Neutron Characterization
in support of the
Carbon
and
Metal Hydride
Centers of Excellence

CbCoE

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This presentation does not contain any proprietary or confidential information

Project ID
ST 25

Overview

Timeline

- Start FY05
- End FY09
- 25% complete

Budget

	Carbon	MH
• FY05	$130k	$125k
• FY06	$208k	$156k
• FY07	$216k	$276k requested

Total DOE project funding through FY06 - $619k

NIST has provided 230 instrument days to date and 2 FTE's/year

Barriers

- Barriers addressed

N. Lack of understanding of H Physisorption and Chemisorption

M. Hydrogen Capacity and Reversibility

Partners

- **Carbon Center**

NREL, Penn State, ORNL, Michigan, *etc.*

- **MH Center**

JPL, HRL, Caltech, Sandia, Hawaii, GE, *etc.*

Objectives

Overall: Support the development of hydrogen storage materials by providing timely, comprehensive characterization of Center-developed materials and storage systems using neutron methods. Use this information to speed the rational development and optimization of hydrogen storage materials that can be used to meet the 2010 DOE goal of 6 wt% and 45 g/L capacities.

2006: Characterize structures, compositions and adsorption/absorption site interaction potentials for hydrogen in/on several candidate materials. Calphad calculations of potentially promising alloy-hydride phase relationships.

2007: Refine understanding of these interactions. Extend characterization/calculations to new materials.

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Approach

- **Neutron methods:**
  - Elemental compositions of the materials
  - Location and bonding of hydrogen
  - Adsorption sites
  - Diffusion mechanisms
- **Calphad based computations:**
  - Stabilities/phases of new alloy-hydrides?
  - Hydrogen content, heats of reaction, and phase-reaction sequences during cycling

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Technical Results

NREL tubes	Atom % Boron	Atom % Ni	Atom % Co
Laser	1.2(1)	1.2(1)	-
Arc	0.6(1)	0.4(1)	0.04(1)

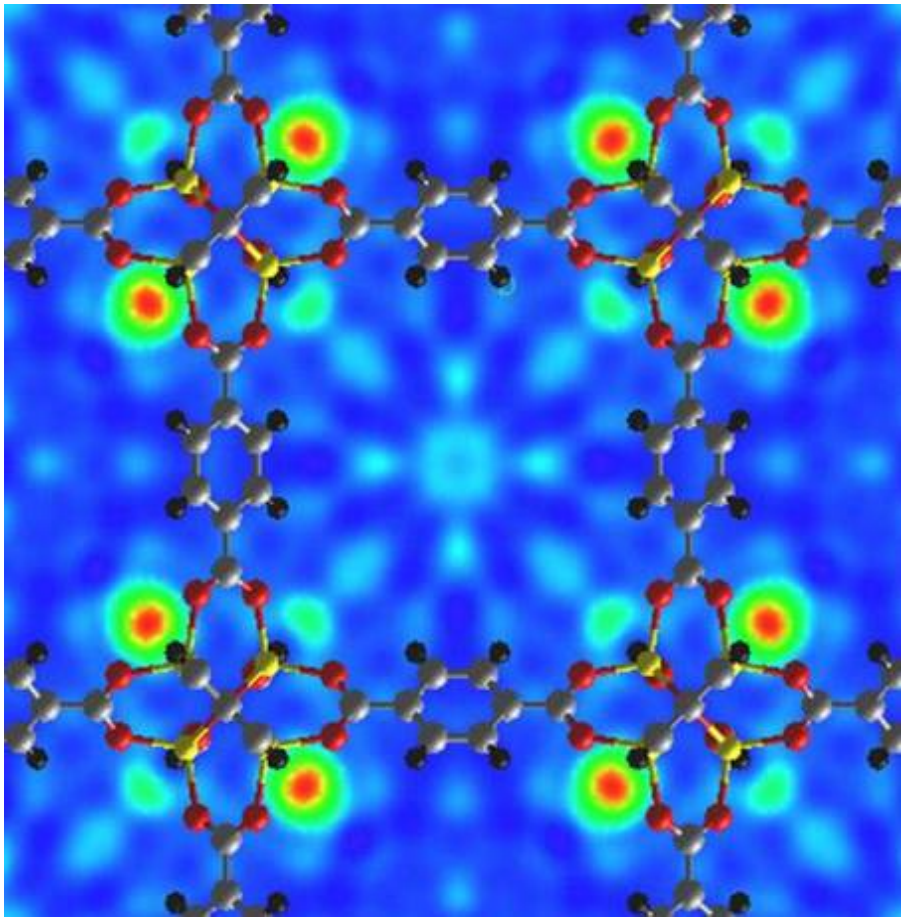
ORNL	Atom % Boron	Atom % Cl	Atom % Pt	Wt.% Pt
Nanohorns	0.248(3)	~$4e^{-5}$	0.0	0.0
Pt-NH	0.252(x)	~$7e^{-6}$	0.832(14)	13.5(2)

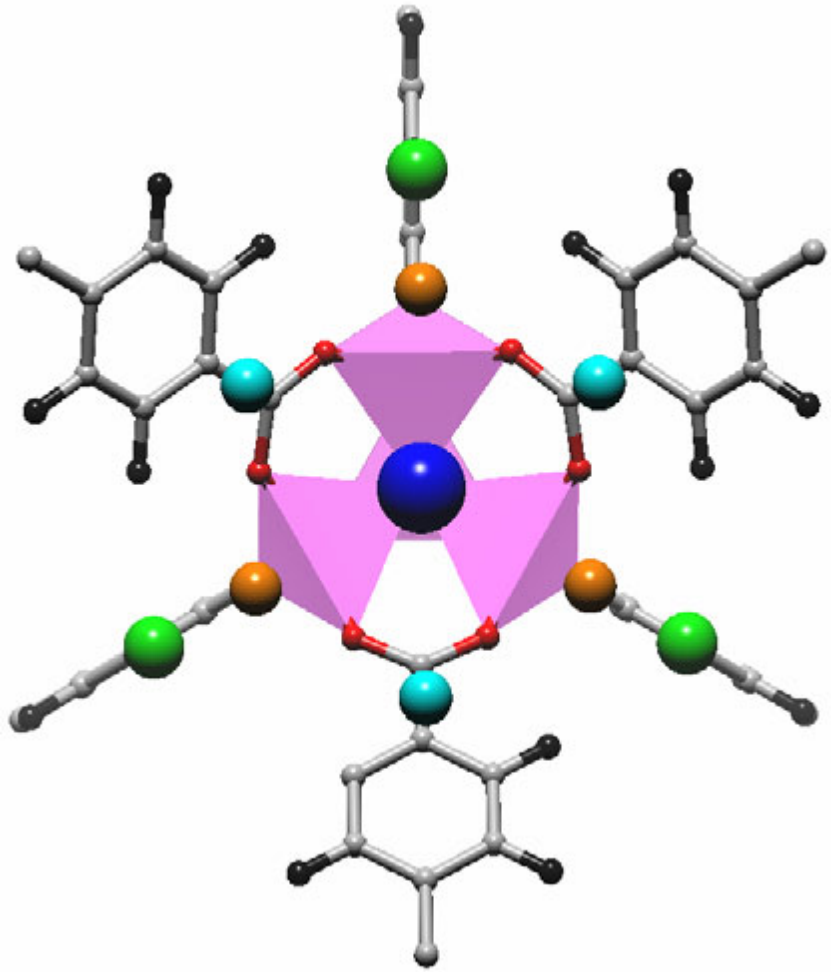
B:Graphite	Atom % Boron	Atom % Cl
Sample 1	0.95(3)	0.002(1)
Sample 2	1.6(2)	0.004(1)

Provide accurate compositions of samples synthesized in Partner Labs.

