SAND2019-3713C

Overview of Tritium and Helium-3 Behavior in Rare Earth Metal Tritides

PRESENTED BY

Clark S. Snow, Sandia National Labs NM

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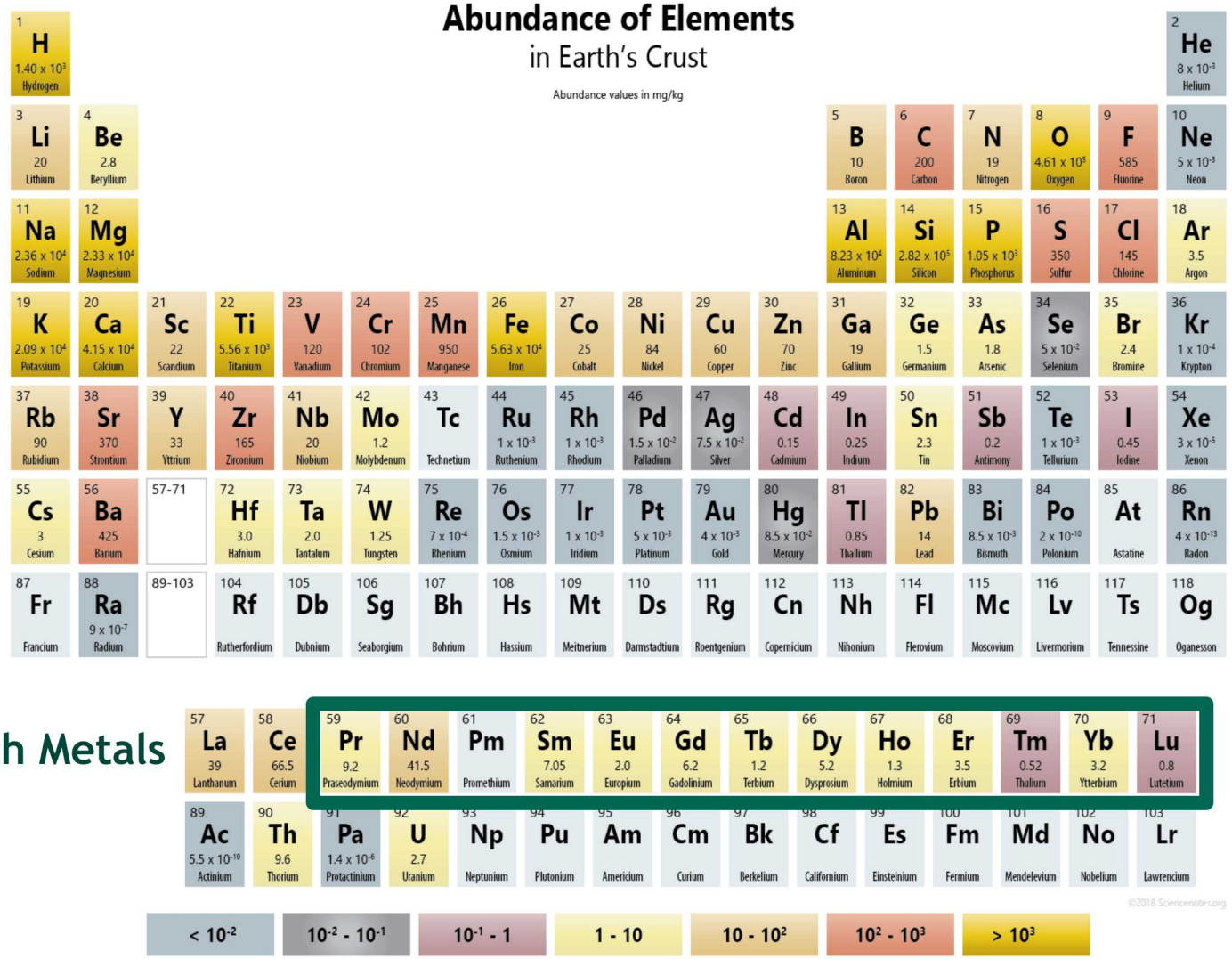
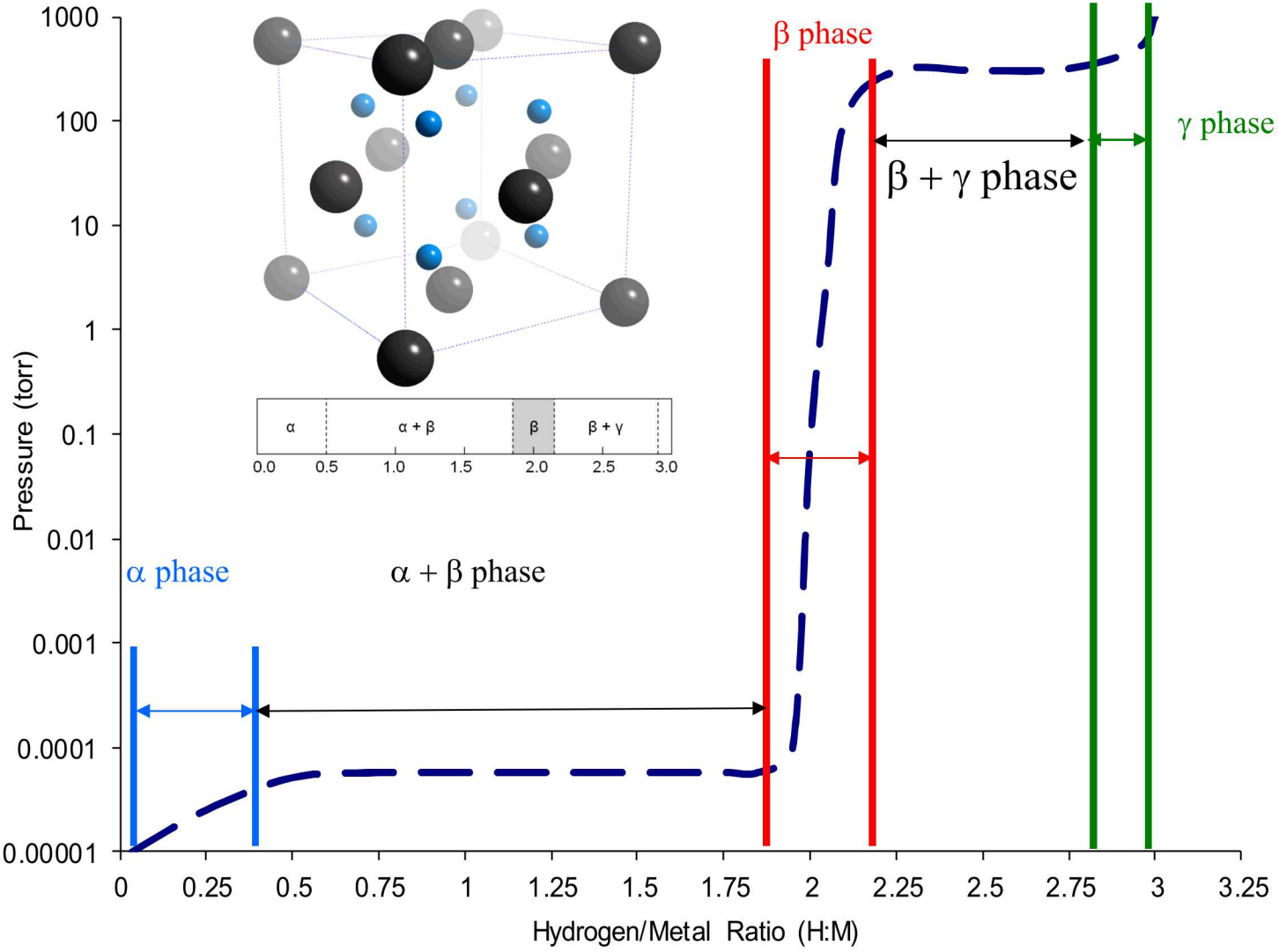
The scope of this presentation



Rare Earth Metals

The phase diagram of the rare-earth metal tritides



Stoichiometric deficiency

Peter Vajda studied the α+β : β phase boundary and found that the boundary approached 2.0 as the purity of the metal increased.

