Helium Distribution in Erbium Tritide Films

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Collaborators

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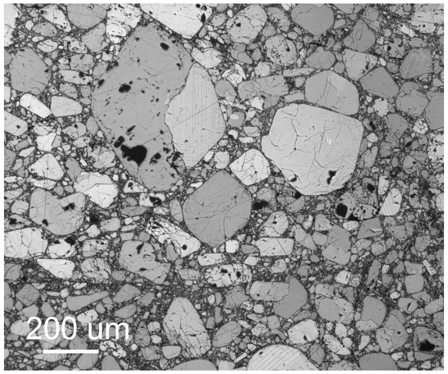
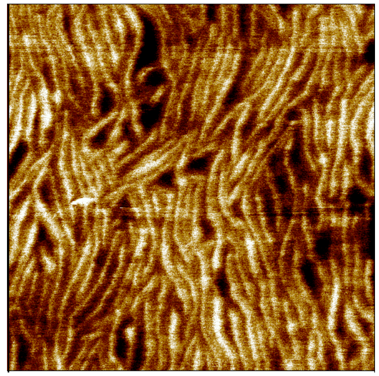
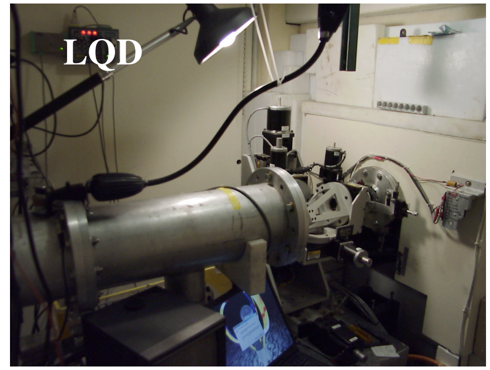
Long Length Scales Program



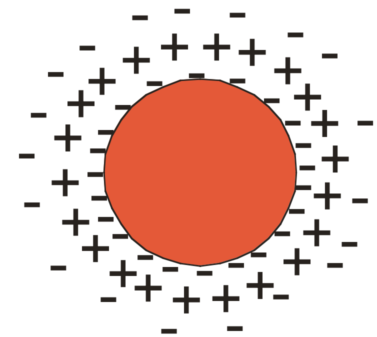
Defects Structure



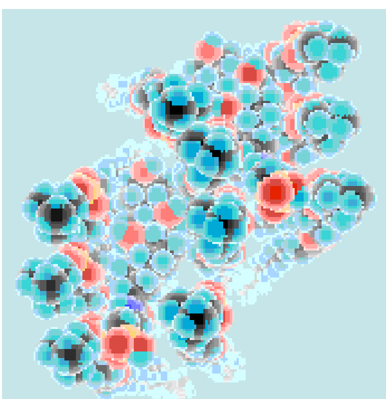
Domain-structured & filled polymers



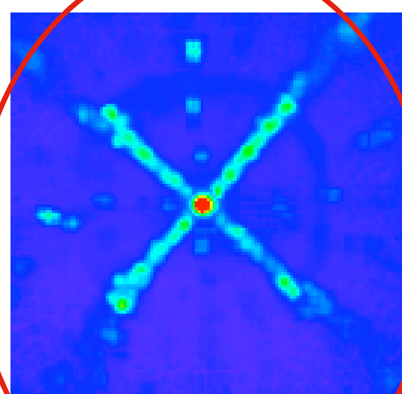
Instrumentation, methods & analysis



Colloid interactions

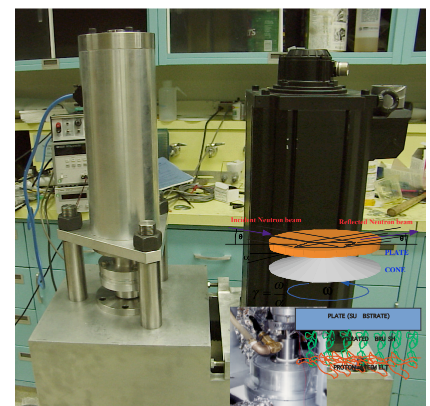


Surfactant self-assembly



Helium bubbles

Molecular motors



Polymer dynamic response

Objective

Show morphology and distribution of hydrogen bubbles formed in Erbuim hydride films and how this may determine the distribution of ^3He, using neutron small-angle scattering measurements and transmission electron microscopy.

Topics

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}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,**

$$d + T \rightarrow \alpha + n + 17.6\,\mathrm{MeV}$$

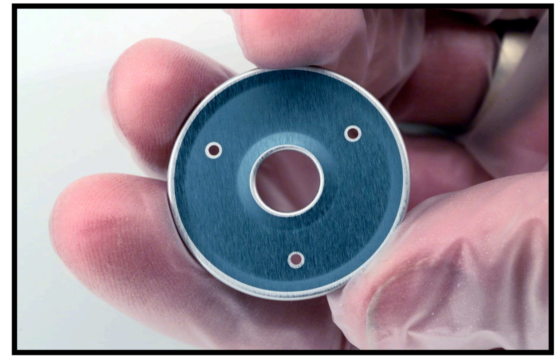
$$d + d \rightarrow {}^{3}He + n + 3.3\,\mathrm{MeV}$$

to provide 14 or 2.5MeV neutrons, respectively.