Technical Accomplishment

Difference Fourier techniques were utilized to determine the hydrogen adsorption sites within a metal-organic framework





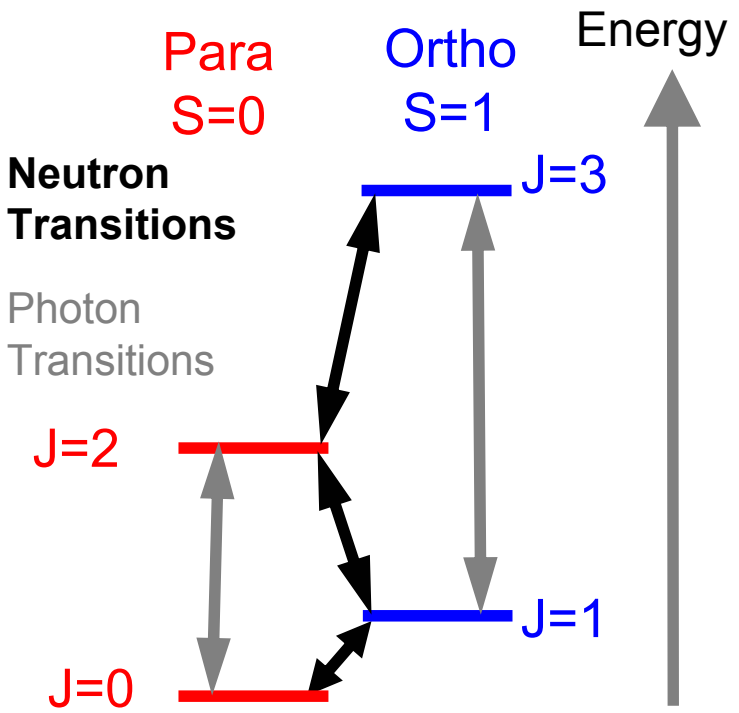
T. Yildirim & M.R. Hartman, PRL **95**, 215504 (2005).

Background – Rotational Dynamics of H_2

Rotational excitations are extremely sensitive to local environment

- hydrogen bound as a molecule
- number of different binding sites
- intensity proportional to the number of H_2 at each site
- temperature dependence yields relative binding energies

$E_J = B\,J(J+1)$, $B_{H_2} = 7.35$ meV

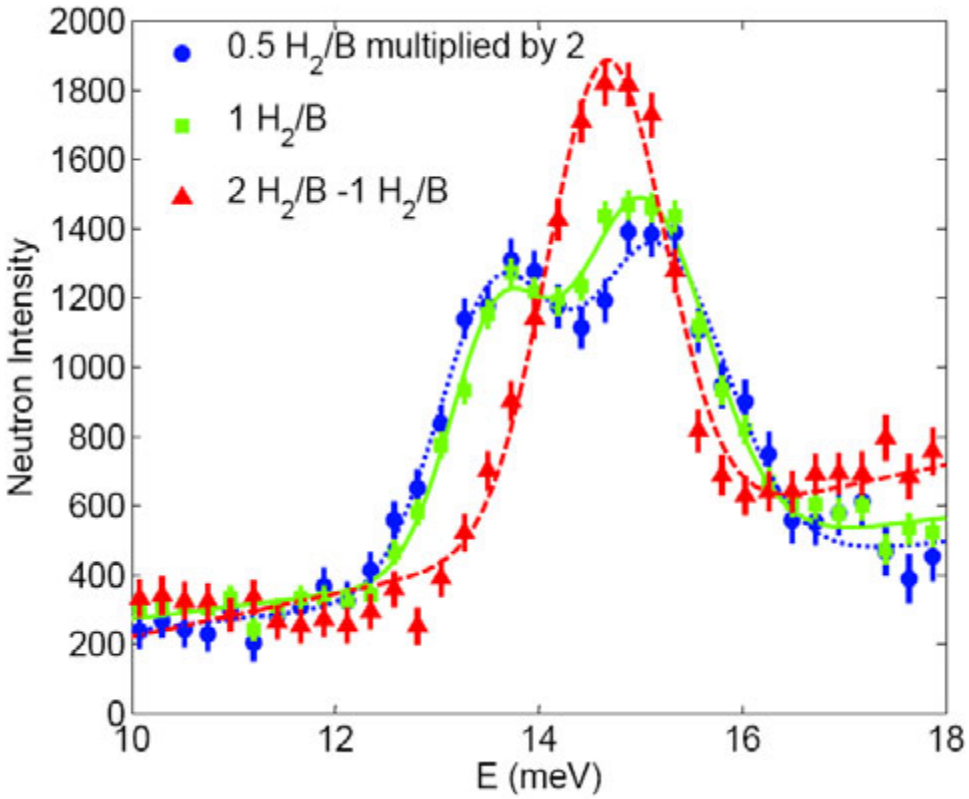


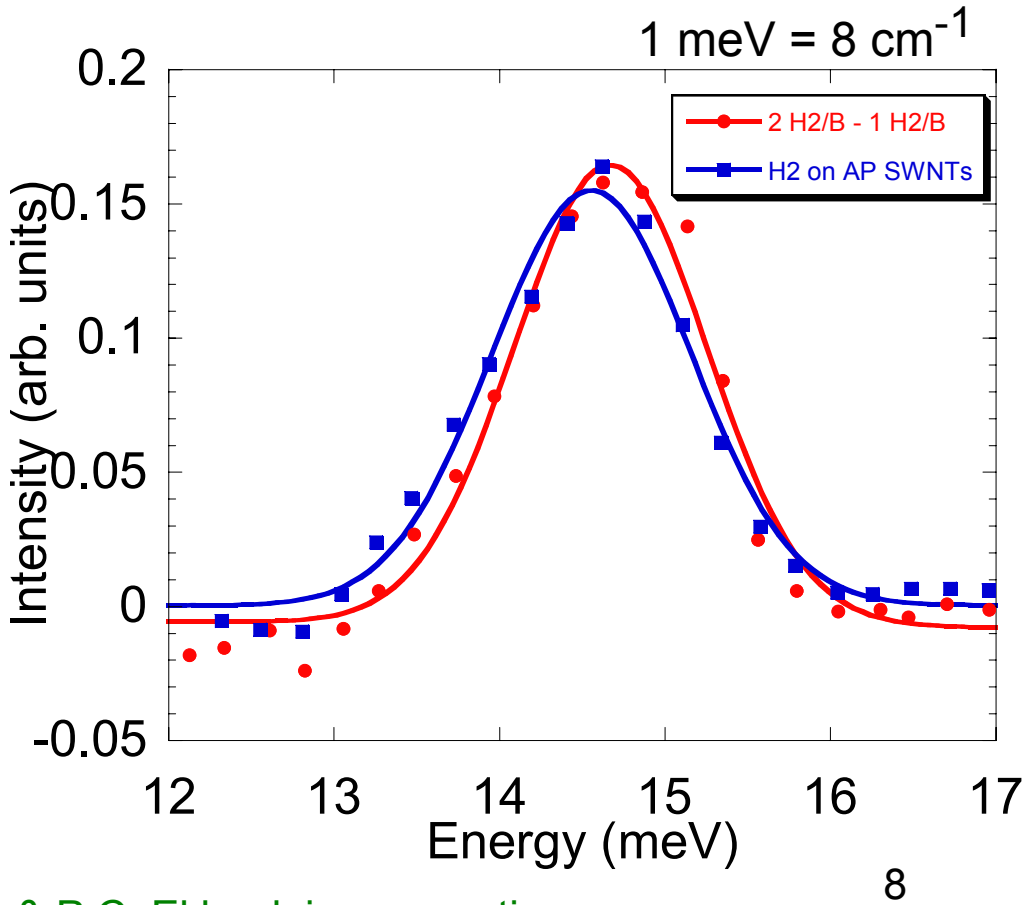
- Para has a nuclear spin S=0. This constrains J to be even.
- Ortho has a nuclear spin S=1. This constrains J to be odd.

