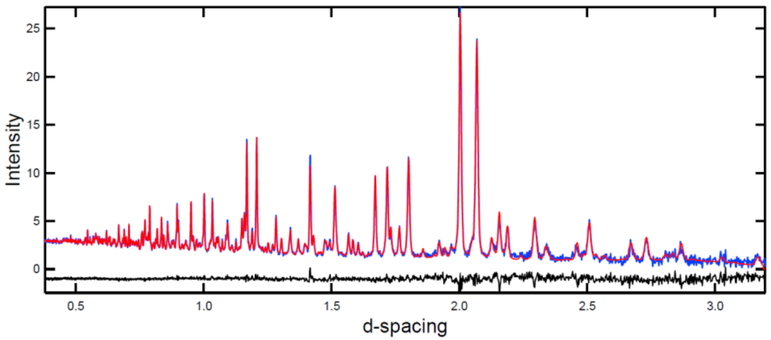
First Discovery of Different Molybdenum Oxidation States in a Small Band Gap Semiconductor





$d_{Mo\text{-}Mo}$ = 2.2 Å $d_{Mo\text{-}Mo}$ = 2.7 Å

Half of the molybdenum ions have a low valence of 3+ (brown squares), while the other half have a high valence of 5+ (grey octahedra).



Scientific Achievement

A new metal oxide was discovered, La_2MoO_5, in which two different types of molybdenum cations co-exist in different valence states.

Significance and Impact

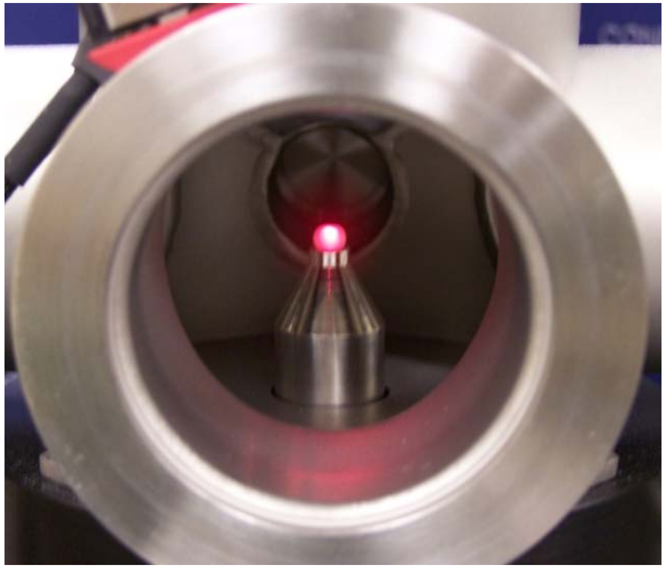
The occurrence of two different Mo valences within a single structure has never been observed before and provides the possibility for strong optical transitions between these two sites, and could lead to applications in infrared sensing.

Research Details

- Powder samples were prepared by reduction of La_2MoO_6.
- Neutron diffraction data were collected at several temperatures on the POWGEN instrument at SNS.
- High resolution X-ray powder diffraction was collected on the 11-BM beam line at APS.
- The position of oxygen atoms were based on neutron data and allowed Mo valences to be determined using the Bond Valence Sum method.
- High level density functional theory (DFT) calculations were used to characterize and study the electronic structure of this material.

D. M. Colabello, F. E. Camino, A. Huq, M. Hybertsen, and P. G. Khalifah. *JACS.* 137, 3 (2015).

Multi-phase High-Entropy Alloys Retain Enhanced Mechanical Properties



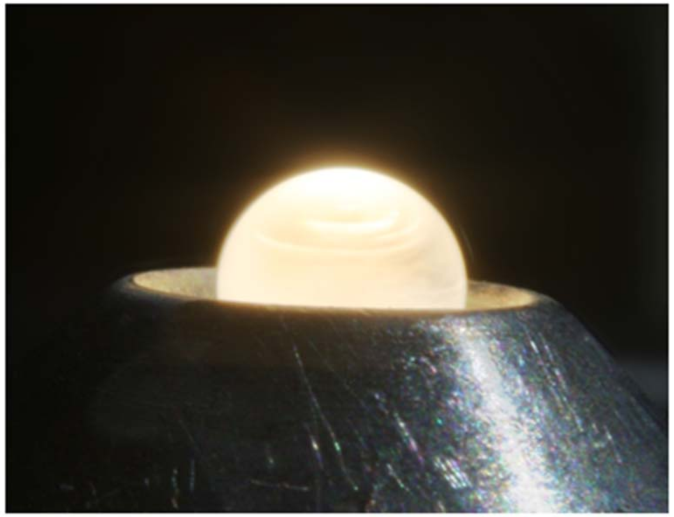


Photo : Lawrie Skinner

Scientific Achievement

Complementary neutron, electron, and X-ray synchrotron scattering techniques demonstrate that high-entropy alloys, containing multiple elements in near-equimolar concentrations, retain enhanced mechanical properties even in the presence of elemental segregation and chemical ordering.