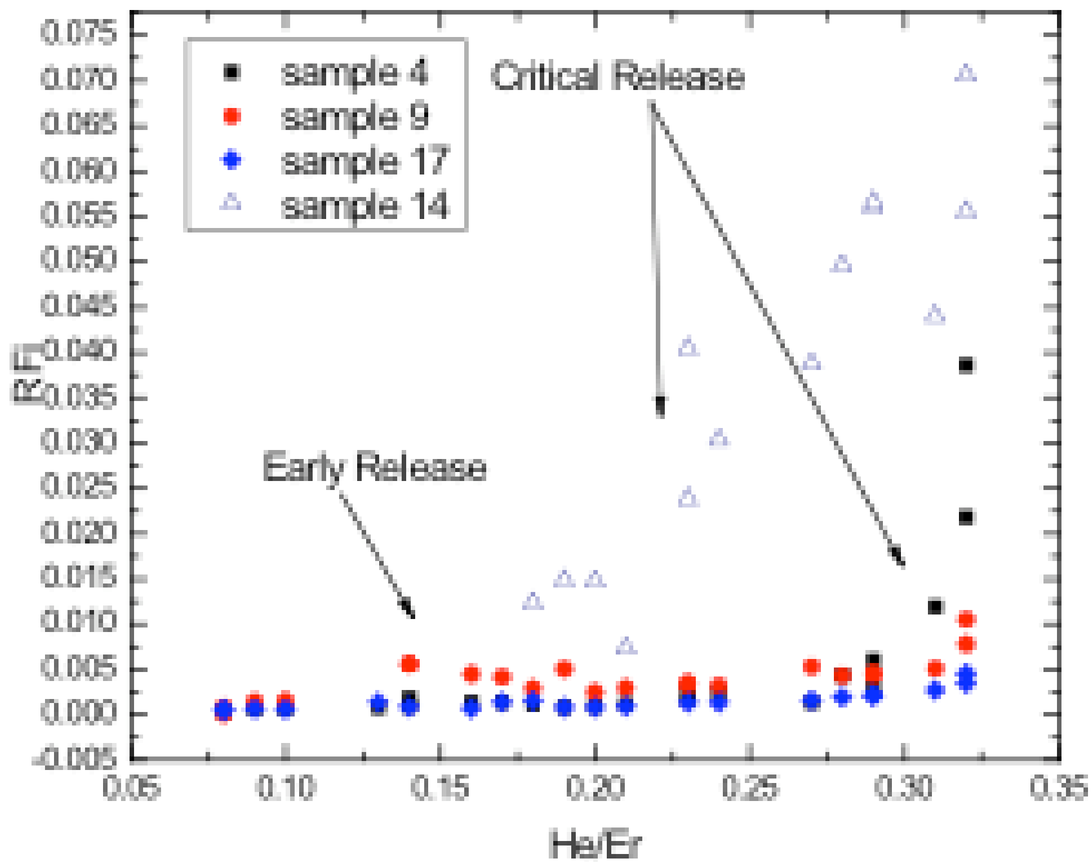
- **They are used in,**
  - Bore hole logging
  - Medical research
  - Defense systems
  - Contraband detection systems
- **There are strict requirements of the defined operational characteristics and life.**

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 ($\tau_{1/2}$ = 12.3 yr), these binary hydride systems transform into ternary systems with time.
- ^{3}He is generated at a rate given by the time rate of decay of tritium and may be expressed as
  - $G(t) = N_O(1 - e^{-\lambda t})$
- It is well known that much of the ^{3}He 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.

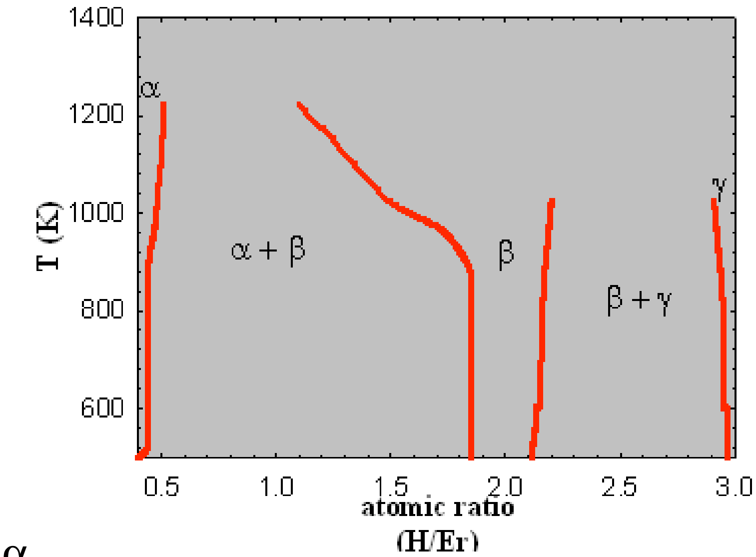


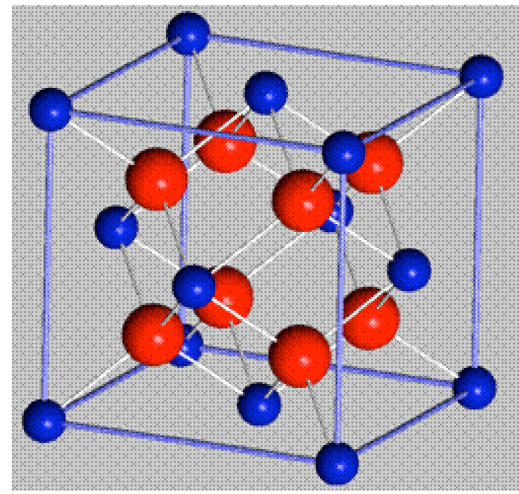
- He is eventually released into the vacuum envelope.
- Significant variation in point of release.

Program Objective

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



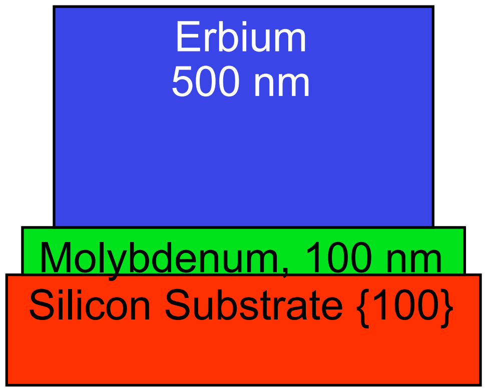


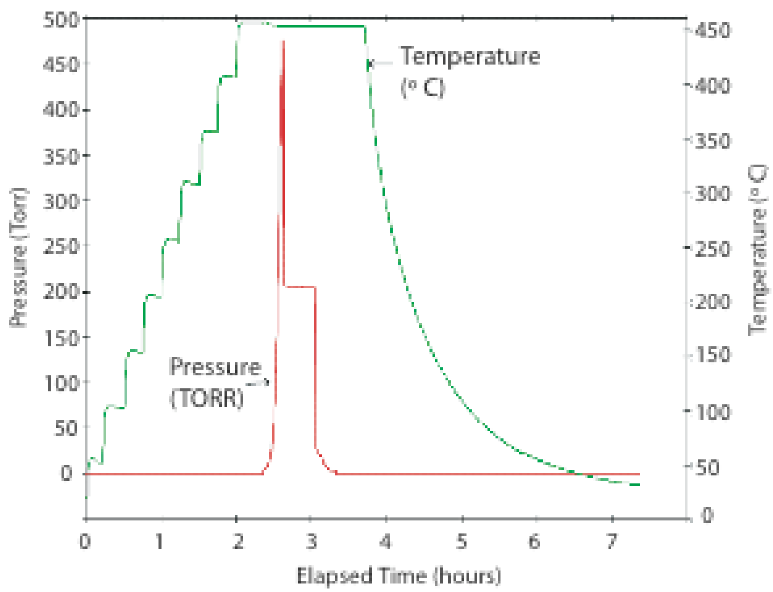
? α.
  - a solid solution phase of hydrogen in the hcp Erbium lattice.
  - H/Er < 0.5.

