Helium Distribution in Erbium Tritide Films

Rex P. Hjelm
hjelm@lanl.gov

Lujan Neutron Scattering Center
Los Alamos National Laboratory

Sandia Metal Hydride Workshop
Albuquerque, New Mexico
2 October 2005
Collaborators

James Browning
Sandia National Laboratories

Gillian Bond
New Mexico Institute of Mining and Technology
Defects Structure

Domain-structured & filled polymers

Instrumentation, methods & analysis

Colloid interactions

Surfactant self-assembly

Helium bubbles

Molecular motors

Polymer dynamic response
Objective

Show morphology and distribution of hydrogen bubbles formed in Erbium hydride films and how this may determine the distribution of $^3$He, using neutron small-angle scattering measurements and transmission electron microscopy.
The neutron generator:
A small-linear deuterium ion accelerator with a deuterium/tritium target utilizing the d+T and d+d fusion reactions to generate neutrons.

Erbium hydride formation and the release of $^3\text{He}$:
The decay of tritium to helium-three and the subsequent release of helium. We want to understand the factors governing helium release.

The small-angle scattering experiment:
Neutrons provide good light element contrast. The small-angle geometry provides a probe for structure between 1 and 100 nm.

A remarkable result:
Hydride formation introduces plate-like defects along preferred directions and distances to form a long length scale quasi-lattice. These may serve as retention sites for helium.

The effect may be observed in other metal hydrides:
Similar, reversible effects may have been observed in palladium hydrides.
Applications of Erbium Tritide films in Neutron Generators

• A neutron generator is a small electrostatic accelerator incorporating an ion source, ion optics and a target in a compact vacuum envelope.

• Deuterium ions (D+) derived from a plasma source are accelerated in electric fields to impact tritium atoms (T) in a target to yield neutrons through nuclear reactions,
  \[ d + T \rightarrow \alpha + n + 17.6\text{MeV} \]
  \[ d + d \rightarrow ^3\text{He} + n + 3.3\text{MeV} \]

  to provide 14 or 2.5MeV neutrons, respectively.

• They are used in,
  – Bore hole logging
  – Medical research
  – Defense systems
  – Contraband detection systems

• There are strict requirements of the defined operational characteristics and life.
Target films are ErD_xT_y

- Erbium hydride, as is the case with all rare earth hydrides, possesses the ability to accommodate hydrogen concentrations up to three times the atomic concentration of erbium.
- The dihydride phase assumes the CaF_2 structure with hydrogen atoms occupying tetrahedral sites.
- Because tritium is radioactive (τ_{1/2} = 12.3 yr), these binary hydride systems transform into ternary systems with time.
- ^3He is generated at a rate given by the time rate of decay of tritium and may be expressed as:
  \[ G(t) = N_0(1 - e^{-\lambda t}) \]
- It is well known that much of the ^3He generated does not readily diffuse from the film, but remains trapped within the polycrystalline material.
- Trapping mechanism is not understood.
A fundamental understanding of helium release is required to predict the expected life of neutron generator.

- He is eventually released into the vacuum envelope.
- Significant variation in point of release.
Program Objective

- Provide a fundamental understanding of the behavior of $^3\text{He}$ in erbium dihydride systems.
  - In order to optimize target film characteristics such that we minimize $^3\text{He}$ release from the film, i.e., maximize $^3\text{He}$ retention.

- Determine how process parameters influence this behavior.
  - Materials properties are driven by structure, which in turn can be influenced by process parameters.
Three known hydride phases in Erbium

\( \alpha \):
- a solid solution phase of hydrogen in the hcp Erbium lattice.
- \( H/Er < 0.5 \).

\( \beta \):
- a distinct chemical entity, \( \text{ErH}_2 \).
- Forms an fcc (\( \text{CaF}_2 \)) lattice with hydrogen at the tetrahedral sites.
- 7% volume increase hcp->fcc.
- \( H/Er \approx 1.8 \) to 2.2.
- Coexists with the \( \alpha \) and \( \gamma \) phases

\( \gamma \):
- \( H/Er \approx 2.9 \) to 3.0
Erbium film and hydride formation

- **Erbium film:**
  - Electron beam physical vapor deposition at 450°C 1 nm/sec.
  - A 100nm Mo layer deposited on silicon substrate {100}.
  - A 500nm Er layer deposited onto the Mo layer.