Significance and Impact

Single-phase high-entropy alloys are desired for their enhanced properties like high temperature strength and radiological resistance. Our discovery that enhanced properties are maintained in multi-phase or partially-ordered solids suggests that the high-entropy-alloy-design strategy for novel applications can be extended beyond the present goal of creating single-phase solid solutions.

Work was performed at the ORNL Spallation Neutron Source's POWGEN and NOMAD instruments. SNS is a DOE Office of Science User Facility.

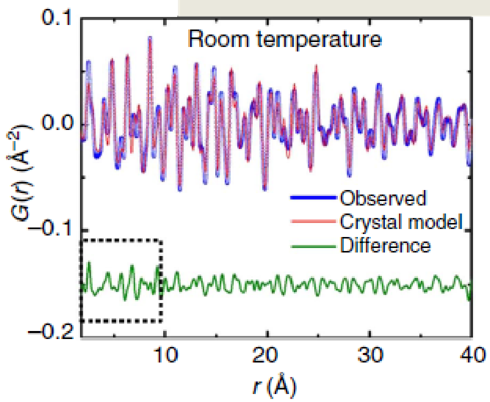
Microscopy studies were performed at the ORNL Center for Nanophase Materials Sciences.

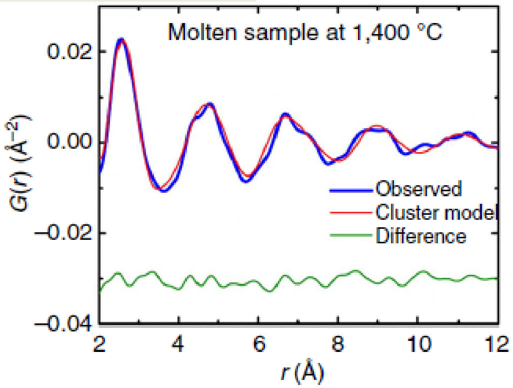
L. J. Santodonato, Y. Zhang, M. Feygenson, C. M. Parish, M. C. Gao, R. J.K. Weber, J. C. Neuefeind, Z. Tang, and P. K. Liaw. *Nature Communications.* 6 (2015): 5964.

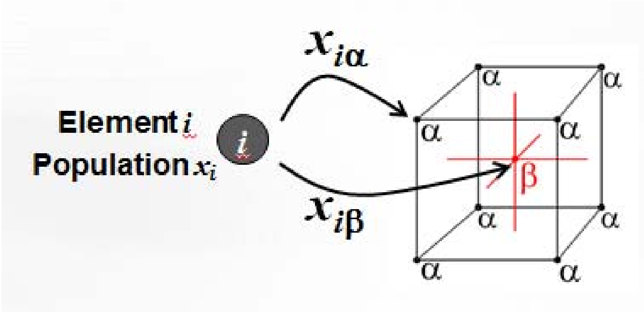
Deviation from high-entropy configurations in $Al_{1.3}CoCrCuFeNi$

