Effect of Trace Elements on Long-Term Cycling/Aging Properties and Thermodynamic Studies of Complex Hydrides for Hydrogen Storage

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This presentation does not contain any proprietary or confidential information
Overview

Timeline
- Project start date – FY05
- Project end date – FY10
- Percent complete – ~96%

Barriers Addressed
- A. System Weight and Volume
- D. Durability/Operability
- E. Charge/Discharge Rates

Budget
- Total project funding (5yrs.) : $ 1,920,352
- DOE share (5yrs.) : $ 1,536,278
- Contractor share (5yrs.) : $ 384,074
- Funding received in FY2007 : $ 520,000 (includes instrument)
- Funding received in FY2008: $ 350,000
- Funding received in FY2009: $ 391,278

MHCoE Partners

Active Current Collaboration
- Sandia National Laboratories, CA – L. Klebanoff and M. Allendorf
- Ohio State University – Dr. J.C. Zhao
- Oak Ridge National Laboratory, Neutron Center, Dr. A. Huq
- University of Geneva, Switzerland, Prof K. Yvon, Dr. R. Cerny, Dr. D. Phanon, Dr. N. Penin
- University of Rome, Prof. R. Cantelli
- University of Paris/CNRS- Dr. M. Latroche and J-C Crivello

Future Collaboration
- NIST Gaithersburg, Maryland - Dr. Terry Udovic
- Brookhaven National Laboratories, NY – Dr. James Reilly
- Oak Ridge National Laboratory- Dr. Gilbert Brown
Relevance

General

- "Grand Challenge" Program: Launched by DOE for R&D of hydrogen storage technologies - designed to meet targets for commercially viable vehicular systems.
- Metal Hydrides Center of Excellence (MHCoE): Three Centers of Excellence exist; we work on on-board hydrogen storage technical barriers.
- Study Topics at Uni. of Nevada, Reno (UNR): (1) System weight and volume, (2) Durability/operability, and (3) Charging and discharging Rates and part of life cycle assessment addressing the environmental impact for hydrogen storage (excluding costs).

Impact of Impurities on Long-term Durability and Understanding Reaction Pathways of the Complex Hydrides

1. Objectives:

- Effect of ppm and higher level impurities in H₂ gas.
- Li-N-H light weight based compounds used to evaluate long-term durability.
- To develop new materials with enhanced hydriding properties, by modifying or controlling reaction pathways.
- To develop longer cycle life complex hydrides, with lower hydrogen release temperatures and improved kinetics.

2. Relevance to Addressing On-board Hydrogen Storage Specific Technical barriers:

- Durability: Addressed these issues by using industrial hydrogen as well as various individual impurity gas mixtures in hydrogen gas.
- Charging /Discharging: Reaction pathways found.
- Life cycle assessments: Addressed environmental impact of hydrogen storage via impurity gas effect; example N₂, O₂, H₂O, CO, CO₂, NH₃ and other gases.
A. Basis for Selection of Li-N-H system Was To Address the barrier on System weight:

- Light-weight Li-N-H system has ~10.5 wt.%H-capacity and long cycle life: During loading of pure hydrogen in Li3N, 5 compounds form, depending on the conditions. In fully loaded condition the major phase is LiNH2 (8.78 wt.%H) along with residual LiH (~12 wt.%H) phase which adds up to ~10.5 wt.%H.

- This study is expected to have Broader Impact on hydride research: Research is expected to give insight to other hydrides (mixtures of amides-alanates, amide-magnesium hydrides and others). In addition, mixing H2 with N2 changes the thermodynamic paths leading to significant changes in cycle ability.

B. Durability/Operability and Life cycle environmental effects

- Trace Impurity Impact on Long-term Durability: In practical applications, trace impurities in commercial hydrogen gas (such as dispensed at future H2 gas stations) will have an impact on the hydrogen loading capacities during periodic recharging with fresh hydrogen.