Technical Accomplishment

Evidence of a possible route to enhanced physisorption

Neutron spectroscopy was used to show that H_2 preferentially binds to the boron sites in B-doped nanotubes



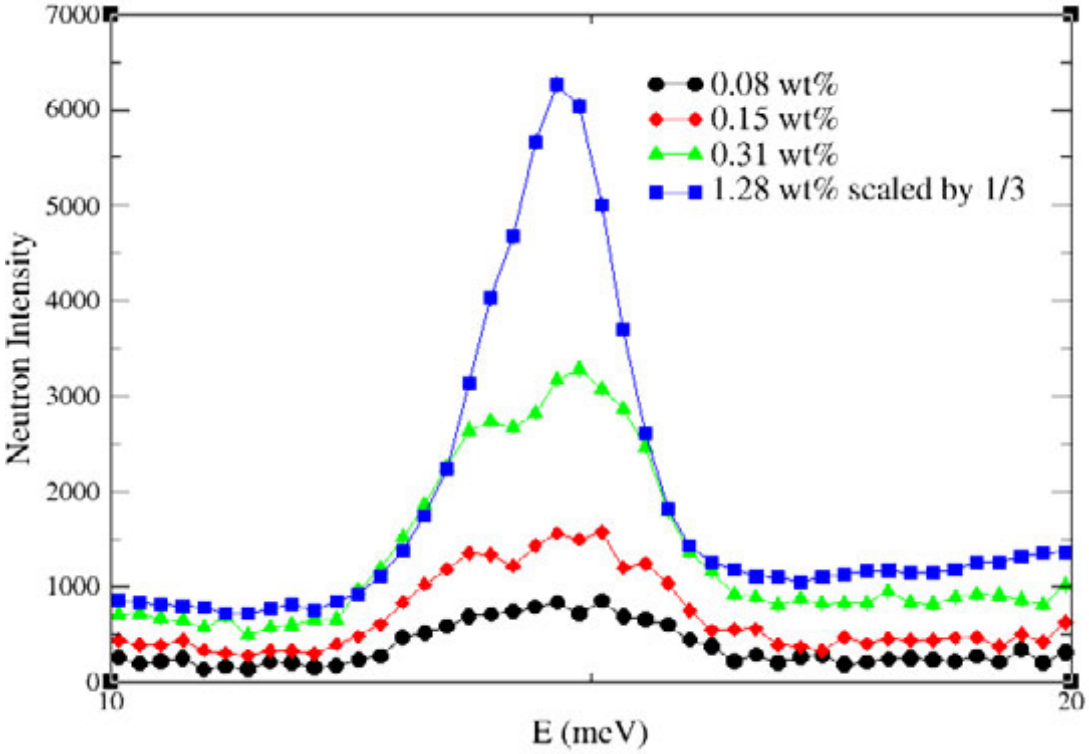


Y. Liu, D.G. Narehood, C.M. Brown, D.A. Neumann, & P.C. Eklund, in preparation.

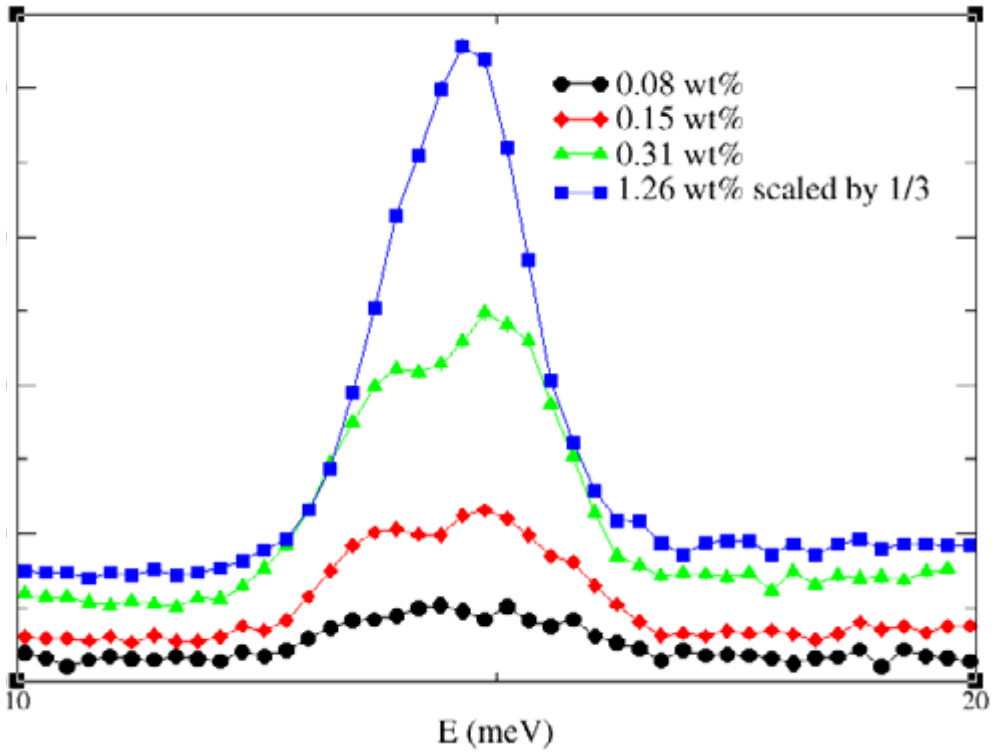
Technical Accomplishment

Neutron spectroscopy was used to characterize the low temperature binding sites on unopened B-doped nanohorns

nanohorns



Pt-nanohorns



H_2 sits on the same locations on both samples

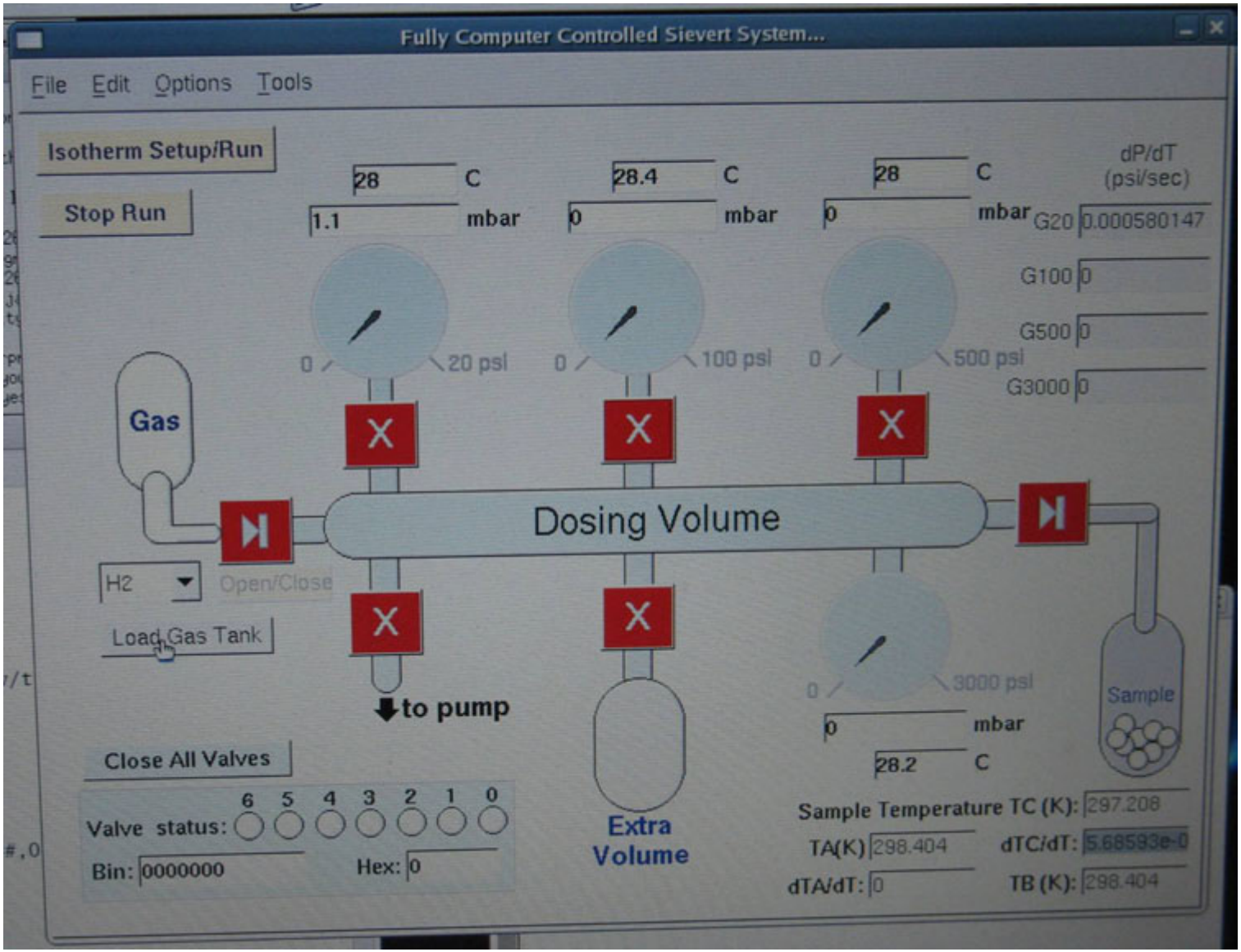
Technical Progress

Neutrons can characterize materials in real world operating conditions

Developed neutron scattering testing cell that enables *in-situ* measurement to 100 bar of hydrogen pressure.