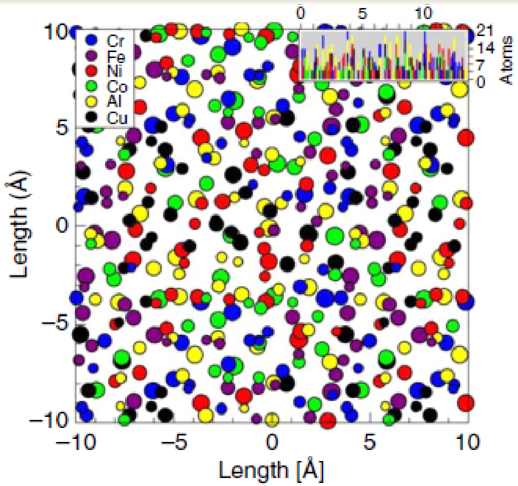
Research Details

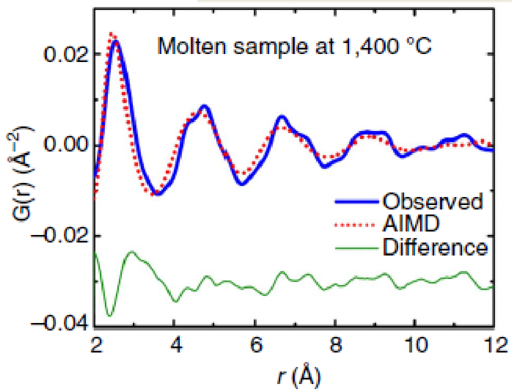
- Performed neutron scattering experiments from room temperature all the way to the molten state (1,400° C).
- Used aerodynamic sample levitation and laser heating.
- Quantified the configurational entropy of mixing by fitting neutron scattering data to structural models.
- A deviation from random atomic mixing was observed in the molten alloy, which is inherited by the solid phases.

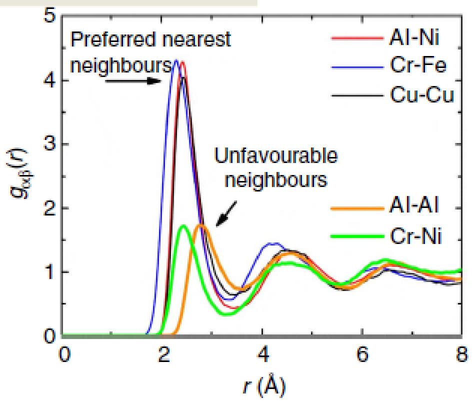












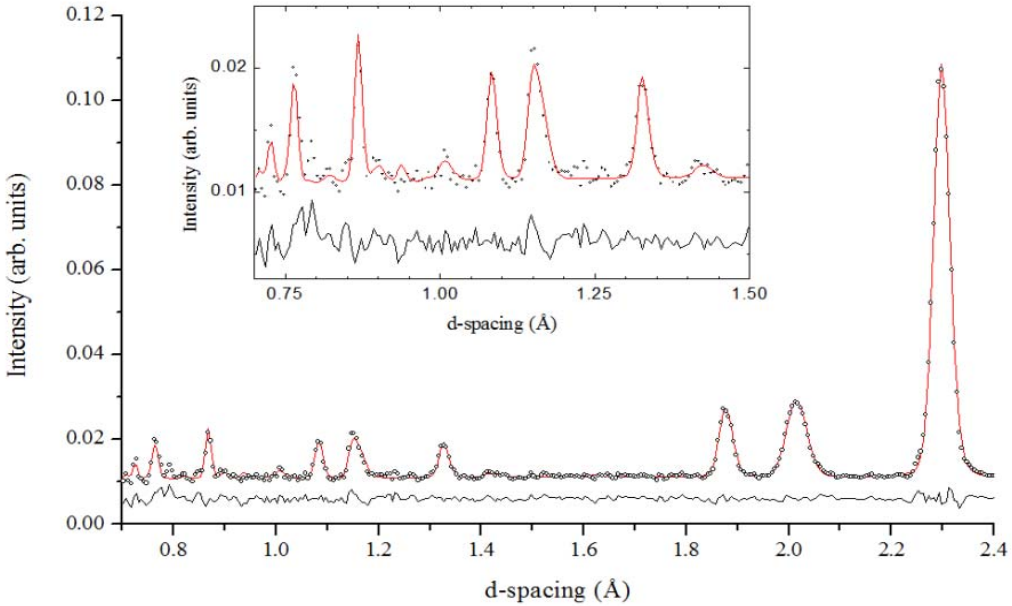
High Pressure: SNS DAC Development Program

Pressure makes structure the experimental variable…

Unique Capabilities

- Powder diffraction at ~1 Mbar.
- Powder diffraction at 30 GPa and 13 K.