? β:
  - a distinct chemical entity, ErH_2.
  - Forms an fcc (CaF_2) lattice with hydrogen at the tetrahedral sites.
  - 7% volume increase hcp->fcc.
  - H/Er ≈ 1.8 to 2.2.
  - Coexists with the α and γ phases

? γ: H/Er ≈ 2.9 to 3.0

Erbium film and hydride formation



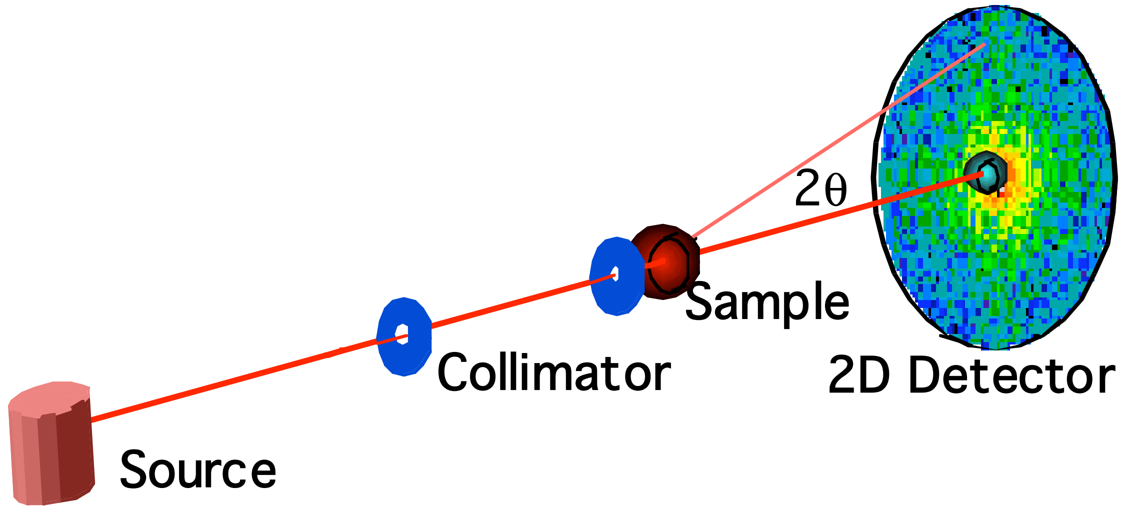


- **Erbium film:**
  - Electron beam physical vapor deposition at 450^{o}C 1 nm/sec.
  - A 100nm Mo layer deposited on silicon substrate {100}.
  - A 500nm Er layer deposited onto the Mo layer.
- **Hydride formation:**
  - ? β-phase:
    - ErT_2 (Savannah River Technology Site).
    - ErD_2 (Los Alamos National Laboratory).
  - tritium pressure of approximately 200Torr.
  - temperature of 475^{o}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.**

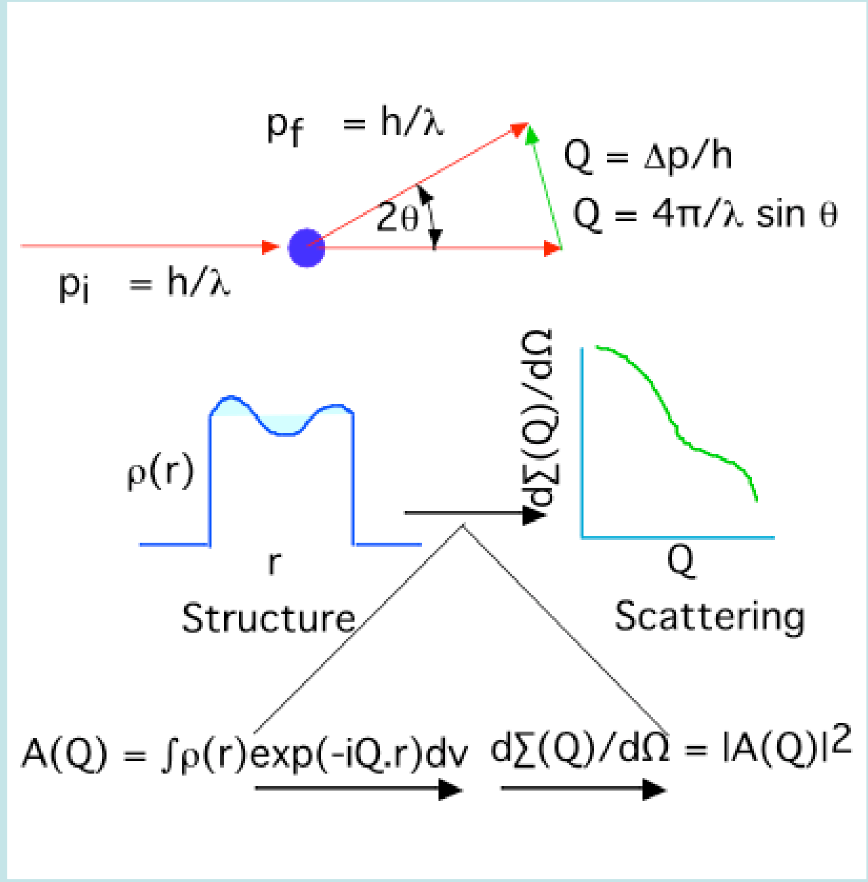
Fundamentals of the Small-angle Scattering Technique