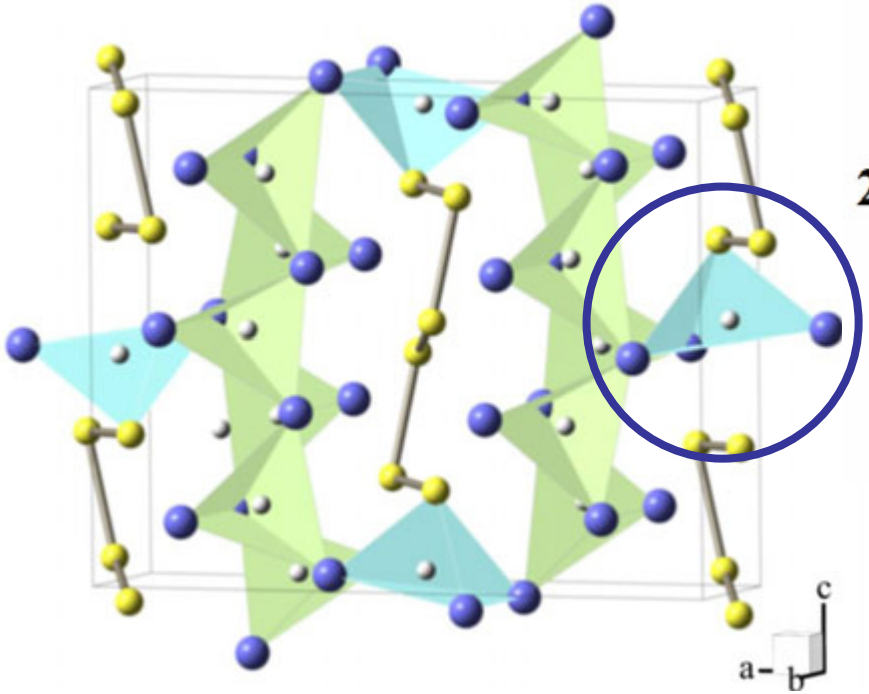
Technical Progress

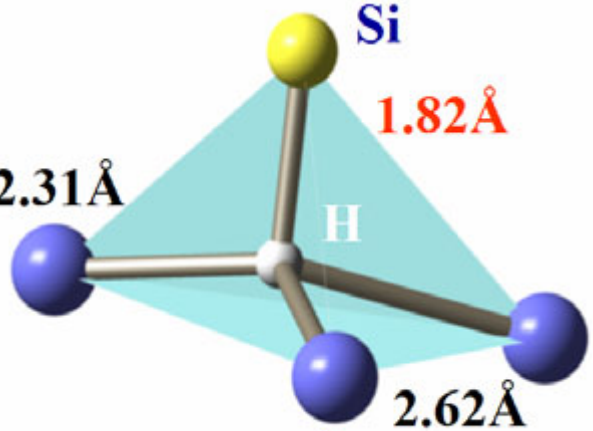
Neutrons can characterize materials in real world operating conditions

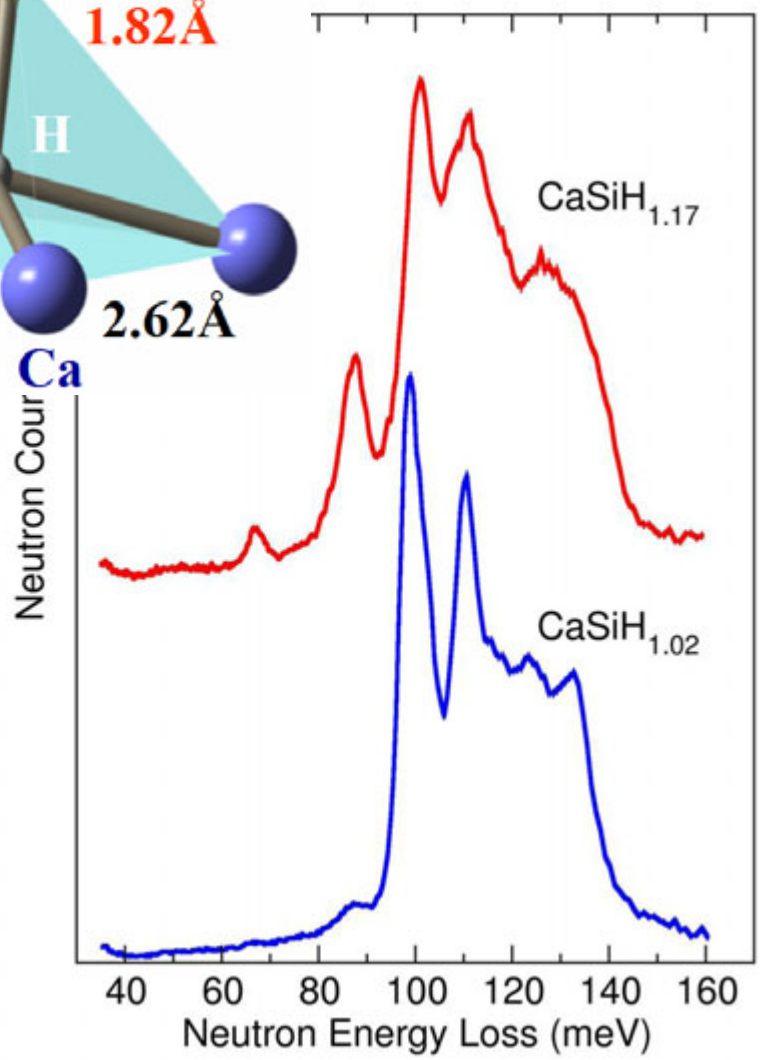


Developed a fully automated Sievert system that enables *in-situ* measurement to 60 bars of hydrogen pressure.