- Approach: To determine the effects of gaseous trace impurities (ppm levels of O2, CO, H2O, CH4, NH3, N2 in H2gas) on complex hydrides after prolonged hydrogen pressure cycling and thermal aging. Note: NH3 is not a common impurity in H2 gas itself, but there is an potential of ppm level emission at higher temperatures, so we checked its environmental effect (last period’s work).

- Update: Effects of using Nitrogen gas as an impurity in hydrogen gas to enhance the reversible hydrogen capacity have shown promise, and are presented here.

- Objectives: Specifically, the emphasis of this year’s study was to evaluate the following (Best Results:*80/20):
  1. Long-term effects of four Nitrogen Mixtures with Hydrogen and compare with H2 alone:
     (1) H2-No Nitrogen (2) H2-100 ppm Nitrogen (3) *80/20 molar H2/N2 (4) 50/50 molar H2/N2 (5) 25/75 molar H2/N2
  2. New Phase Evolution – Li1.5NH1.5
  3. Modeling – Li1.5NH1.5 and Li4NH

C. Addressing Charging/Discharging Rates and Applied Thermodynamic Studies

- Difficulties in Interpreting Our Earlier Neutron and X-ray diffraction Data: These difficulties implied understanding of the phase equilibria of the system. So, CALPHAD thermodynamic modeling calculations were performed.

- Pressure-Composition Isotherms: Thermodynamic and Structural analyses performed to obtain phase stability information, and formation of new phases. Agreements between experimental and thermodynamic results found.
Li-N-H System (Gas Impurity effects)
- Completed cycling tests on Li-N-H system to determine the effect of various gaseous impurities in H₂ (100 ppm level of O₂, CO, H₂O, CH₄, NH₃) to simulate the charge/discharge with fresh H₂ in Li-N-H hydrides.
- The effect of NH₃ gas impurity – isothermal (255°C) and isobaric aging at 6.2 bar H₂ performed using 100 ppm NH₃ in H₂ revealed no loss in hydrogen capacity.

Applied Thermodynamics and Crystallographic Studies
- Critical phase reaction pathways determined using progressive incremental loading of hydrogen in Li₃N, supported by the CALPHAD developed Li-N-H Phase diagrams:

<table>
<thead>
<tr>
<th>Phase Fields Obtained from equilibrium Li-N-H Ternary Phase Diagrams (From 2009 Presentation Slide 10)</th>
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<tbody>
<tr>
<td>225°C</td>
</tr>
<tr>
<td>Li₃N(s) + H₂(g) → Li₃N(s) + Li₂NH(s) + Li(l) →</td>
</tr>
<tr>
<td>9 atm.</td>
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<tr>
<td>25°C</td>
</tr>
<tr>
<td>Li₃N(s) + H₂(g) → Li₃N(s) + Li₂NH(s) + Li₄NH(s) →</td>
</tr>
<tr>
<td>9 atm.</td>
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</table>

- Li₄NH phase at room temperature; stable up to ~5 wt.%H and peritectically decomposes at 25°C.
- The amount of LiH phase formed under equilibrium loading of hydrogen was determined.
- New higher hydrogen capacity (5.8 wt.%H) cubic phase of Li₂₋ₓNH₁₊ₓ (x=1/2) type was found.
- X-ray diffraction pattern was also obtained of this solid solution intermediate phase.
- Improved kinetics were observed at higher pressures in the Li-N-H system.
Summary of This Year’s Accomplishments

**Li-N-H System (New results on Gas Impurity effects)**

- **Significant Result** → Nitrogen gas compensation during cycling improved H-capacity. (Earlier studies revealed significant loss of N\textsubscript{2} from the solids during cycling)

- **Hydrogen Absorption Capacity** → Varied depending on the amount of N\textsubscript{2} mixed with H\textsubscript{2}; in particular H\textsubscript{2}/N\textsubscript{2} = 80/20 molar ratio yields ~10 wt.%H absorption.

- **ppm Level N\textsubscript{2} Added Improves H-Capacity** → Even 100ppm N\textsubscript{2} in H\textsubscript{2} significantly improved the hydrogen absorption as a function of number of cycles (~8 wt.%H); much more than with just H\textsubscript{2}.