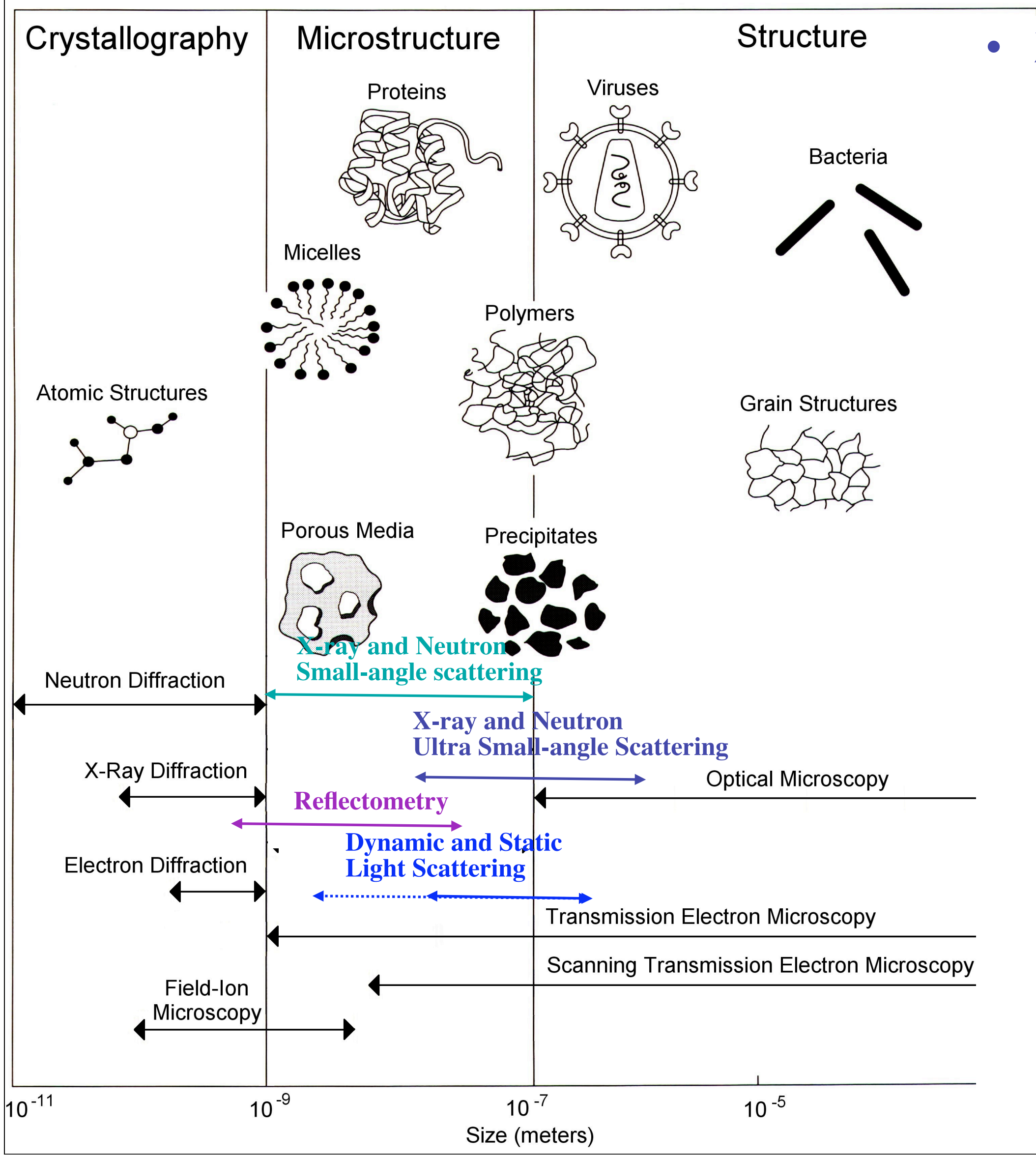
- A schematic of a typical small-angle scattering instrument:
- An x-ray or neutron source is collimated into a beam with defined direction, typically using two pinholes.
- The beam is scattering from the sample and the scattering is detected as scattering intensity as a function of scattering angle, 2θ, on a two dimensional detector.

Small-angle Scattering Probes Large Scale Structure

- 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, ρ(r).

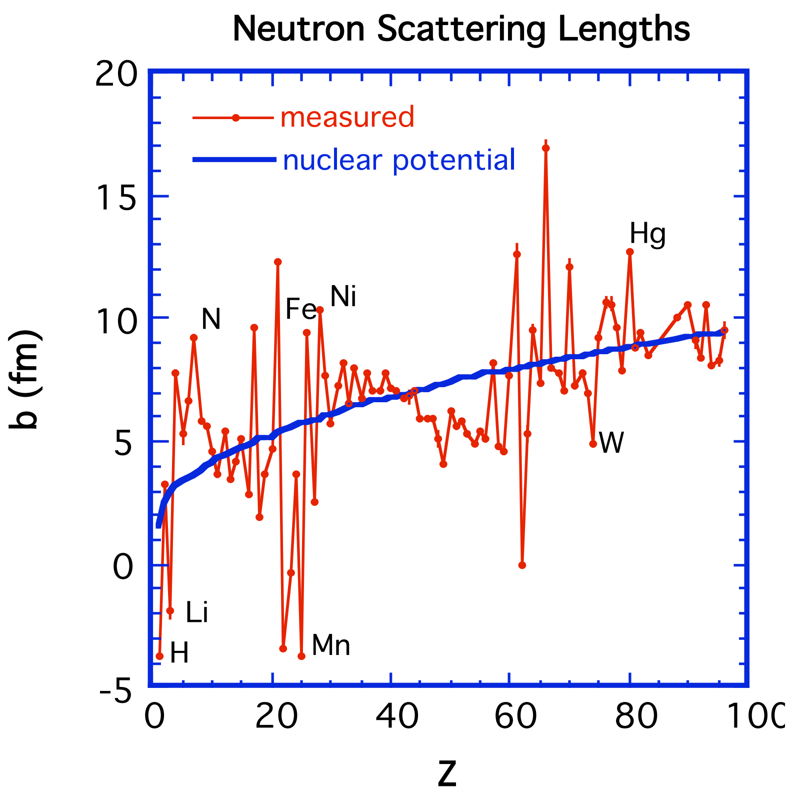


SAS as a Structural Probe



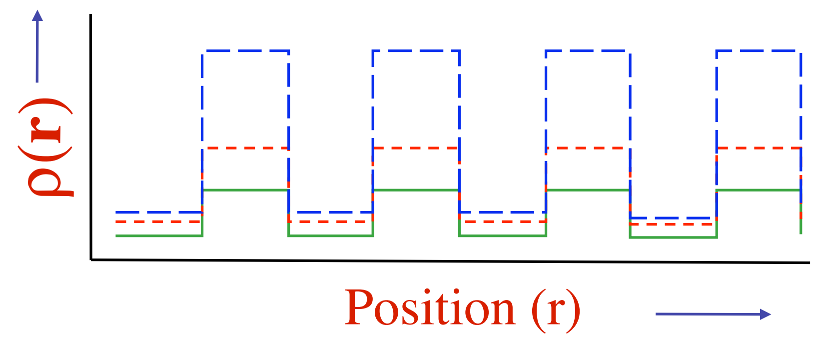
- **X-ray and neutron SAS:**
  - structures on length scales of 1-100 nm.
  - Bulk properties.
  - Three-dimensional structures.
  - Particulate and continuous phase morphology.
  - Neutrons:
    - Useful to study bulk samples because they penetrate matter easily.
    - Sensitive to light elements, such 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