Technical Accomplishment

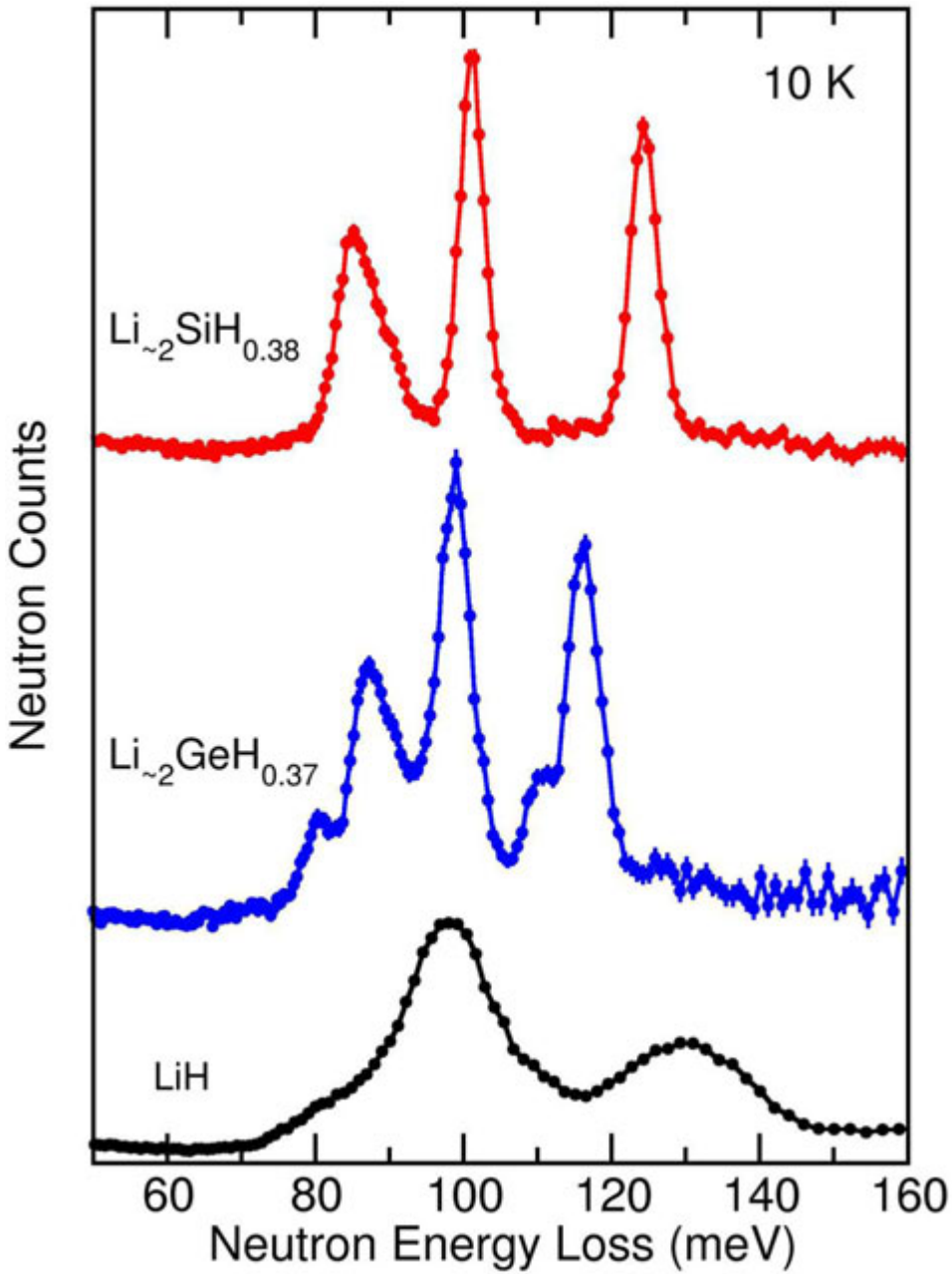






- Determined structures of newly synthesized ternary $CaSiD_x$ phases
- The degree of covalency of the Si-H bonding in the x>1 structure may be less than predicted by first-principles calculations.

Technical Accomplishment



- Synthesized a new $Li_xGe_yH_z$ ternary phase
- The new $Li_xGe_yH_z$ ternary phase is similar in structure to $Li_xSi_yH_z$ ternary phase
- The Li/Ge and Li/Si ratios for the ternary phases are ≈ 2

Collaboration with JPL, HRL, and Caltech

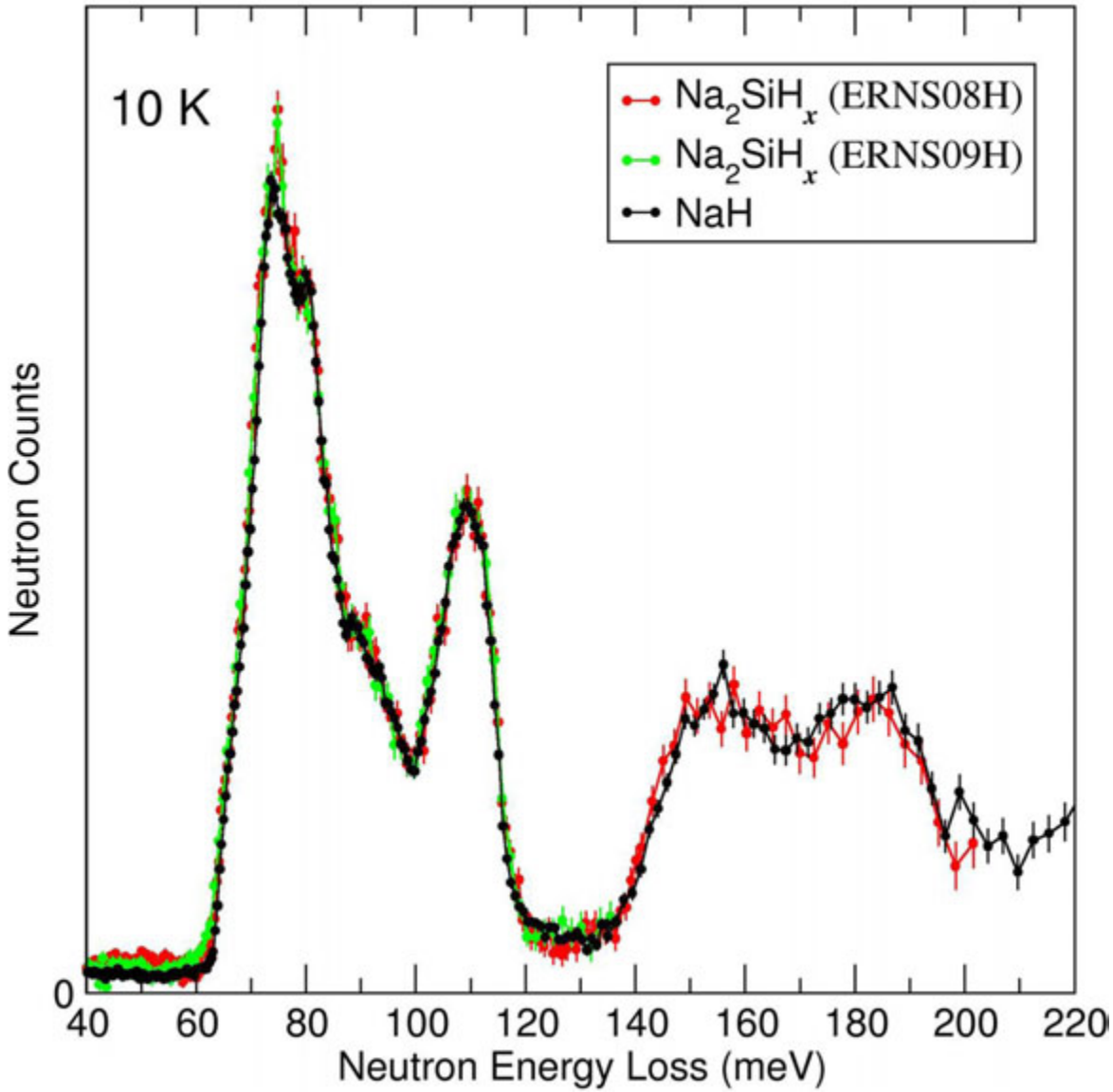
1 meV = 8 cm^{-1}

Technical Accomplishment

METAL HYDRIDE CENTER OF EXCELLENCE

- PGAA indicates H/Na atomic ratios of 0.94(2) & 0.97(1)
- Comparison with NaH spectrum indicated that essentially all absorbed hydrogen in these samples exists as NaH