- *….opportunities for high-pressure INS*



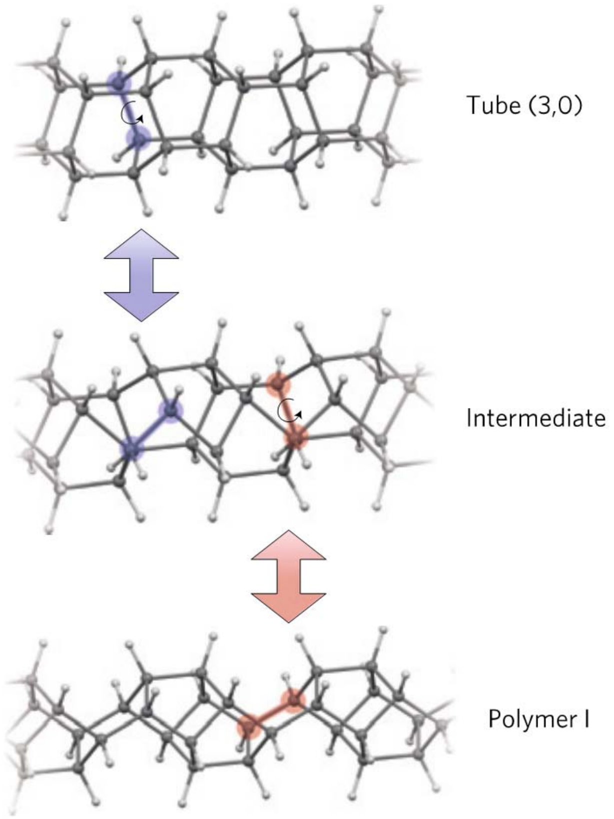
D_2O Ice VII refineable data up to ~45 GPa sample mass 50 μg.