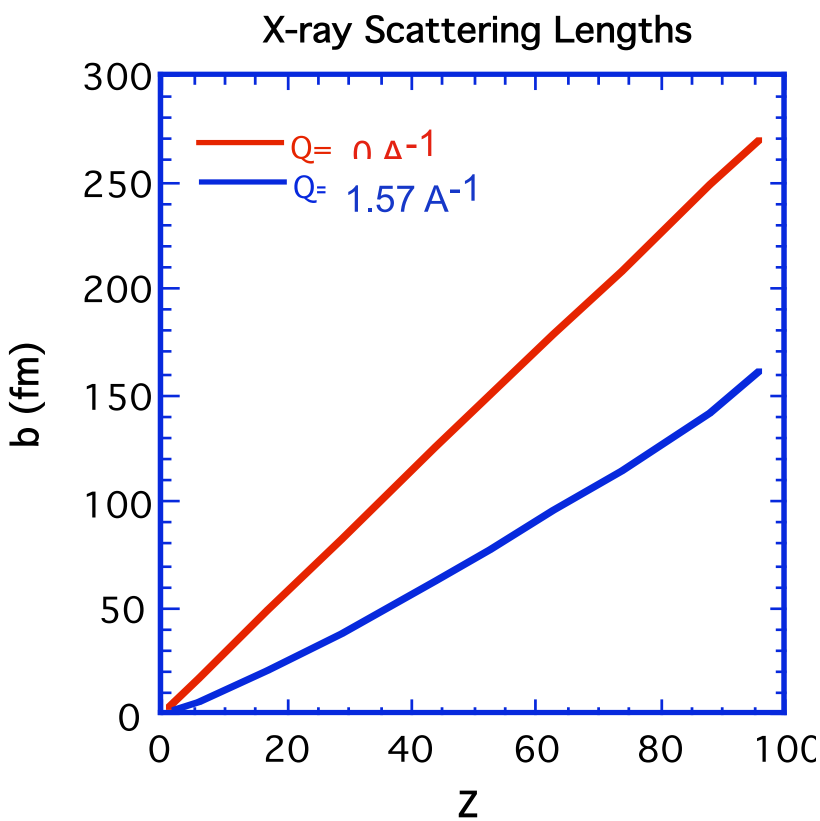
Hydrogen Isotope	Scattering Length (b) in (fm)
^{1}H	-3.7409 (11)
^{2}D	6.674 (6)
^{3}T	4.792 (27)

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



- **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*.**

Scattering Length for X-rays

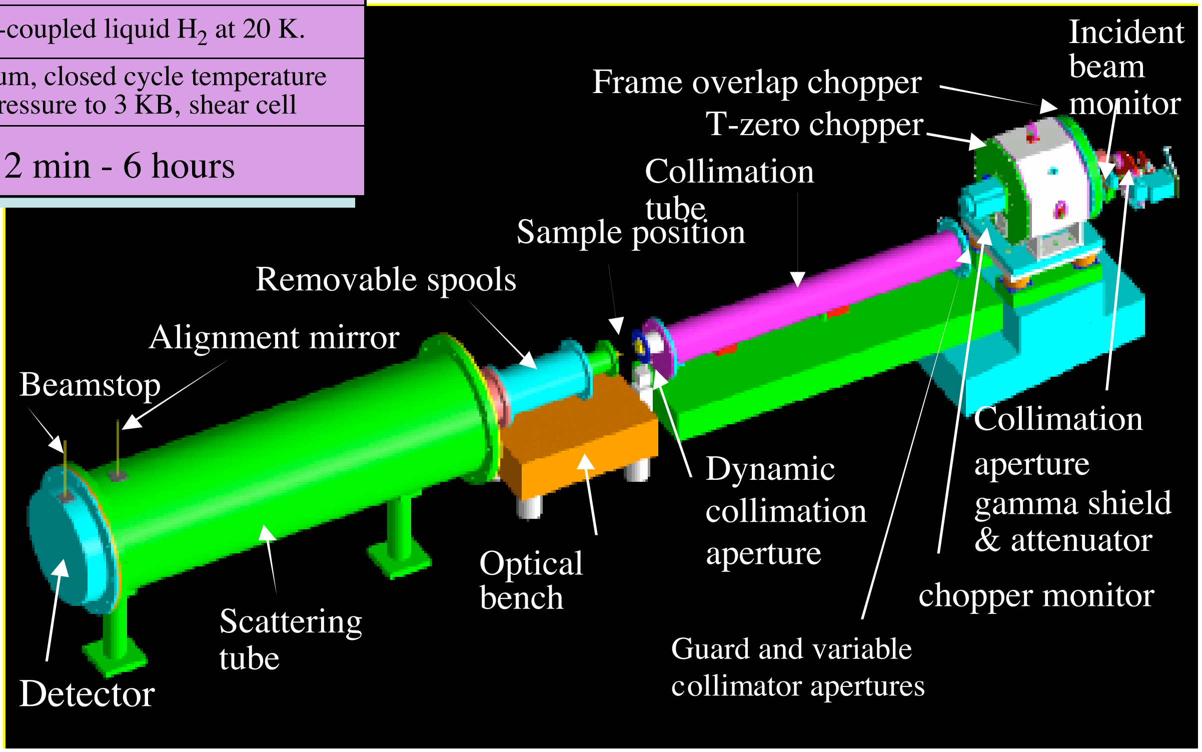


- X-ray scattering lengths monotonic with Z $\propto \rho$.
- Large difference in scattering length between light and heavy elements.
- X-ray scattering lengths large.
- X-ray form factors a function of Q.