Collaboration with Sandia

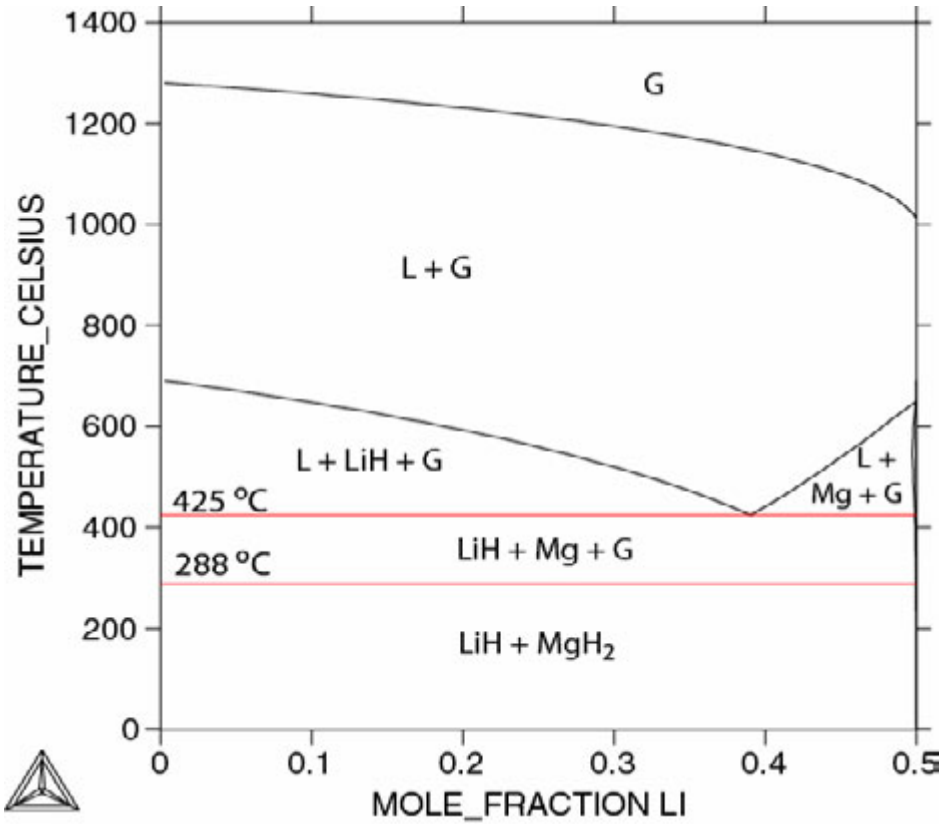


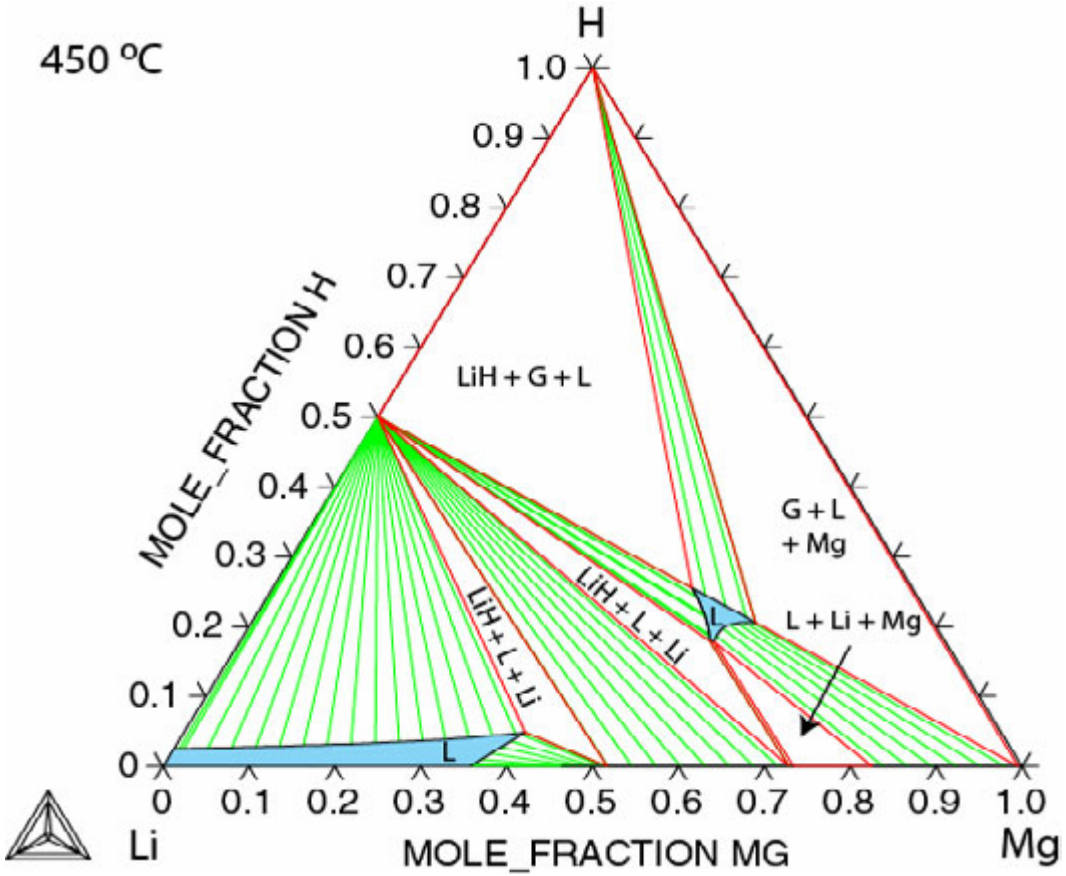
1 meV = 8 cm^{-1}

Technical Accomplishment

METAL HYDRIDE CENTER OF EXCELLENCE

Calphad thermodynamic descriptions of multi-component hydride systems





Addition of Mg to LiH reduces reaction temperature

The reaction involves a H-rich liquid phase

=> reduces effective storage capacity

Future Work
(Carbon Center)

Remainder of FY 2006:

Continue neutron scattering studies of various carbon-based systems

- Complete analysis of neutron spectroscopy data.
- Confirm hydrogen rotational spectra of as-prepared nanotubes to remove possible uncertainties in morphologies due to production methods
- Perform higher temperature loading of Pt doped samples to look of signs of spillover
- Complete 2006 milestones
- Go/No-Go 3rd quarter of FY06 - Demonstrate usefulness of neutron scattering techniques to the Center

FY 2007:

- Provide elemental analysis of prepared samples
- Isolate the origins of the increased hydrogen binding potential
- Characterize spillover effects
- Speed the development of materials that can be used in systems meeting the 2010 DOE goals

Future Work

Remainder of FY 2006:

Continue neutron scattering studies of various metal-hydride systems

- Complete analysis of structure and bonding associated with the ternary Li-Si-H and Li-Ge-H compounds (JPL,HRL,Caltech)
- Continue the characterization of H bonding in the Ca-Si system (JPL)
- Aiding other partners with such systems as destabilized MgH_2, Li-Mg-B-H (w/JPL/HRL/Caltech), Na-Si-H, $Ca(BH_4)_2$ (Sandia)
- Continue investigating the vibrational spectroscopy of the alanes (Hawaii)
- Completed characterization of $NaBH_4$
- Go/No-Go by 3rd quarter of FY06 - Demonstrate usefulness of neutron scattering techniques to the Center

FY 2007:

- Characterize destabilized alkali and alkaline earth hydrides and other systems developed by MHCoE members in order to speed the development of materials that can be used in systems meeting the 2010 DOE goals

Future Work

METAL HYDRIDE CENTER OF EXCELLENCE

Thermodynamics Computations

Remainder of FY 2006:

- Develop description for the Li-B system in collaboration with the University of Pittsburgh
- Evaluate literature for addition of Ca-X systems to the H-Li-Mg-B-Si database

FY 2007:

- Include additional light elements in the database and evaluate new materials that show promise for use in systems that meet the2010 DOE systems goals

Summary

Neutron methods provide crucial, non-destructive characterization tools for the Carbon and Metal Hydride Centers

Carbon Center

Evidence of a possible route to enhanced physisorption of hydrogen on carbons

Elemental composition and neutron scattering measurements of multiple carbon based samples of interest to the center

Metal Hydride Center

Characterized new Li-Si-H and Li-Ge-H ternary phases

Characterized a large fraction of the Ca-Si-H phase diagram using multiple neutron techniques

Thermodynamics Computations

A thermodynamic database for H-Li-Mg-B-Si has been developed

Collaboration with the University of Pittsburgh has been initiated to obtain the missing quantities for the Li-B system

Back-up Slides (Not presented)

Milestones
(Carbon Center)

March 31, 2006 (Completed)

1) Survey of materials of interest to the Center. Continue isothermal gas loading, inelastic neutron scattering, neutron powder diffraction, and prompt gamma hydrogen content measurements. Samples would include at least four from the following: MOFs; aerogels; polymers; graphitic nanofibers; carbon nanotubes; hybrid B-N-C systems; and doped carbon materials.

2) Design a suitable gas loading system and sample cell that satisfies NCNR safety regulations and can apply 100 atmospheres of hydrogen gas at variable temperature.

3) Detailed neutron studies. Evaluate the effects of controlled synthesis on materials such as MOFs and metal decorated nanotubes. The precise materials will be selected through discussions with the leadership of the Center.

4) Provide detailed characterizations of the molecular structures of adsorbents showing promising adsorption properties and

Demonstrate importance of neutron techniques to mission of the Center (Go/No Go: 3Q Year 2)

September 30, 2006 (On track to complete)

1) Build in-situ apparatus for real world conditions. A room-temperature apparatus will be constructed that reflects in-situ operating conditions for a hydrogen-storage medium.

2) Detailed neutron studies in support of the Center's go/no-go analysis. A thorough analysis of the three or four materials that are the most promising in terms of meeting the FY2007 go/no-go decisions will be completed.

Milestones
(Metal Hydride Center)

March 31, 2006 (Completed)

1) *Detailed neutron studies*. Evaluate structural and bonding properties of new materials selected through discussions with the leadership of the Center. Continue the characterization the hydrogen bonding potentials associated with destabilized LiH and MgH2 systems.

2) *Thermodynamic evaluations.* Provide further Calphad analyses of promising metal-hydride systems

Demonstrating importance of Calphad calculations to mission of the Center (Go/No Go: 3Q Year 2)
Demonstrate importance of neutron techniques to mission of the Center (Go/No Go: 3Q Year 2)

September 30, 2006 (On track to complete)

1) Detailed neutron studies in support of the Center's go/no-go analysis. A thorough analysis of the materials that are the most promising in terms of meeting the Phase 1 go/no-go decisions.

2) Continue Calphad evaluations of new materials.

