

IV.A.4g Neutron Scattering Characterization and Thermodynamic Modeling of Advanced Metal Hydrides for Reversible Hydrogen Storage

Terrence J. Udovic (Primary Contact),
Ursula Kattner
National Institute of Standards and Technology (NIST)
100 Bureau Dr., MS 8562
Gaithersburg, MD 20899-8562
Phone: (301) 975-6241; Fax: (301) 921-9847
E-mail: udovic@nist.gov

DOE Technology Development Manager:
Carole Read
Phone: (202) 586-3152; Fax: (202) 586-9811
E-mail: Carole.Read@ee.doe.gov

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Introduction

The Metal Hydride Center of Excellence (MHCoe) has been investigating the possibilities of destabilizing the light-metal alkali and alkaline-earth hydrides by doping with Group IV A elements. Using neutron-based probes, NIST has provided diffraction and spectroscopic characterization of LiH, NaH, and CaH₂ destabilized with Si or Ge. Such information is being used to help understand the effect of doping on the structure and hydrogen bonding associated with these systems, since doping ultimately influences hydride stabilities and hydrogen-cycling properties.

Calculation of phase diagrams (Calphad) thermodynamic modeling provides critical assessments of hydrogen content, character and heats of reaction, and phase-reaction sequences during hydrogen charge-discharge cycling of MHCoe-developed metal-hydride systems. NIST has developed a thermodynamic database, including the elements Li, Mg, B, Si, and H and their respective binary phases, for the Calphad modeling of metal-hydrogen systems. This database has been used to calculate the reactions in ternary hydrogen systems. These results are the basis for the evaluation of the suitability of third element additions for destabilization of the binary hydrides LiH and MgH₂.

Approach

The key to improved hydrogen-storage materials is a detailed understanding of the atomic-scale locations and lattice interactions of the hydrogen. We are applying

our state-of-the-art neutron measurement capabilities and expertise at the NIST Center for Neutron Research (NCNR) to the promising materials being developed by the MHCoe. This work will enable Center partners to obtain unique insights into the atomic- and molecular-scale properties that are responsible for the hydrogen-storage properties of these candidate materials.

In addition, we are performing Calphad thermodynamic modeling. The available literature has been evaluated for thermodynamic data and analytical descriptions of the thermodynamic functions of the relevant phases. The data and functions are compiled into a consistent database describing the multi-component systems. Missing quantities are identified and descriptions are being developed in collaboration with MHCoe partners.

Results

We have focused the majority of our neutron measurements on destabilized light-metal hydrides in order to gain a more fundamental understanding of the role of the destabilizer element. In a collaboration with Jet Propulsion Laboratory, HRL, and Caltech, we were finally able to synthesize a ternary Li_xSi_yH_z+Si two-phase sample (without LiH) by starting with a ballmilled LiH+Si 1:1 mixture, desorbing H₂ at 773 K, reabsorbing H₂ at 723 K, and finally partially desorbing H₂ and annealing at 723 K for an extended period. Also, we synthesized a new Li_xGe_yH_z ternary phase via ball milling/desorption/absorption of a 2LiH+Ge mixture. Neutron powder diffraction (NPD), neutron vibrational spectroscopy (NVS) (Figure 1), and prompt-gamma activation analysis (PGAA) measurements indicate that the new Li_xGe_yH_z phase is similar in structure to the Li_xSi_yH_z phase and suggest that the Li/Ge and Li/Si ratios ≈2 and the H/Li ratios ≈0.2. Although the ternary structure appears to be orthorhombic, the exact structure has still not been solved despite continuing efforts.

We have also synthesized CaSiH_y phases (0<x<1.2) via ball milling/desorption/absorption of CaH₂+Si mixtures. For CaSiD_{1+x}, we have determined the *Pnma* crystal structure by NPD (Figure 2). Both NPD and NVS suggest that the degree of covalency of the Si-H bonding predicted in the x>1 structure by first-principles calculations [1] may be in error, since the 1.82 Å Si-D bond length found is ≈0.24 Å larger than the calculated value.