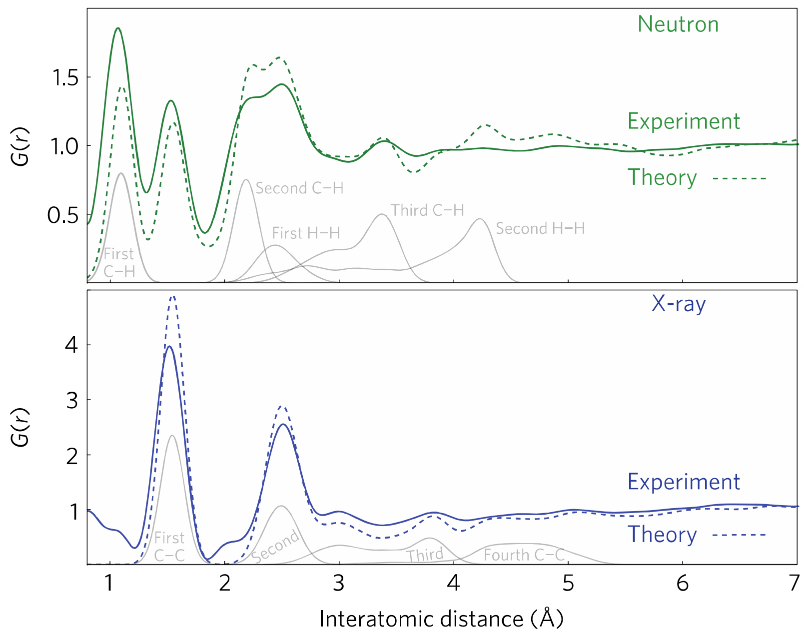
2008 2013 2014

Liquid Benzene Squeezed to Form Diamond Nanothreads

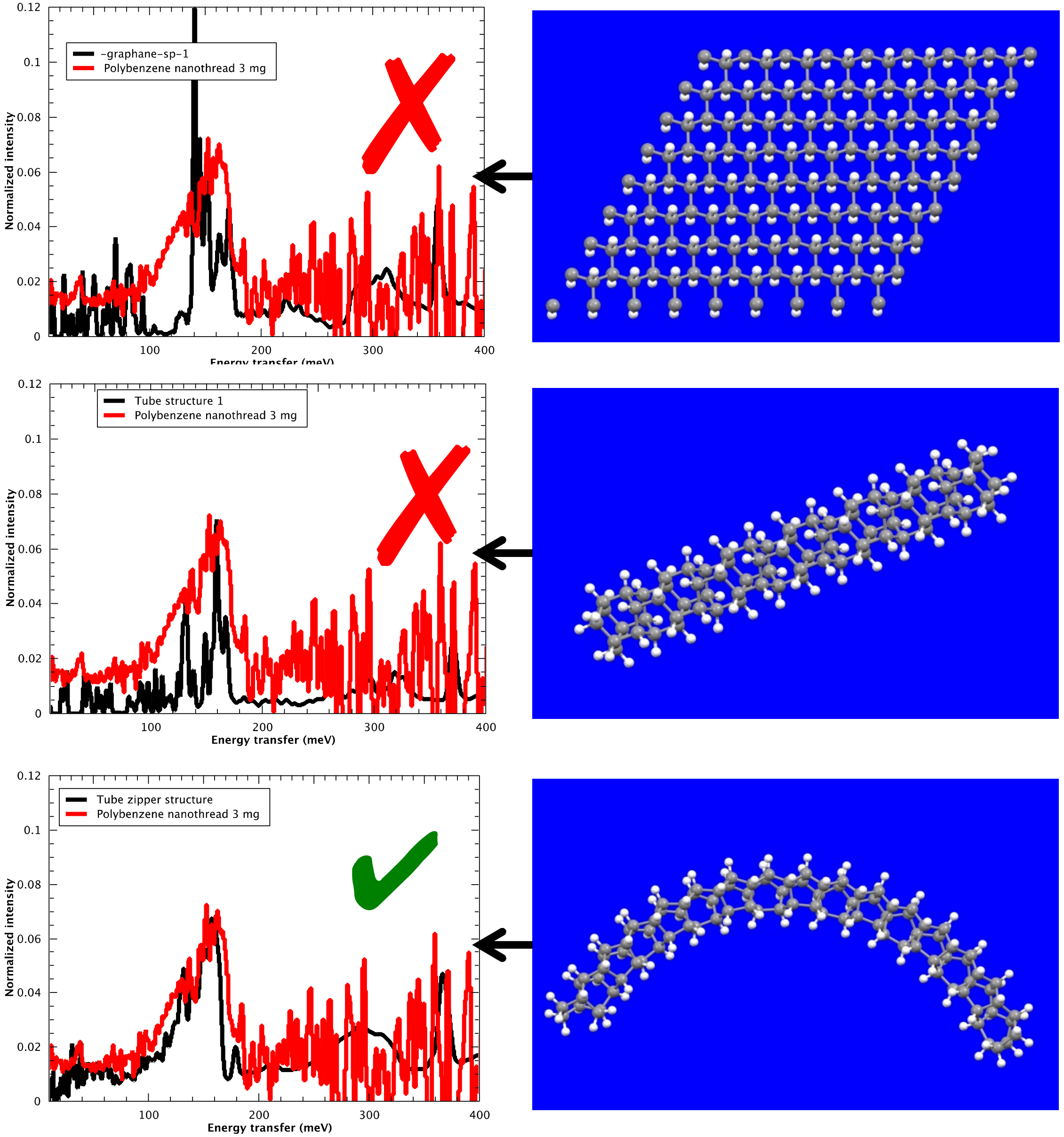
Research Details

- High-pressure synthesis of polymerized benzene samples was performed at 20 GPa and room temperature using large-volume Paris-Edinburgh cell at the SNAP instrument at SNS.
- A relatively large sample (0.02 mL) of nanothreads was recovered at ambient pressure, permitting the use of X-ray and neutron diffraction; Raman spectroscopy; solid-state NMR; and transmission electron microscopy.
- Neutron data were collected on the NOMAD instrument at SNS and beamline 16ID-B at APS.