- **Terminal Phase During Desorption 80/20 H\textsubscript{2}/H\textsubscript{2}** → Significant increase in Li\textsubscript{2}NH phase and decrease in the LiH phase (as compared to pure H\textsubscript{2} loading).

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**Applied Thermodynamics and Crystallographic Studies**

- **New Phase Detected Experimentally**: An intermediate phase Li\textsubscript{1.5}NH\textsubscript{1.5} (F-43m), a= 05.027 Å, and vol.=127.04 Å\textsuperscript{3}. determined.

  General formula = Li\textsubscript{2-x}NH\textsubscript{1+x} @ x=1/2 at H-5.8 wt.%; forms between imide (x=0) and amide (x=1) phases.

  Modeling performed on this compound

  Other investigators have reported another cubic phase, but details or compositions were not reported (W. David et al.).

- **In-situ synchrotron x-ray diffraction Studies**: To elucidate phase equilibria details, work in progress.

- **Modeling Results**: Band structure, density of states, Electron Localized function determined of the Li\textsubscript{1.5}NH\textsubscript{1.5} phase and compared with others.

  Published in *Phys Rev B* in 2010 (IEA collaboration)

- **CALPHAD Modeling of Li-N-H System**: Critical phase reaction pathways determined with *progressive incremental loading of hydrogen* in Li\textsubscript{3}N.
Technical Accomplishments and Progress -1

- Isotherm (Abs.) obtained from Li₃N-H at 255°C (at Uni. of Geneva)
- The low pressure isotherm (inset) was obtained at UNR, Reno, showing compositions of different Phases formation; for example, LiNH₂ forms at 1.3 bar H. This plot is included to furnish background information.

Summary of Isotherm @ 255°C
- Li₃N-H solid solubility
- Progressive formation Li₂NH, Li₂₋ₓNH₁₊ₓ, and then LiNH₂ along with LiH.
- Note: Li₄NH does not form at 255°C and precipitates at room temperature.
- Note: Desorption from ~10.5 wt.% H stops at ~5.8 wt.% H.
Phase Evolution Summary of the Li-N-H system

**Li$_3$N**
- **Li$_3$N (ss)**
- **Li$_4$NH**
  - **Li$_4$NH** (Li Coordinated Compound) not a complex hydride
- **LiNH$_4$** Composition: 2.46 wt.%H

**General Formula for Complex Hydrides**
- **Li$_{2-x}$NH$_{1+x}$**

**1st Complex Hydride**
- **Li$_{2-x}$NH$_{1+x}$** @x=0 = **Li$_2$NH**
  - N-H Disordered Bonds
  - Structure: Slide 16
  - 3.48 wt.%H

**2nd Complex Hydride**
- **Li$_{1.5}$NH$_{1.5}$** @x=1/2
  - *SS= Solid Solution compound
  - x=1/2
  - N-H+N-H$_2$ Intermediate Compound
  - Ordering at x=1/2
  - Structure Slide 17
  - 3.48 to ~5.8 wt.% H

**3rd Complex Hydride**
- **LiNH$_2$** @x=1
  - N-H$_2$ Ordered Bonds
  - Structure: Slide 16
  - 8.78 wt.%H

Li$_3$N $\rightarrow$ Li$_3$N (ss) $\rightarrow$ Li$_4$NH $\rightarrow$ Li$_2$NH $\rightarrow$ Li$_{1.5}$NH$_{1.5}$ $\rightarrow$ LiNH$_2$
- **LiH**
  - **SS** $\rightarrow$ 5.8 wt.%H
Comparison of PCI curves obtained under hydrogen and H₂/N₂ - 80/20 at 255°C

- Equilibrium pressure (up to ~4 wt.% H) is increased using N₂/H₂ mixtures as compared to pure H₂ (in Red).
- Cycling results show good absorption properties (Please see Slide 11).

Sample Vial
Homogeneous White Powder with N₂/H₂ mixtures—No Slag—mass: 33 mg after the experiment.