- **Hydride formation:**
  - β-phase:
    - ErT$_2$ (Savannah River Technology Site).
    - ErD$_2$ (Los Alamos National Laboratory).
  - tritium pressure of approximately 200Torr.
  - temperature of 475°C.
Summary

- Neutron generator technology plays a key role in a wide range of applications including national defense and security.
- Understanding the physical mechanism of neutron tube target aging is critical to our mission.
- The application of various neutron scattering techniques provides not only a unique way of investigating $^3$He behavior in materials, but provides critical data necessary in the development of a fundamental understanding of such systems.
Fundamentals of the Small-angle Scattering Technique

- A schematic of a typical small-angle scattering instrument:
- An x-ray or neutron source is collimated into a beam with defined direction, typically using two pinholes.
- The beam is scattering from the sample and the scattering is detected as scattering intensity as a function of scattering angle, $2\theta$, on a two dimensional detector.
- Scattering due to fluctuations in scattering length density.
- Scattering intensity measured as a function of momentum transfer, $Q$.
- Inverse relationship between $Q$ and real space length scales probed.
- Small-angle (low-$Q$) scattering probes large length scales.
- Scattered intensity, Fourier transform squared of structure, $\rho(r)$. 

\[ Q = \frac{4\pi}{\lambda} \sin \theta \]

\[ A(Q) = \int \rho(r) \exp(-iQ.r) \, dv \quad \frac{d\Sigma(Q)}{d\Omega} = |A(Q)|^2 \]
SAS as a Structural Probe

- **X-ray and neutron SAS:**
  - structures on length scales of 1-100 nm.
  - Bulk properties.
  - Three-dimensional structures.
  - Particulate and continuous phase morphology.

- Neutrons:
  - Useful to study bulk samples because they penetrate matter easily.
  - Sensitive to light elements, such as hydrogen, carbon and nitrogen.
  - Sensitive to isotopes, such as hydrogen and deuterium.

- **X-rays:**
  - Electron scattering—sensitive to atomic number.
  - High fluxes.
Neutron scattering: Light Element and Isotope Contrast

Hydrogen Isotope Scattering Lengths (b) in (fm):

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Scattering Length (b) in (fm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1H$</td>
<td>-3.7409 (11)</td>
</tr>
<tr>
<td>$^2D$</td>
<td>6.674 (6)</td>
</tr>
<tr>
<td>$^3T$</td>
<td>4.792 (27)</td>
</tr>
</tbody>
</table>

Scattering Length Density: $\rho = \sum b_i/V$

- Good light element contrast and isotopic labeling.
- Light and heavy elements have similar scattering lengths.
- Good sample penetrability and no radiation damage.
- Wavelengths comparable with atomic and molecular length scales.
- Energies comparable with atomic vibrations and molecular dynamic energies.
- Atomic form factor constant in $Q$. 

Los Alamos National Laboratory

Rex Hjelm
Scattering Length for X-rays

- X-ray scattering lengths monotonic with $Z \propto \rho$.
- Large difference in scattering length between light and heavy elements.
- X-ray scattering lengths large.
- X-ray form factors a function of $Q$. 
LQD: a state of the art TOF-SANS

<table>
<thead>
<tr>
<th>LQD Specifications</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength Range</td>
<td>2 - 15 Å</td>
</tr>
<tr>
<td>Angular Range</td>
<td>4 - 60 mrad</td>
</tr>
<tr>
<td>Q-range</td>
<td>0.0023 - 0.5 Å⁻¹</td>
</tr>
<tr>
<td>Typical Sample Size</td>
<td>10 x 13 mm</td>
</tr>
<tr>
<td>Detector</td>
<td>Two dimensional proportional counter</td>
</tr>
<tr>
<td>Moderator</td>
<td>Partially-coupled liquid H₂ at 20 K.</td>
</tr>
<tr>
<td>Sample Environments</td>
<td>Air, vacuum, closed cycle temperature control, pressure to 3 KB, shear cell</td>
</tr>
<tr>
<td>Typical Measurement Times</td>
<td>2 min - 6 hours</td>
</tr>
</tbody>
</table>

- **Brightest pulsed spallation cold moderator.**
- **Advanced background suppression.**
- **Advanced optics and count rate control.**

LQD Specifications:
- Brightest pulsed spallation cold moderator.
- Advanced background suppression.
- Advanced optics and count rate control.

In the diagram:
- Incident beam monitor
- Frame overlap chopper
- T-zero chopper
- Collimation tube
- Sample position
- Removable spools
- Alignment mirror
- Beamstop
- Detector
- Scattering tube
- Optical bench
- Dynamic collimation aperture
- Collimation aperture
- Gamma shield & attenuator
- Chopper monitor
- Guard and variable collimator apertures
In situ structure and aging with small-angle neutron scattering

- **Small-angle neutron scattering:**
  - Sample chamber sealed with Conflat™ flanges containing fused silica neutron windows.
  - 18-27 samples mounted in transmission geometry along the beam by the silicon support.
  - Silica and silicon are nearly transparent to neutron beam.
  - Neutrons are non-destructive.