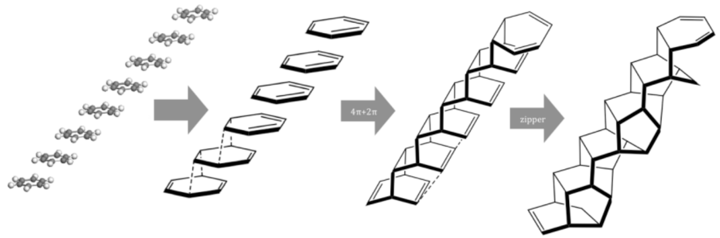


Polybenzene nanothreads on VISION



Research Details

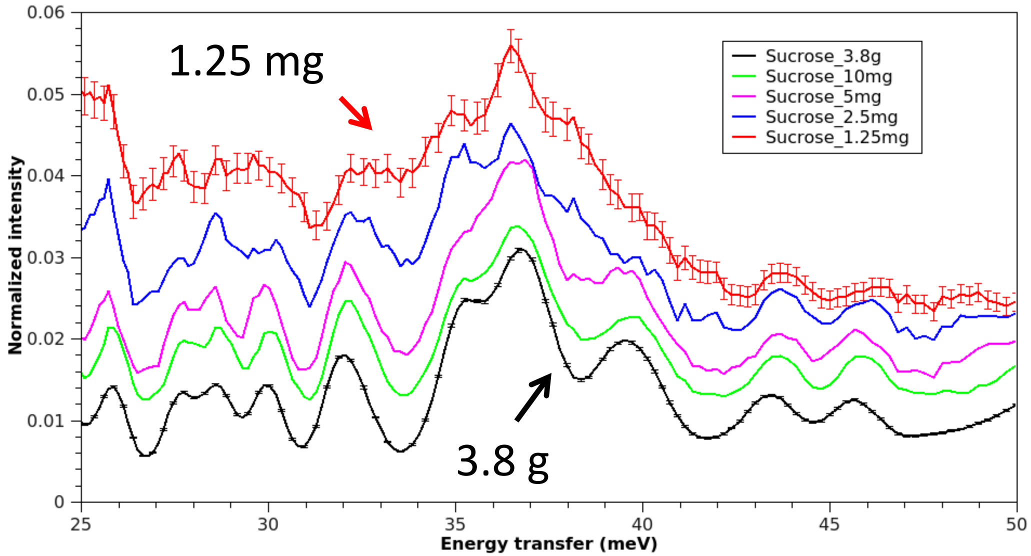
- 3 mg sample of compression-induced polymerized benzene measured using VISION .
- Data compared with series of DFT calculations of hypothetical structures with sp3 carbon and 1:1 H:C ratio
- Computer modelling vital (calculations took ~36 hours utilizing 1024 cores).
- Proposed “zipper” structure provides best agreement between calculation and experiment.



VISION: Opportunities for Real-Time Chemistry

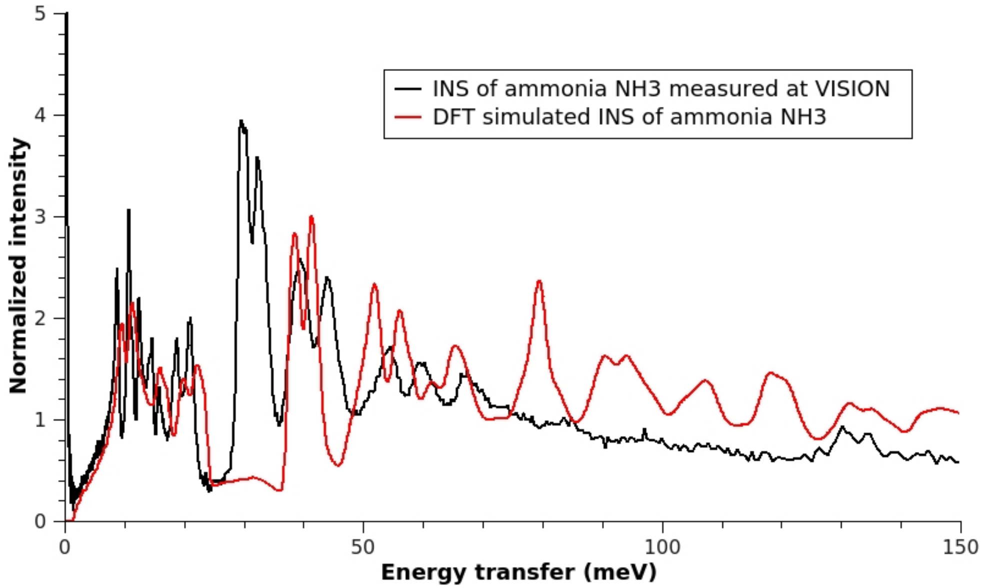
- **1.25 mg of sucrose (table sugar)**

Sugar grains on Al foil (magnified, the total volume of the grains is about 0.8 mm^3)