PCT with H₂/N₂ (80/20):
- 1st test: ΔP = 0.2 bar
- 2nd test: ΔP = 0.4 bar

<table>
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<th>wt.% LiNH₂</th>
<th>wt.% Li₂NH</th>
<th>wt.% Li₂xNH₁₋ₓ</th>
<th>wt.% Li₃N</th>
<th>wt.% Li₂O</th>
<th>wt.% LiH</th>
<th>wt.% Li₄NH</th>
<th>a Li₂ₓNH₁₋ₓ (Å)</th>
<th>Occ. Li</th>
<th>Occ. H</th>
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<td>1 Fm-3m</td>
<td>0</td>
<td>5.5</td>
<td>27.5</td>
<td>0</td>
<td>5.0458</td>
<td>1.14</td>
<td>1.86</td>
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T=255°C
1. Partial loading of H to observe the phases formed showed that at ~8.2 wt.%H, 2 phases LiNH₂ Li₁.₅NH₁.₅ and LiH formed (isotherm intentionally terminated).

2. Fully loaded (isotherm –right) the Li₁.₅NH₁.₅ virtually disappears and increases the amount of Li₂NH.
Increased H-capacity with higher N₂ Content by using 80/20 H₂/N₂ Mixtures During Pressure cycling

- **80/20 molar H₂/N₂ shows High H-capacity:** The 345 and 516 cycles show as good a capacity of ~10 wt.% as the starting isotherm 0-cycle, which is remarkable.

- **Possible reason for Decrease in H-capacity after 850 cycles:** XRD pattern (left) shows increased oxide formation; O₂ might have been accidentally introduced in the system during transferring the sample holder after the 516th cycle (from the cycling machine to the Sieverts apparatus). This 850 cycles experiment needs to be repeated.

- **Replenishing the lost N₂ from Li-N-H compounds:** Prior results showed loss of nitrogen possibly due to evacuation /loading cycles.
Effect Mixing trace amount of Nitrogen (100ppm) in H₂ on the Cycle ability of Li₃N-H

- **Isotherm 0 (H₂):** Starting material-Li₃N isotherm is designated zero cycle.
- **Isotherm 1 (H₂):** This starts at Li₁.₅NH₁.₅ + LiH and ends at LiNH₂.
  - **Isotherm 506 (H₂):** This yields 4.2 wt.%H, with increased amount of LiH.
  - **Isotherm 345 (100 ppm N₂-H₂):** Shows 6.2 wt.% H, better than 1 cycle (5.8 wt.%H) or 506 cycles (4.2 wt.%H) with only H₂.
  - **Isotherm 853 (100 ppm N₂-H₂):** Increased H capacity (8.2 wt.%) as compared to the 345 cycle capacity of ~7.3 wt.%H.
  - **Isotherm 1359 (100 ppm N₂-H₂):** Shows slight lowering (7 wt.%H) of capacity even with nitrogen.

**Conclusions**

- Mixing 100 ppm level of N₂ with H₂ shows much higher ultimate H-capacity as compared to even 1 cycled material with H₂ alone. All isotherms taken at 255°C.
- There is more Li₂NH formed in the mixed 100ppm-H₂ materials based on XRD measurements.
- The decrease after 1359 cycles is due to the formation Li₂O perhaps impurities in N₂ gas.
Comparison of Desorption Isotherms Obtained after Cycling H₂-100 ppm N₂

Summary:

- **Significant Increases in H-Capacity During Desorption:** H- capacity much greater than 1 cycle material (H₂) and increases from 345 to 853 Pr.-cycles with H₂-100ppm N₂.

- **Accumulation of Li₂NH phase During Desorption cycles:** XRD results obtained after 1359 absorption/desorption cycles shows significantly more Li₂NH phase and less LiH phase as compared to cycling with H₂ alone. We believe that the Li₂O phase formation is due to trace O₂ impurity in N₂ gas added.
High partial pressure of N\textsubscript{2} in H\textsubscript{2} gas there is an abrupt change in pressure at H\textsubscript{2} conc. @ ~1.38 wt.%H in isotherm (right) taken with 25/75 H\textsubscript{2}/N\textsubscript{2} molar or H\textsubscript{2}/N\textsubscript{2}= 0.02/0.98 wt. fraction.