LQD: a state of the art TOF-SANS

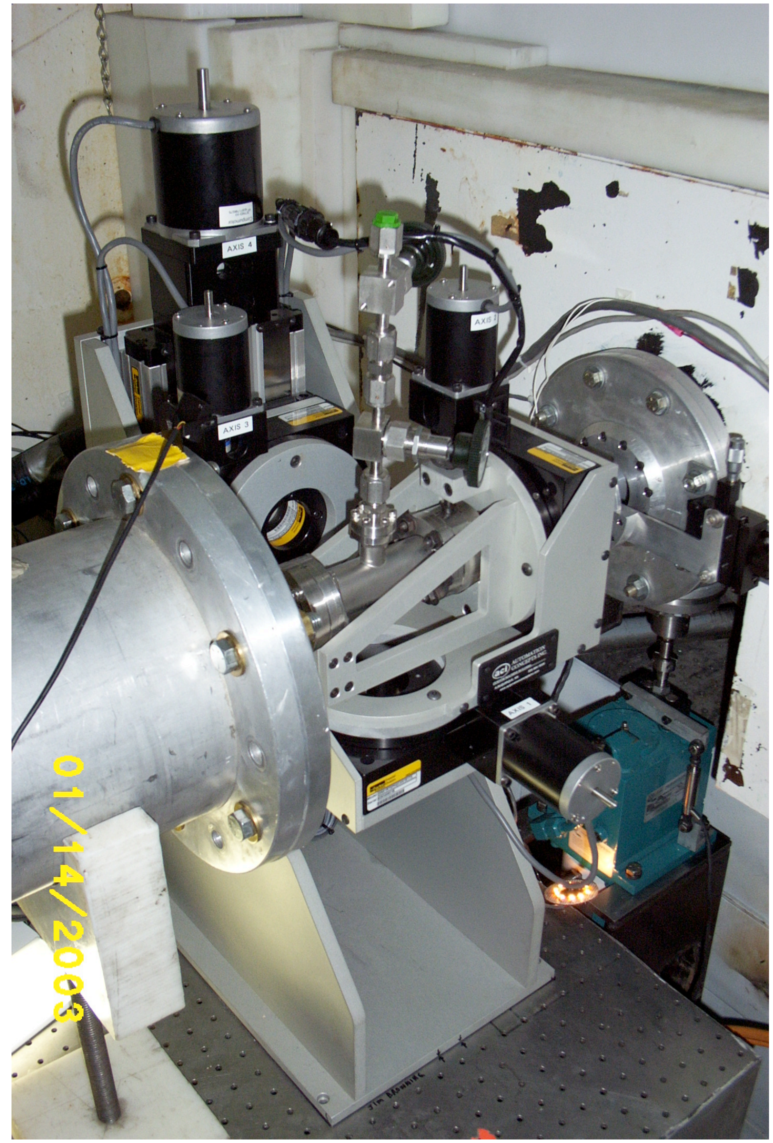
LQD Specifications	
Wavelength Range	2 - 15 Å
Angular Range	4 - 60 mrad
Q-range	0.0023 - 0.5 $Å^{-1}$
Typical Sample Size	10 x 13 mm
Detector	Two dimensional proportional counter
Moderator	Partially-coupled liquid H_2 at 20 K.
Sample Environments	Air, vacuum, closed cycle temperature control, pressure to 3 KB, shear cell
Typical Measurement Times	2 min - 6 hours

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



In situ structure and aging with small-angle neutron scattering

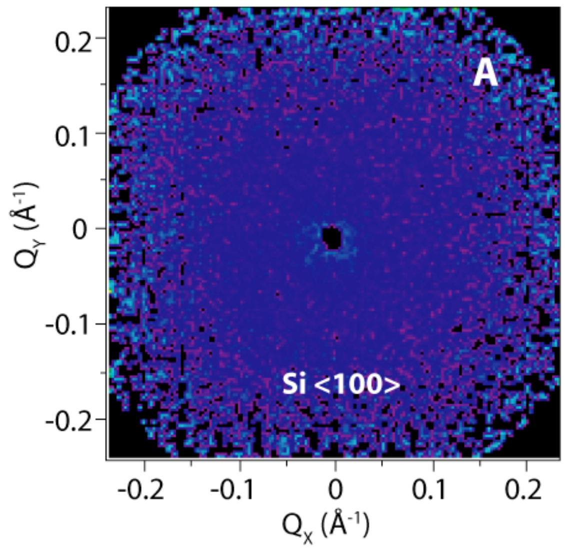
- **Small-angle neutron scattering:**
  - Sample chamber sealed with Conflat™ flanges containing fused silica neutron windows.
  - 18-27 samples mounted in transmission geometry along the beam by the silicon support.
  - Silica and silicon are nearly transparent to neutron beam.
  - Neutrons are non-destructive.
- **Samples:**
  - ErT_2 (β-phase): evolution of structure as $T \rightarrow {}^3He + \beta^- + \nu$, forming $ErHe_xT_y$.
  - 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 λ.
- A few diffraction

s



Hydriding process introduces a large scale quasi-lattice into the film

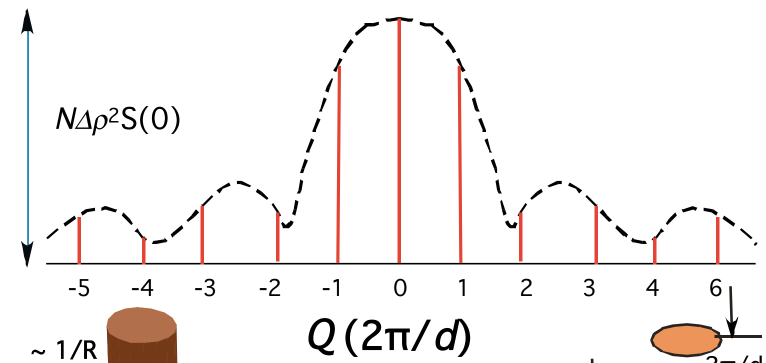
- **Scattering Intensity – Product of four terms:**