Response to Last Year's Review

NA - New project in 2005

Accomplishments, Progress & Results
(Carbon Center)

- *Evidence* of a possible route to enhanced physisorption of hydrogen on carbons.
- Elemental composition and neutron scattering measurements of multiple carbon based samples of interest to the center:
  - Boron-nanotubes (PSU, NREL)
  - Boron-graphite (PSU)
  - Nanohorns and Pt-Nanohorns (ORNL)
  - Search for spillover in bridged materials (Mich.)
- On target for completion of 2006 milestones.

Accomplishments, Progress & Results

- Isolated and characterized new Li-Si-H and Li-Ge-H ternary phases
- Characterized a large fraction of the Ca-Si-H phase diagram
- Completed study of $NaBH_4$ and exploring mixed hydrides
- Performed multiple characterizations on samples of interest to the center

- A thermodynamic database for H-Li-Mg-B-Si has been constructed and used to calculate ternary phase diagrams along with hydrogenation temperatures & pressures for the H-Mg-Si, H-Li-Mg, H-Mg-B and H-Li-Si systems.
- The effect of the accuracy of the descriptions of the binary intermediate compounds on the hydrogenation temperatures and pressures was evaluated.

Publications and Presentations

PAPERS:

- T. Yildirim and M.R. Hartman, “Direct observation of hydrogen adsorption sites and nano-cage formation in metal-organic frameworks (MOF)”, Phys. Rev. Lett., 95, 215504 (2005).
- D.A. Neumann, “Neutron Scattering and Hydrogenous Materials”, Materials today, 9 (1-2), 34 (2006).
- Y. Liu, D.G. Narehood, C.M. Brown, D. A. Neumann, and P.C. Eklund, “Inelastic Neutron Scattering of H_2 Adsorbed on Boron Doped (≤ 1%) Single Walled Carbon Nanotubes”, In preparation.

TALKS:

- M.R. Hartman, T. Yildirim, T.J. Udovic, and C.M. Brown, "Hydrogen Adsorption and Dynamics in Metal-Organic Framework (MOF) Materials," presented at the Materials Research Society Fall 2005 Meeting, Boston, MA (2005) (#A9.51)
- D.G. Narehood, Y. Liu, C.M. Brown, D.A. Neumann, and P.C. Eklund, “Inelastic Neutron Scattering of H_2 Adsorbed on Boron Doped (≤ 1%) Single Walled Carbon Nanotubes”, March meeting of the American Physical Society (2006).
- D.A.Neumann, Neutron Metrologies for the hydrogen economy, ACS Fall meeting, Washington, DC, August 2005.
- D.A.Neumann, Neutron Metrologies for the hydrogen economy, MRS Fall Meeting, Boston, MA, November 2005.
- Y. Liu, T. Yildirim, “Quantum Dynamics of H2 in Metal-Organics Frameworks MOF5”, presented at the Materials Research Society Spring 2006 Meeting, San Francisco, CA (2006) (#EE6.9)
- P. Eklund, D.G. Narehood, U. Kim, X. Liu, Y. Liu, C.M. Brown, D.A. Neumann and H. Gutierrez, “Boron-doped Single-walled Carbon Nanotubes for Enhanced Hydrogen-tube Interaction”, 209th Meeting of The Electrochemical Society, Colorado May, (2006).
- C.M. Brown *et. al,* ”Hydrogen Rotation in Carbon Materials”, American Conference on Neutron Scattering, June 2006.

POSTERS:

- Y. Liu, C. M. Brown, M. R. Hartman, V. K. Peterson, D. A. Neumann, T. Udovic, D. Narehood , P. Eklund, S. S. Kaye, J. R. Long, “Investigating structural and dynamical information of H_2 inside materials” , Annual Sigma-Xi Postdoctoral Poster Presentation, 2006 (#62)
- T. Yildirim and M. R. Hartman, “Direct Observation of Adsorption Sites and Hydrogen Nano-Cage Formation in Metal-Organic Frameworks,” presented at the *Materials Research Society Fall 2005 Meeting*, Boston, MA (2005) (#A9.40)

Publications and Presentations

TALKS:

- M.R. Hartman, T.J. Udovic, J.J. Rush, R.C. Bowman, Jr., J.J. Vajo, C.C. Ahn, "Neutron Scattering Investigations of a Destabilized LiH:Si Systems for Hydrogen Storage Applications," presented at the *Materials Research Society Fall 2005 Meeting*, Boston, MA (2005).
- R.C. Bowman, S.-J. Hwang, C.C. Ahn, A. Dailly, M.R. Hartman, T.J. Udovic, J.J. Rush, J.J. Vajo, "Reversibility and Phase Compositions of Destabilized Hydrides Formed from LiH", presented at the Materials Research Society Spring 2006 Meeting, San Francisco, CA (2006) (#EE7.5)
- U.R. Kattner, "A Thermodynamic Database for Metal-Hydrogen Systems," Advanced Materials for Energy Conversion III Symposium at the TMS 2006 Annual Meeting, San Antonio, TX, March (2006)
- T.J. Udovic, "Probing Structure and Bonding in Hydrogen- Storage Materials by Combined Neutron- Scattering Techniques and First- Principles Calculations", The 2006 Meeting of the American Crystallographic Association, Honolulu, Hawaii, (2006) (13.01.02)
- R.C. Bowman, Jr., J. Kulleck, S.-J. Hwang, M.R. Hartman, T.J. Udovic, J.J. Rush, "Characterization of Phase Compositions and Structures for Metal Hydrides Used in Hydrogen Storage", The 2006 Meeting of the American Crystallographic Association, Honolulu, Hawaii (2006) (13.01.04)
- Y. Gao, J. Rijssenbeek, "Crystal Structure and Reaction Mechanism of Complex Metal Hydrides Studied by in-situ Synchrotron and Neutron Techniques", The 2006 Meeting of the American Crystallographic Association, Honolulu, Hawaii (2006) (13.01.05)

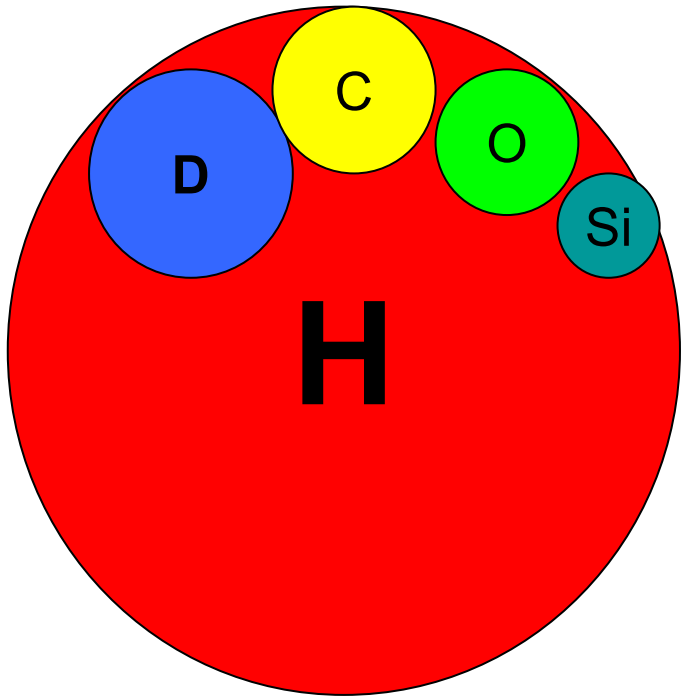
POSTERS:

- H. Wu, T.J. Udovic, J.J. Rush, "Hydrogen Storage Properties and Phase Variation Studies in the Destabilized CaH_2+Si System", presented at the Materials Research Society Spring 2006 Meeting, San Francisco, CA (2006) (#EE3.31)
- M.R. Hartman, J.J. Rush, T.J. Udovic, "Investigation of the Dynamics of Hydrogen in Lithium Borohydride using Quasielastic Neutron Scattering", presented at the Materials Research Society Spring 2006 Meeting, San Francisco, CA (2006) (#EE3.1)