- **CALPHAD** modeling of Li-N-H model phase diagram (left) shows a change in phase field in the Li-N-H diagram:
  - Li\textsubscript{3}N + Li\textsubscript{2}NH + gas (blue region) → Li\textsubscript{2}NH + gas (white area) using 25/75 H\textsubscript{2}/N\textsubscript{2} gas (see enlarged area –right).
  - Li\textsubscript{2}NH phase does not change >1.38 wt.%H, but there is more gas resulting abrupt increase in pressure.
  - Ideally there should no LiH, but there is ~2 wt% LiH present in the final sample; due to the initial formation near the Li\textsubscript{3}N-LiH-Li\textsubscript{2}NH phase field in the ternary diagram.
The Effect of Intrinsic Thermal (Temperature) Cycling on the H-capacity with starting material as LiNH₂ in H₂/N₂ 50/50 Molar Between 23°C and 255°C

- Increased H-capacity: Temp. cycling (top) shows a decrease in gas pressure (blue points) and clearly shows increased H-capacity, during cycling.
- 25 of 55 – 2 hours cycles shown (top-middle).
- The H-capacity increased from a ~4.0 wt% to ~4.5 wt%H after 55 thermal cycles (isotherm-Blue circles).
- H-capacity: Expected to increase with further cycling.
- Isotherm (left-with pure H₂ in red triangles) taken after 1 cycle is included for comparison.
- Large amount Li₂NH phase with H₂/N₂ cycling and some Li₂O phase (XRD)

Conclusion:
- Even high N₂ in H₂ (50/50) tends to increase H-capacity during cycling; but yields less than H₂/N₂ 80/20 (see slide 11)
Summary of the Density of states of Li$_4$NH, Li$_2$NH and LiNH$_2$ showing Different Interactions

**Summary:**
- Modeling data of known Li$_2$NH and LiNH$_2$ compared reasonably well with other investigators.
- Results of Li$_4$NH Published (*Phys. Rev. B*- ref.1)
- Note that Li$_4$NH is not a complex hydride, but Li Hydride –Nitride with Li-N and Li-H interactions.


Density of States showing both N-H and N-H₂ interactions in Li_{1.5}NH_{1.5}

Structure and proposed models for Li_{1.5}NH_{1.5}

Calculated electronic localization function (ELF) for Li₄NH, Li₂NH, Li_{1.5}NH₁₁.₅ and LiNH₂

Li_{1.5}NH₁₁.₅ DOS and Structure results from our modeling work (ref.1) show *N-H* and *N-H₂* interactions and ordering. Prior work of W.I.F David et. al. *J. Am. Chem. Soc*, 129, 1594 (2007) is cited.

Ab initio calculations - Li$_4$NH Electronic Structure (Semiconductor)

- Li$_4$NH is a Li coordinated Compound (semiconductor with Band Gap ~ 2eV)
- Li$_4$NH not a complex hydride
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<th>Institution</th>
<th>Collaboration</th>
<th>Primary Contact</th>
<th>Extent</th>
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<tr>
<td>University of Genéve</td>
<td>IEA Collaboration</td>
<td>Prof. K. Yvon</td>
<td>PI’s sabbatical leave research, Type of Institution: University</td>
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<td>Uni. of Paris/CNRS</td>
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<td>Dr. M. Latroche</td>
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<td>University of Rome</td>
<td>IEA/IPHE Collaboration</td>
<td>Prof. R. Cantelli</td>
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<td>on characterization of Defect structure DOE H₂ program.</td>
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<td>Heat capacity measurements</td>
<td>Dr. Jason Lashley</td>
<td>Type of Institution: US National Laboratory Extent: Low temperature</td>
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<td>Dr. L. Klebanoff, M. Allendorf</td>
<td>Primary Contacts: Dr. L. Klebanoff , and M. Allendorf Type of</td>
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<td>coordination on complex hydrides</td>
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Proposed Future Work

1. **Effect of Impurities on Complex Hydrides and Defect Structure analyses**
   - We plan to continue defect structure studies on Li$_3$N by introducing transition metals in Li$_3$N by two different methods. These defect structures are expected to reduce the Hydriding temperature.