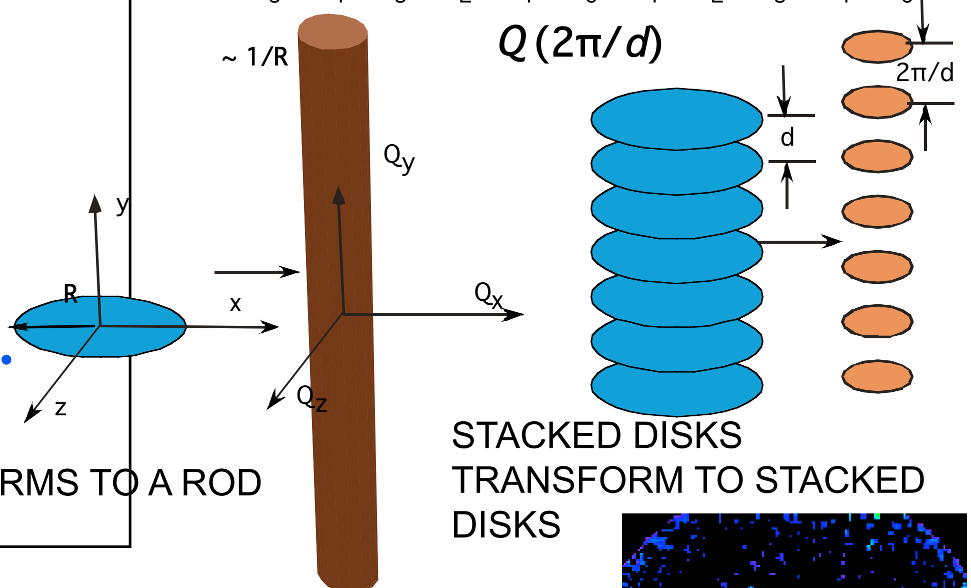
$$I(Q) = N\Delta\rho^2 V^2 P(Q) S(Q)$$

- ***N*: number of objects.**

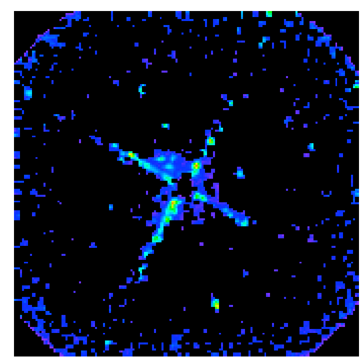
? $\Delta\rho = \rho_A - \rho_B$: scattering length density contrast.

- ***V*: object volume.**
- **P(*Q*): object form factor.**
- **S(*Q*): object structure factor.**

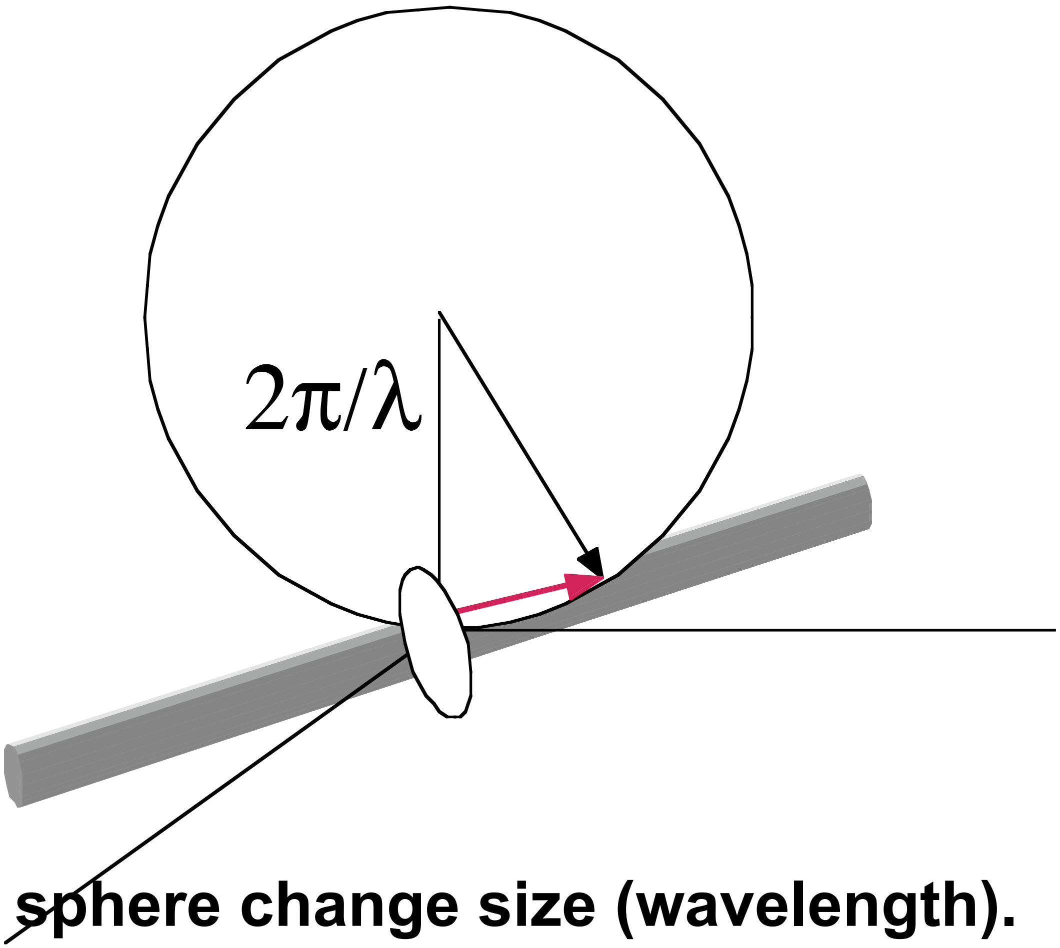




Given the properties of the Fourier transform we must be looking at families of stacked planes at 90º viewed edge on.