As an example of characterization of samples from other partners, we have investigated two Na₂SiH_x samples provided by Sandia National Laboratory

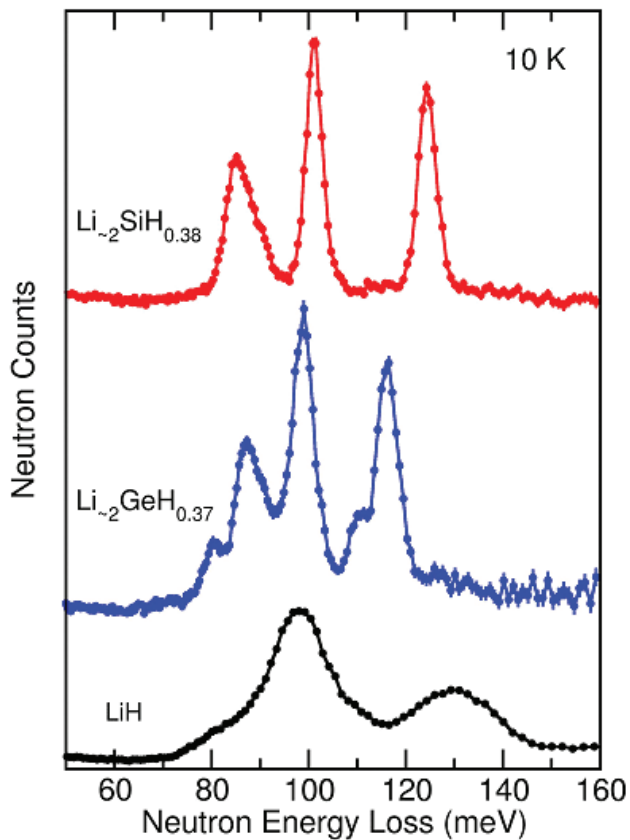


FIGURE 1. NV Spectra for LiH and the New Ternary Hydrides of Li-Si and Li-Ge Alloys

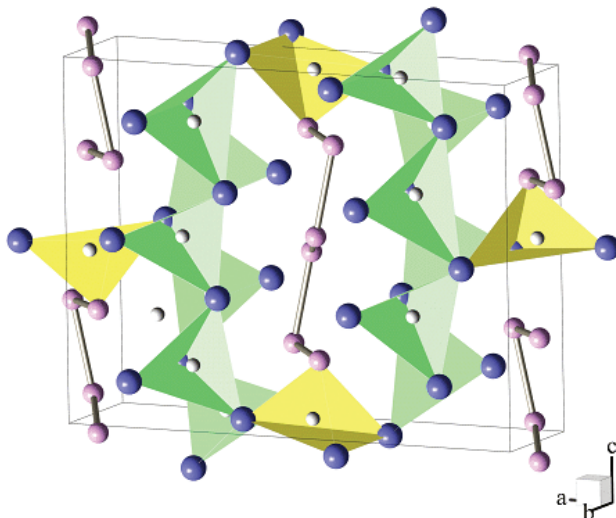


FIGURE 2. *Pnma* crystal structure of $\text{CaSiD}_{1.2}$. Blue, pink, and white spheres represent Ca, Si, and D atoms, respectively. Ca_4 -site tetrahedra are in green, Ca_3Si -site tetrahedra in yellow.

(SNL). SNL saw indications by x-ray diffraction (XRD) that a new hydride phase may have formed. An NVS comparison of these samples with the NaH spectrum (Figure 3) indicate that essentially all absorbed hydrogen