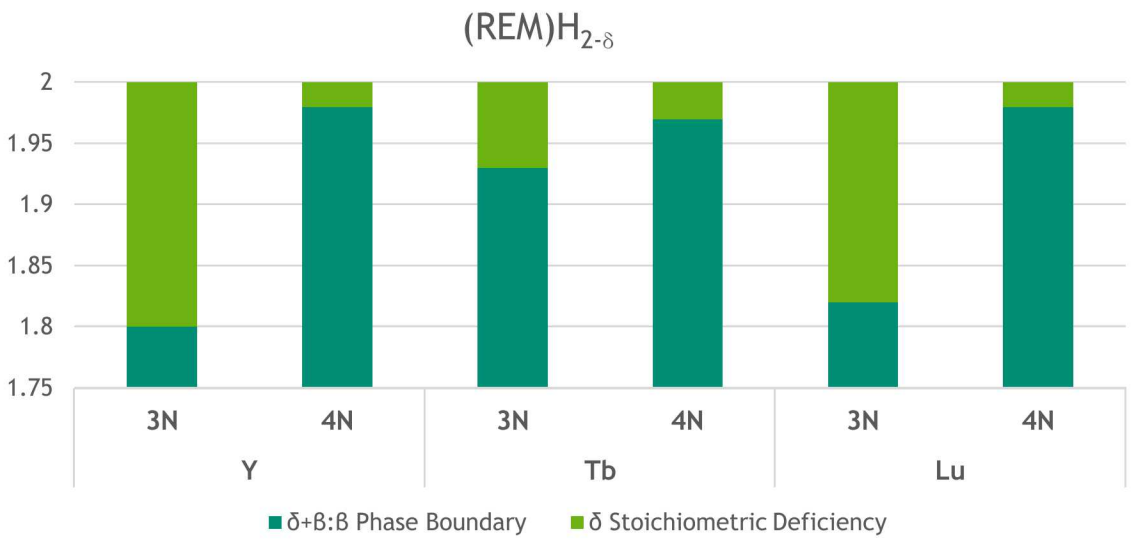
$(REM)H_{2.0+x+\delta}$ where

x = super-stoichiometry amount

δ = stoichiometric deficiency

Stoichiometric Deficiency						
	Y		Tb		Lu	
	3N	4N	3N	4N	3N	4N
2-δ	1.8	1.97-1.99	1.92-1.94	1.96-2.00	1.82	1.97-1.99
	1.9				1.85	
Solid Solution Solubility Limit	0.2	0.1	0.35	0.25	0.25	0.03

P. Vajda, Hydrogen in rare earth metals, including RH2+x phases, in: K. A. Gschneider (Ed.), Handbook on the Physics and Chemistry of Rare Earths, vol. 20, North-Holl., Amsterdam, 1995, p. 207