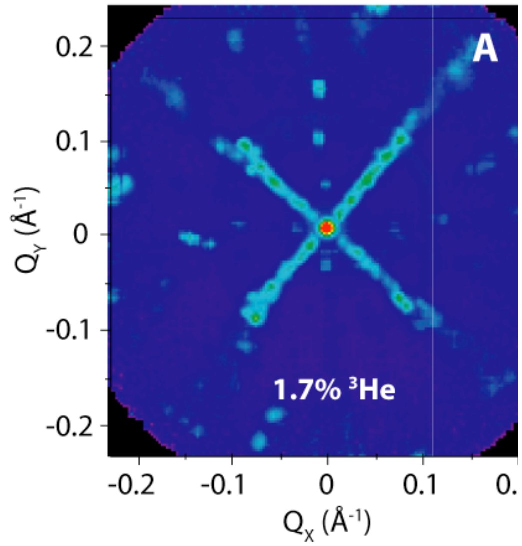


Strong Selection for planes viewed perpendicularly



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

With the evolution of ^{3}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)

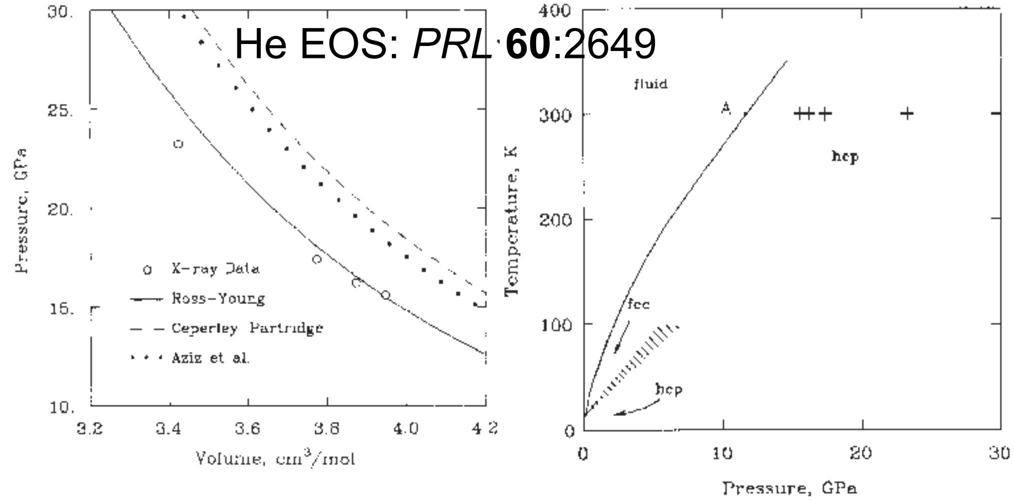
1		2		3		4	
3 mos	2.5 yr	3 mos	2.5 yr	3 mos	2.5 yr	3 mos	2.5 yr
490							
		280	280		260		
	210		200				
160					190	180	170
		150	140	140			140
120	120				120		
100		110	110		100	100	100
	90						
80	80	80	80	80	80		
	70				70		70
60	60			60	60	60	60
50	50		50	50	50	50	50
							40

- **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 ^3He accumulates.
- **Indications:**
  - Defects introduced by hydridization.
  - ^3He may accumulate in defects.

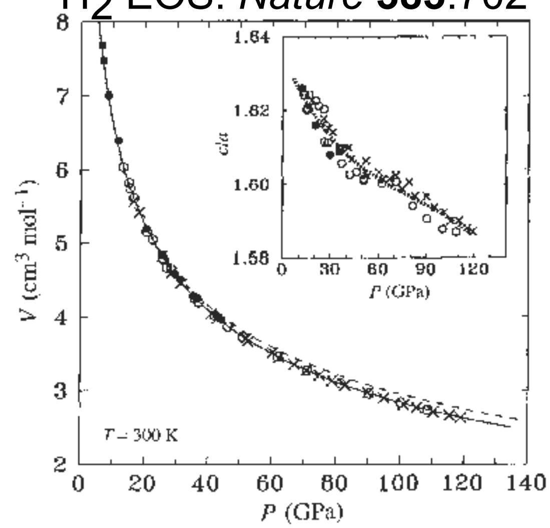
Bubble content: 10 GPa plausible, but no proof.

nucleus	b (fm)	ρ (1010 cm^{-2})		$\Delta\rho^2$ (10^{24} cm^{-4})
			(ErX_2)	
D	6.67	11.5	6.49	25.1
T	4.79	8.24	5.33	8.64
^{3}He	5.74	7.69		5.57
Er	7.79	2.58		

He EOS: *PRL* **60**:2649

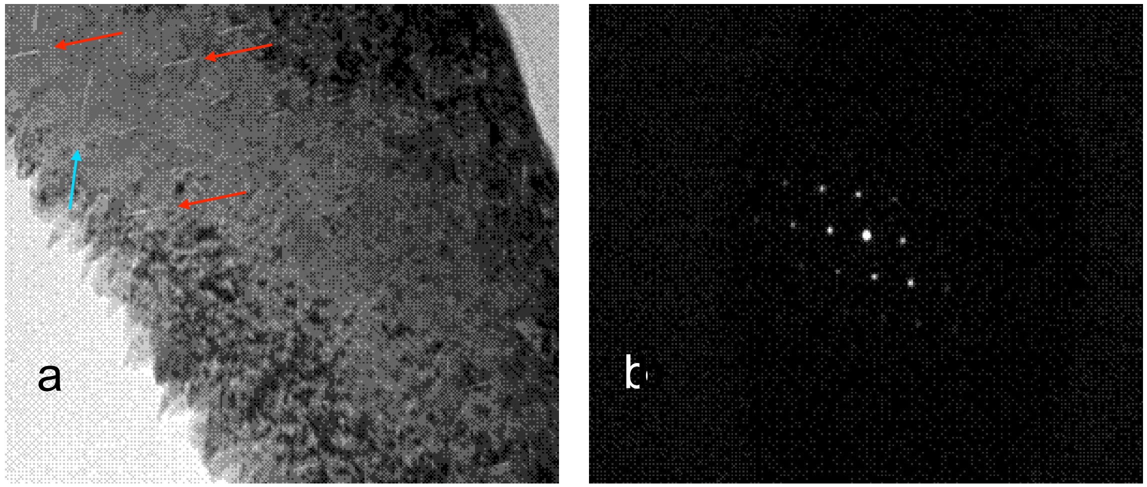


H_2 EOS: *Nature* **383**:702



- **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

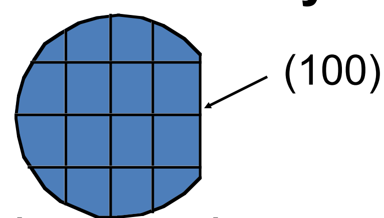
- Two sets of plate-like helium bubbles are visible, at an angle of ~72°
- Helium bubbles appear to lie on {111} planes

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 μm
- Ion milled at ~3.5 - 4° and 5kV until perforation
- Examined in JEOL JEM-2000FX TEM at 200 kV

Issues

- **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 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.