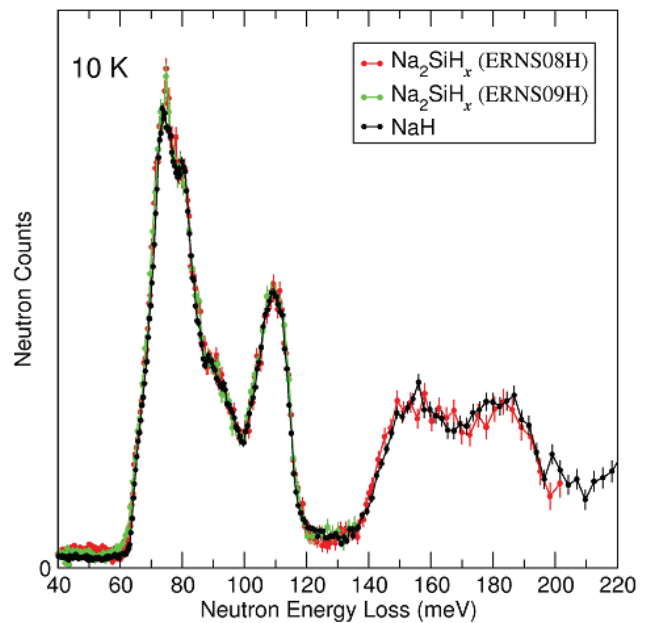


FIGURE 3. Comparison of NV Spectra for NaH and Na_2SiH_x Samples from SNL

in these alloy samples exists as NaH. In addition, PGAA indicates H/Na atomic ratios of 0.94(2) and 0.97(1). We have also synthesized NaSiH_x and Na_2SiH_x via ballmilling/desorption/absorption of NaH + Si mixtures and arrive at similar results.

A thermodynamic Calphad database has been developed and used for calculations of the ternary H-Li-Mg, H-Mg-B and H-Li-Si systems. The results of the calculations show that the addition of a third element reduces the reaction temperature for the hydride decomposition (hydrogen desorption) in all three systems. In the case of the H-Li-Mg system, the hydride destabilization is the result of the formation of a solution phase, while in the cases of the H-Mg-B and H-Li-Si systems, the hydride destabilization is the result of the formation of intermetallic compounds. The temperature reduction in the H-Li-Mg system is insufficient to avoid the formation of a liquid-metal phase. This liquid phase has a significant amount of hydrogen dissolved (Figure 4) thus reducing the available amount of hydrogen even more, making this system unsuitable for hydrogen storage. The addition of B to the Mg-H system reduces the reaction temperatures significantly. However, since the MgH_2 destabilizing phases are Mg-rich (MgB_4 or MgB_7), the amount of available hydrogen is greatly reduced. Although the destabilization of LiH with Si shows the least reduction in hydrogen-storage capacity, the resulting reaction temperature is still fairly high (Figure 5), which makes the feasibility of this system as a hydrogen-storage material questionable. It should be noted that, in this system, liquid metal phase formation is avoided because of the formation of the $\text{Li}_{12}\text{Si}_7$ intermetallic compound.