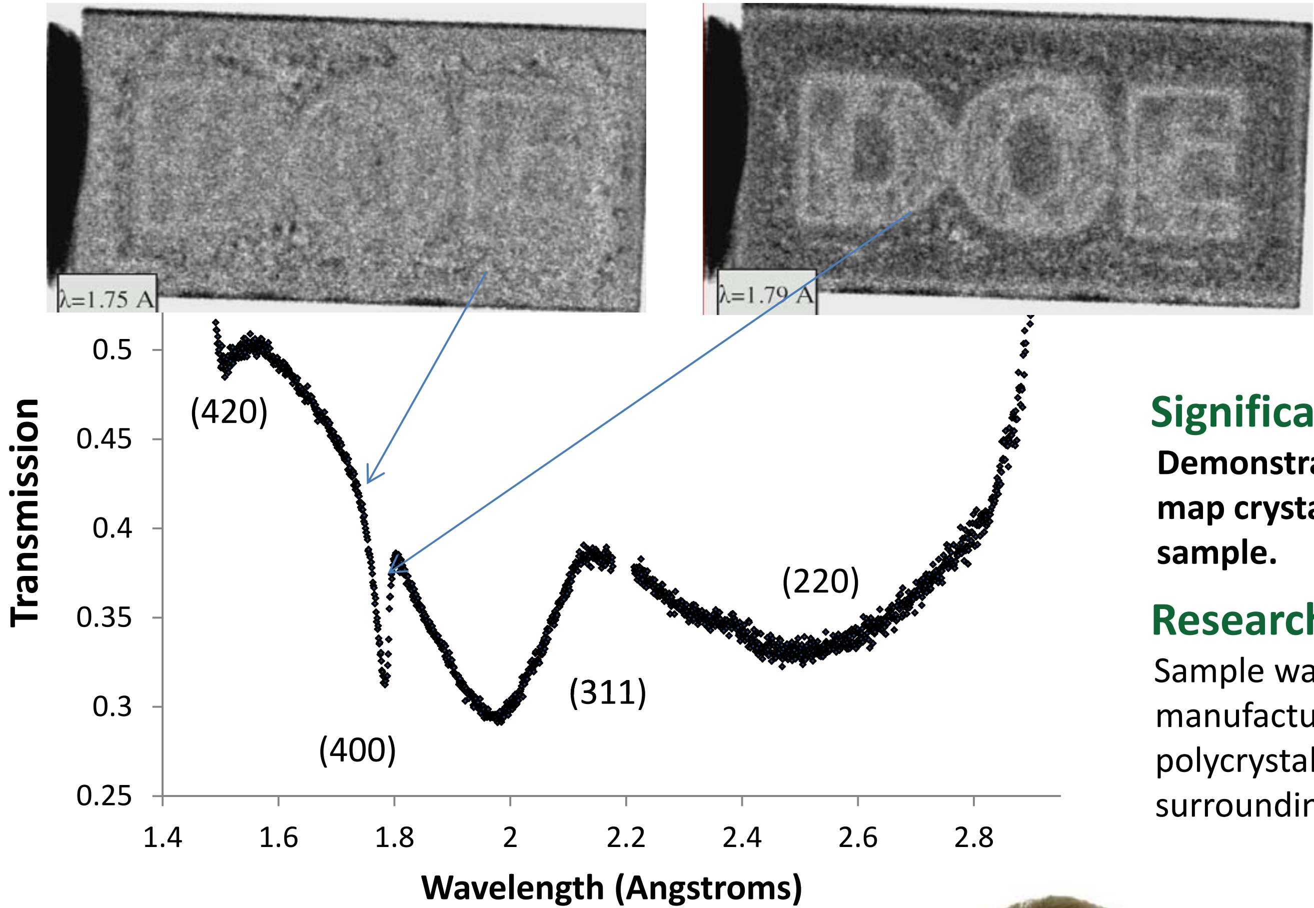


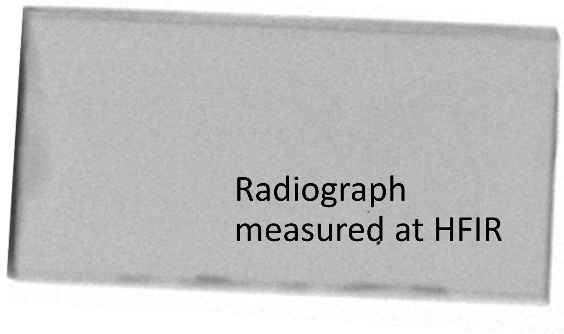
- **Ammonia**

Neutron vibrational spectrum of ammonia (75 microns film) measured at 10 K on VISION at SNS. The red line is a state-of-the-art DFT simulation



Energy-resolved neutron radiography (VULCAN)





Significance and Impact

Demonstration of Bragg-edge imaging to map crystalline planes in a textured sample.

Research Details

Sample was Inconel 738 made by additive manufacturing. “DOE” letters are polycrystalline structures and the surroundings are textured.

Micro-channel plate (MCP) detector temporarily installed on VULCAN

THANK YOU!

Questions?