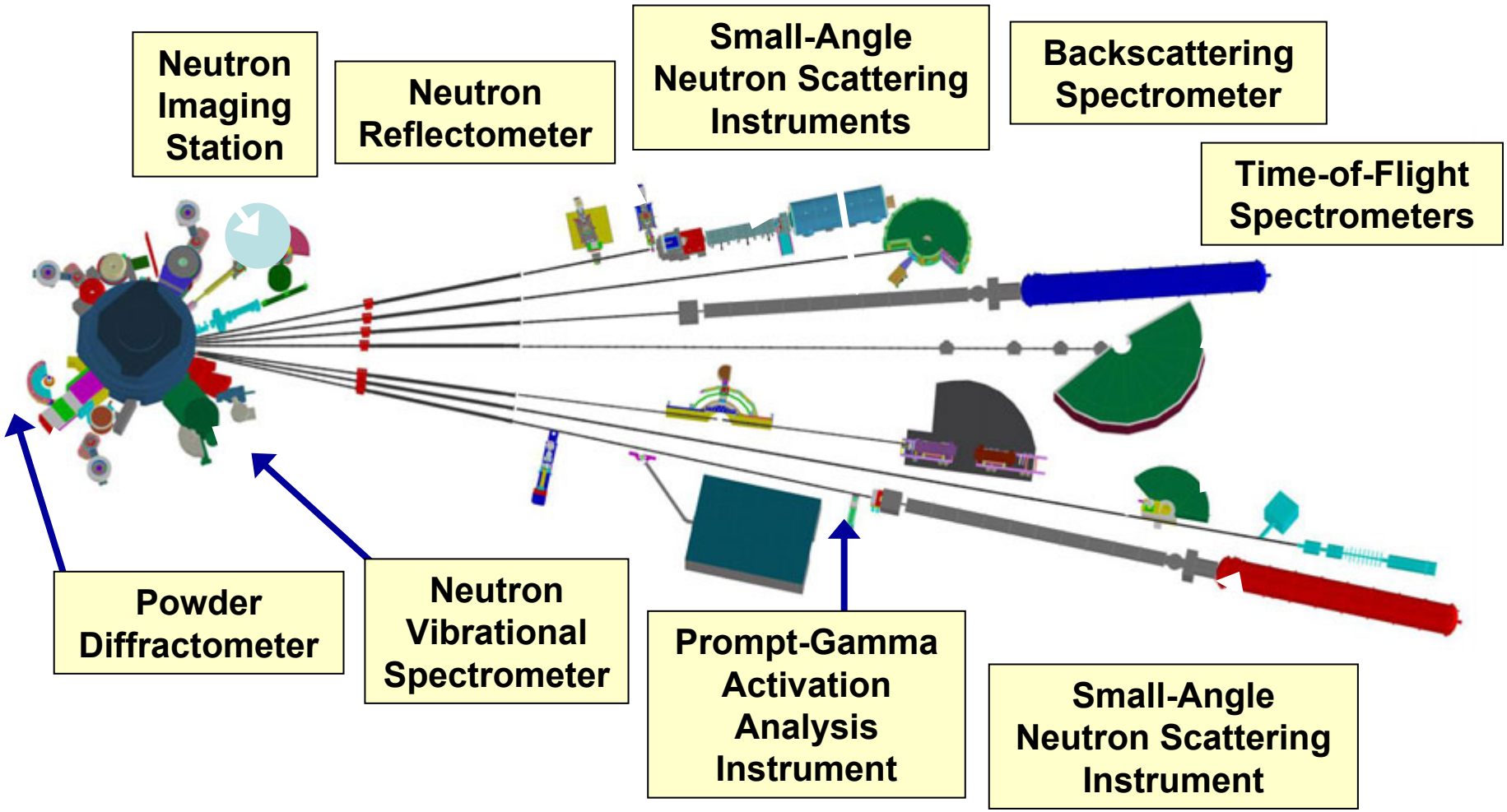
Why Neutrons?

Neutrons are very sensitive to hydrogen!

- Very large H scattering cross-section
- Appropriate wavelength and energy
  => geometry of key motions
- Weak neutron – nucleus interaction
  => penetrating
  => easily modeled



NIST Center for Neutron Research

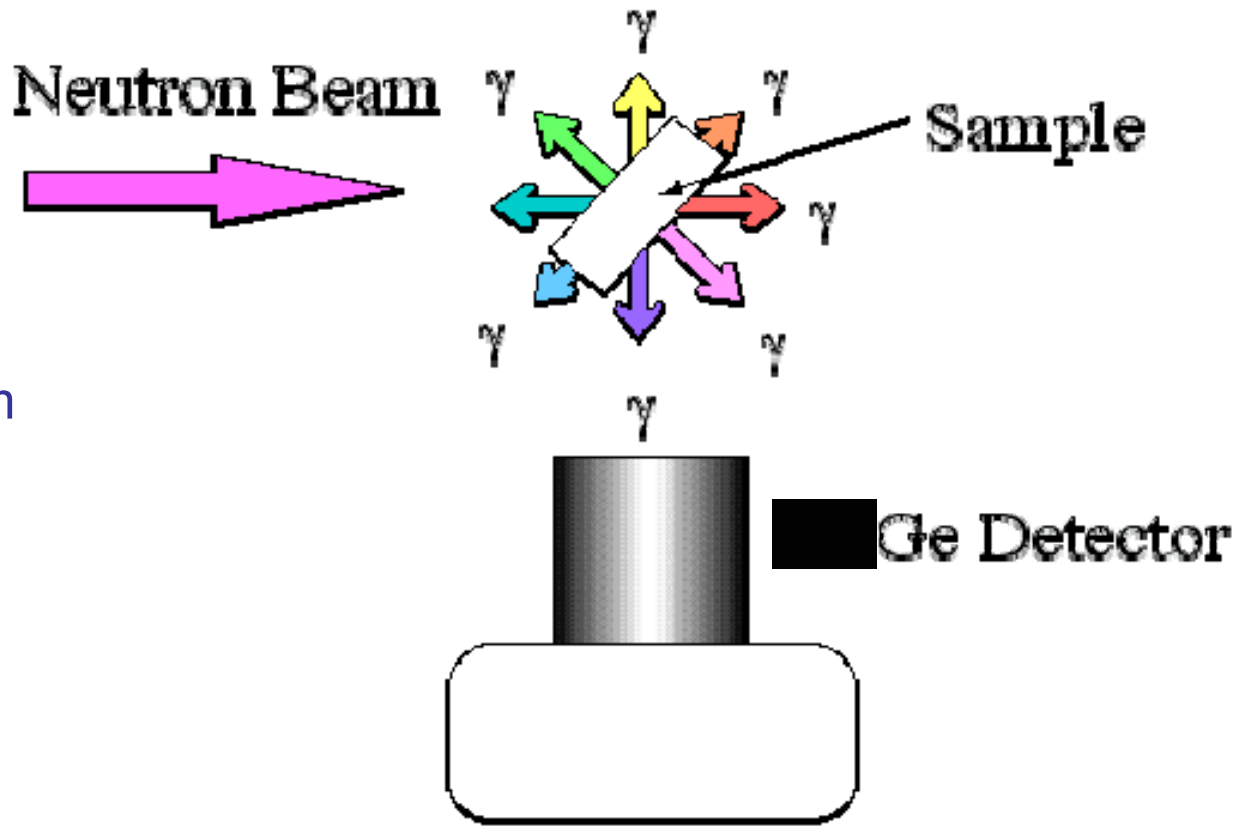


•Neutron Facility Layout

Prompt-γ activation analysis

Elemental Analysis

Information similar to
X-ray fluorescence or
electron microprobe analysis
=> sensitive to H
=> spatial resolution ~0.5 mm



Cold Neutron PGAA

Range in μg	Elements
0.01 - 0.1	**B,** Cd, Sm, Gd
0.1 – 1	Eu, Hg
1 – 10	**H, Cl,** In, Nd
10 – 100	Na, S, K, Sc, **Ti**, V, Cr, Mn, Co, Ni, Cu, Ge, As, Se, Br, Mo, Ag, Te, I, Au
100 – 1000	Mg, Al, Si, P, Ca, Fe, Zn, Ga, Rb, Sr,Y, Zr, Nb, Sb, Ba, La
1000 – 10000	**C**, N, F. Sn, Pb

R.M. Lindstrom & R.L. Paul, J. Radioanal. Nucl. Chem. **243**, 181 (2000).

Critical Assumptions and Issues

Carbon-based

Limited sample quantities hinder rapid neutron spectroscopy assay

MHCoE

Need more financial support to function at peak performance within the center.

Thermodynamics Computations

Quality of enthalpy values of the intermediate compounds is key to the reliability of the results obtained from calculations with the thermodynamic database.

Need input from first principles calculations to obtain enthalpies of intermediate compounds where no experimental data are available or experimental data have large uncertainties.

The Team

CbCoE

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