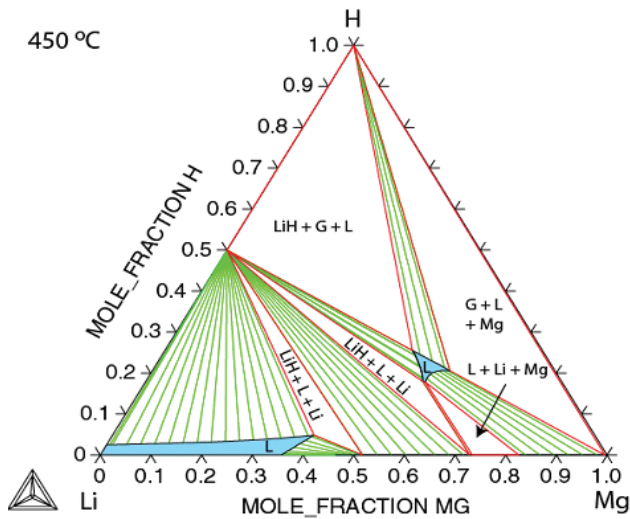


FIGURE 4. Calculated Isothermal Section at 450°C of the H-Li-Mg System

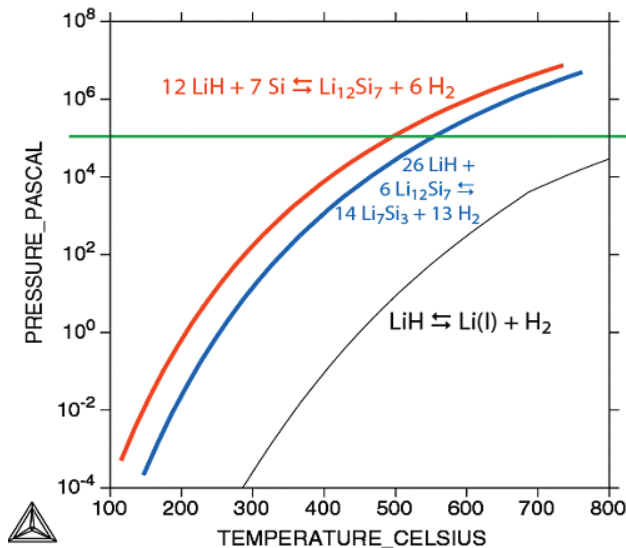


FIGURE 5. Calculated P-T Function of the Hydrogenation Reaction in the H-Li-Si System

Conclusions and Future Directions

1. Neutron metrology (combined with first-principles calculations) has demonstrated its usefulness for characterizing new hydrogen-storage materials investigated by the MHCoe.
2. CaSiH_x results indicate the importance of verifying first-principles results with experiment.
3. The neutron's high sensitivity to H is clearly demonstrated by the NVS results for the Li-Si-H and Li-Ge-H systems (which show clear evidence of a new hydride phase) and for the Na-Si-H system (which does not).

4. We plan to finish neutron characterization of the Ca-Si-H system this year and to begin investigating related ternary (and quaternary) Mg-based systems, if feasible.
5. We plan to characterize structures and H dynamics for BH_4 -related systems, possibly using ^{11}B , in conjunction with MHCoe partners.
6. We will continue to provide neutron metrology to other MHCoe partners on any new hydrogen-storage materials of interest.
7. Calphad calculations are a useful tool for the evaluation of candidate hydrogen-storage materials.
8. The phase equilibria calculations of the H-Li-Mg, H-Mg-B and H-Li-Si show that these ternary systems are not feasible for hydrogen storage.
9. A thermodynamic description of the Li-B system and ternary Li-B-H system will be developed.
10. Thermodynamic descriptions of Ca and its relevant binary systems will be added to the database.

FY 2006 Publications/Presentations

1. 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," MRS Fall 2005 Meeting, Boston, MA (Dec. 2005).
2. M. R. Hartman, "Investigation of Solid-State Hydrogen-Storage Using Neutron Scattering Techniques," North Carolina State University, Nuclear Engineering Dept. Colloquium Series, Raleigh, NC (Jan. 12, 2006).
3. H. Wu, T. J. Udovic, J. J. Rush, "Structure, Phase Variation, and Properties of Hydrogen-Storage Materials in the Ca-Si-H System," The 13th Annual Postdoctoral Poster Presentation, sponsored by the NIST Chapter of Sigma Xi, NIST, Gaithersburg, MD (Feb. 17, 2006).
4. U. R. Kattner, "A Thermodynamic Database for Metal-Hydrogen Systems," TMS 135th Annual Meeting, San Antonio, TX, (Mar. 2006) plenary.
5. 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," MRS Spring 2006 Meeting, San Francisco, CA (Apr. 2006).
6. H. Wu, T. J. Udovic, J. J. Rush, "Hydrogen Storage Properties and Phase Variation Studies in the Destabilized CaH_2 +Si System," MRS Spring 2006 Meeting, San Francisco, CA (Apr. 2006).
7. M. R. Hartman, J. J. Rush, T. J. Udovic, "Investigation of the Dynamics of Hydrogen in Lithium Borohydride using Quasielastic Neutron Scattering," MRS Spring 2006 Meeting, San Francisco, CA (Apr. 2006).
8. 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, (Jul. 2006).

9. 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 (Jul. 2006).

10. 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 (Jul. 2006).

11. H. Wu, W. Zhou, T. J. Udovic, J. J. Rush, T. Yildirim, "Structure and Vibrational Spectra of Calcium Hydride and Deuteride," in the J. Alloys Compd. (in press 2006).

12. H. Wu, W. Zhou, T. J. Udovic, J. J. Rush, T. Yildirim, "Structure and Hydrogen Bonding in CaSiD_{1+x} : Is there Covalent Character?," Phys. Rev. B (submitted 2006).

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1. N. Ohba, M. Aoki, T. Noritake, K.Miwa, S. Towata, Phys. Rev. B **72**, 075104 (2005).