- **Samples:**
  - ErT$_2$ (β-phase): evolution of structure as $T \rightarrow 3\text{He} + \beta^- + \nu$, forming ErHe$_x$T$_y$.
  - ErD$_2$ to check for loading effects.
  - Er and Si baseline studies.

- **In situ structural and aging studies:**
  - Evolution of structure determined from 3 months to 2-1/2 years by measuring samples measured *in situ*.
  - Angular studies for three-dimensional imaging.
Erbium Hydride Structure—a surprise!

- No diffraction from Si <100>—above the Bragg limit for \( \lambda \).
- A few diffraction spots in Erbium films.
- Cruciform Patterns Observed in all Erbium Hydride Samples:
  - Arms at 90º.
  - Sometimes a ropy appearance.
  - Sometimes distinct diffraction spots.
- Very low \( Q \) values—implies large repeats ~10’s nm.
- Oriented structure.
Hydriding process introduces a large scale quasi-lattice into the film

- Scattering Intensity
  - Product of four terms:
    \[ I(Q) = N\Delta\rho^2V^2P(Q)S(Q) \]
  - \( N \): number of objects.
  - \( \Delta\rho = \rho_A - \rho_B \): scattering length density contrast.
  - \( V \): object volume.
  - \( P(Q) \): object form factor.
  - \( S(Q) \): object structure factor.

Given the properties of the Fourier transform we must be looking at families of stacked planes at 90° viewed edge on.
Strong Selection for planes viewed perpendicularly

- Ewald sphere change size (wavelength).
- Orientation.
- See different families of planes

\[ \frac{2\pi}{\lambda} \]
With the evolution of $^3\text{He}$ the diffraction becomes stronger

- Same sample three months and 2.5 years after hydridization.
- Three months:
  - Ropy appearance.
  - Broad, poorly resolved diffraction peaks.
  - Peaks close to equal intensity.
- 2.5 years:
A long scale quasi-lattice

d-spacings (Å)

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 mos</td>
<td>2.5 yr</td>
<td>3 mos</td>
<td>2.5 yr</td>
<td>3 mos</td>
<td>2.5 yr</td>
</tr>
<tr>
<td>490</td>
<td>210</td>
<td>280</td>
<td>280</td>
<td>260</td>
<td></td>
</tr>
<tr>
<td>160</td>
<td>150</td>
<td>140</td>
<td>140</td>
<td>190</td>
<td>180</td>
</tr>
<tr>
<td>120</td>
<td>120</td>
<td>110</td>
<td>110</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>90</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>70</td>
<td>80</td>
<td>80</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>60</td>
<td>50</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

- **Lattice spacings:**
  - Large ~100 Å.
  - Vary with different batches.
  - No obvious d-preference.
  - Ambiguous as to intra and/or inter sample variability.

- **Changes with time:**
  - Observed only in ErT$_2$.
  - Diffraction peaks more distinct as $^3$He accumulates.

- **Indications:**
  - Defects introduced by hydridization.
  - $^3$He may accumulate in defects.
Bubble content: 10 GPa plausible, but no proof.

- Calculation is subject to uncertainties.
- Based on observations from other systems, Bubble pressure ≈ 10 GPa.
- Assume no isotope effect.
- Difficult to determine bubble content.
TEM: Transverse film sections show bubbles on the \{111\} planes

a) Bright-field transmission electron micrograph
b) Selected-area diffraction pattern close to <110> zone axis

- Two sets of plate-like helium bubbles are visible, at an angle of \(~72^\circ\)
- Helium bubbles appear to lie on \{111\} planes

TEM Samples:
- Wafer with films cleaved into strips
- Strips mounted in sandwich configuration
- Cross-section cut, ground and polished
- Sample dimpled until film thickness \(~10\ \mu m\)
- Ion milled at \(~3.5 - 4^\circ\) and 5kV until perforation
- Examined in JEOL JEM-2000FX TEM at 200 kV
• These results came as a surprise.
• Issues:
  – What is determining the preferred orientation?
  – Why are there preferred long range spacings into a quasi-lattice?
  – Why is there four-fold symmetry in the diffraction pattern?
• Supporting data (TEM and XRD) suggest “platelet” like structure populating the (111) planes in similar samples.
• Possible explanation: Defects are controlled by stress field introduced by Si substrate.
  – Si (100) surface.
  – Si cut along (011).
  – Large Mo modulus—could transmit stress between Si and ErH$_2$ lattice.
Conclusions

• **SANS**
  – provides contrast not available by other means.
  – Neutron penetrability allows studies of samples *in situ*.
  – Provides a non-destructive probe.

• **Hydride formation:**
  – introduces plate-like defects along preferred directions and distances to form a long length scale quasi-lattice.
  – These may serve as retention sites for helium.