2. **In-Situ High Resolution X-ray Diffraction Studies on Hydriding/Dehydriding**
   - In-situ X-ray (UNR/ESRF/LBNL) will continue to obtain newly developed hydride samples from MHCoE partners to understand the reaction pathways towards development of improved hydrides for vehicular applications.

3. **Collaboration with the MHCoE Theory Groups**
   - We plan to interact with computational modeling researchers in the MHCoE group to correlate experimental results towards understanding of the structure and the dynamics of hydriding and dehydriding.

4. **International collaboration with Universities and other European Union (EU) Partners**
   - We will continue IEA collaboration with Uni. of Geneva, Paris/CNRS, and Rome. We have started collaboration with the EU team on developing catalyst for the Li based hydride systems.

5. **Correlation of all data and preparation of Manuscripts - Post- DOE annual review 2010 Conference.**
   - We will finalize Journal publications after detailed analyses.
**Summary – 1**

- **Long-term stability of light weight complex hydrides for vehicular applications:** Determine critical aspects related to durability/operability of complex hydrides.

- **Role of ppm gaseous impurities in hydrogen gas:** Studies simulate periodic H₂-filling at a commercial hydrogen gas station for future H₂-vehicles.

- **Practical Issues:** Envision premixed 80/20 H₂/N₂ gas will be used to load the hydride bed and majority of hydrogen will be absorbed by the Li-N compounds.

  Residual N₂ gas over-pressure is expected in the hydride tank; as lost N₂ from the Li-N-H compounds is replenished (as observed experimentally during cycling).

- **H-Capacity Increase During Pr. Cycling:** Typically H-capacity deceases with hydrogen gas (alone), but we observed increased H-capacity with mixed 80/20 H₂/N₂ (molar) yielding ~10 wt.%H.

- **Trace amount of N₂ also increases the cycling capacity:** Mixing 100ppm N₂ in H₂ also significantly improves the hydrogen absorption, although 80/20 H₂/N₂ gave the best results.

- **Increase in Li₂NH Phase and Suppression of LiH Phase During 80/20 H₂/N₂ Pr. Cycling:** Significant increase in the amount of Li₂NH phase in the system after cycling.
**Summary – 2**

**Applied Thermodynamics and Crystallographic Studies**

- **New intermediate Li$_{1.5}$NH$_{1.5}$ identified**: Li$_{2-x}$NH$_{1+x}$ at x=1/2 has a terminal composition of 5.8 wt.%H; phase forms between imide (x=0) and amide (x=1).

  This cubic phase (F-43m) lattice parameter’s are $a = 5.027 \, \text{Å}$ and vol. $127.04 \, \text{Å}^3$. Calculated values are $5.111 \, \text{Å}$. Other investigators have reported another cubic phase, but details or compositions were not reported.

- **Phase equilibria Studies Using In-situ synchrotron X-ray diffractions**: Majority of work done – finalizing manuscript details.

- **Modeling**: Band structure, density of states, ELF’s of the new Li$_{1.5}$NH$_{1.5}$ are compared with other Li-N-H phases; reported in publication Phys Rev B in 2010 (IEA collaboration).

- **CALPAHD Modeling**: Critical phase reaction pathways determined using progressive incremental loading of hydrogen in Li$_3$N.
Acknowledgements

We are very grateful to the US DOE-MHCoE for the support of this Project.

We thank Dr. Gary Sandrock for his valuable comments on NH$_3$ issues in amide-amide system.

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We also thank Dr. Micheal Latroche and Dr. J-C Crivello of CNRS, Paris, and also Prof. Michelle Gupta of Uni. of Paris-Sud for her help in support of the MHCoE work.

Also thank Dr. A. Huq of ORNL for her collaboration on neutron diffraction studies.