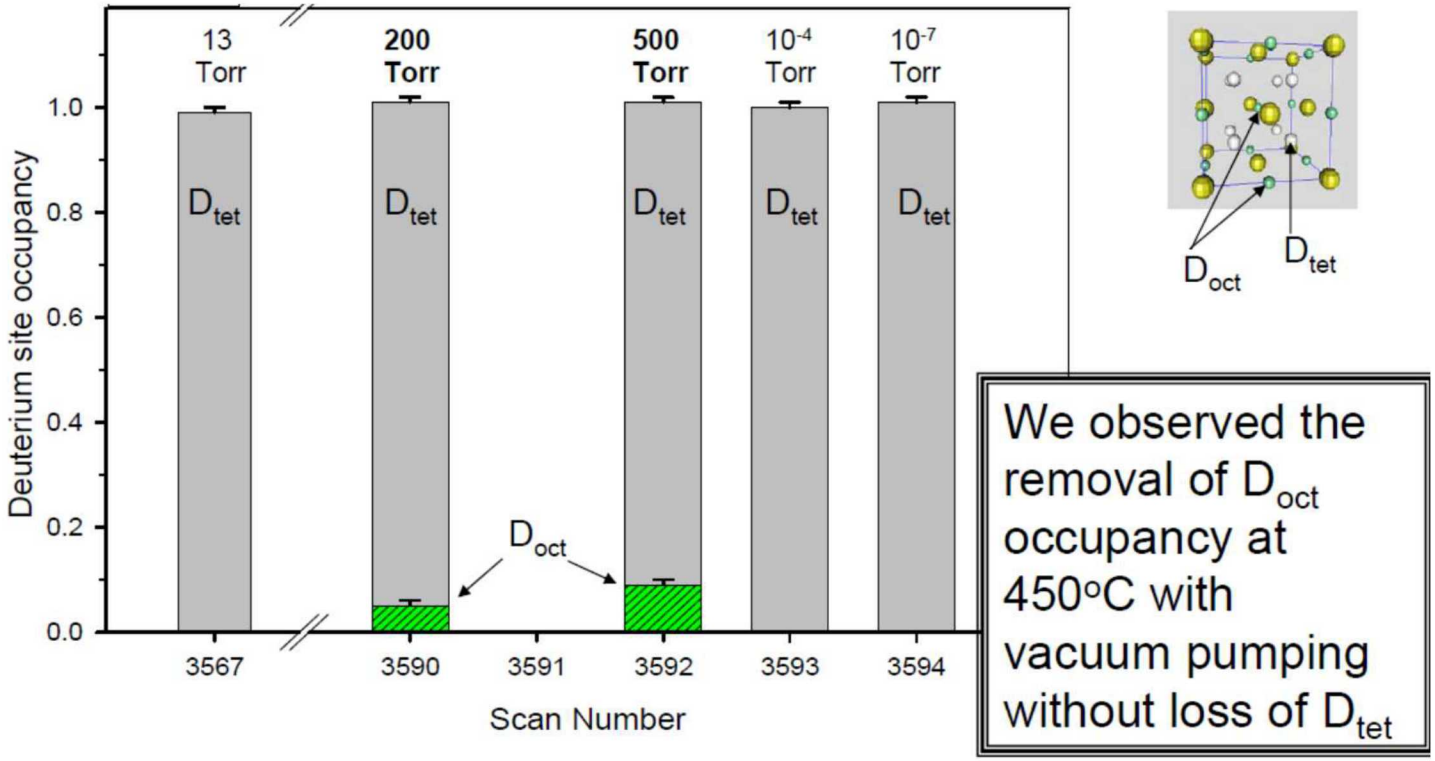
Site stability during gaseous loading

Data taken at 450 C and pure D_2 gas in erbium metal

Structure monitored via neutron diffraction

Octahedral sites begin to be occupied at 200 Torr, higher the pressure more occupancy.

Removing D_2 gas removes the octahedral site occupancy.



Rodriguez et al., "*In-Situ* observation of ErD2 formation during D2 loading via neutron diffraction" in *Powder Diffraction* **26** (2), June 2011 p.144

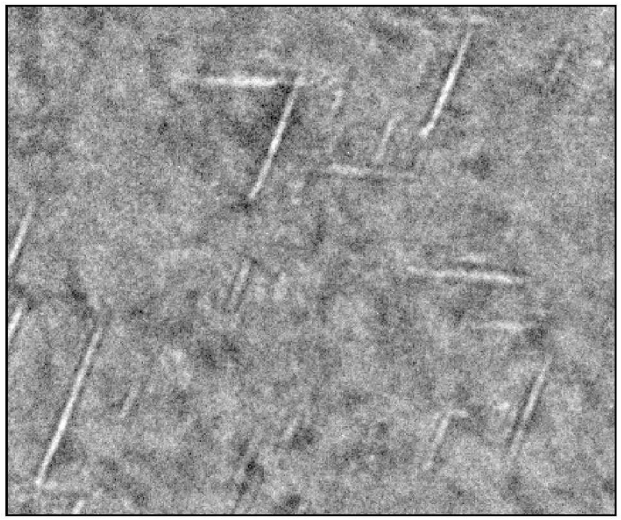
What happens when tritium decays into helium-3: Data from ErT_2

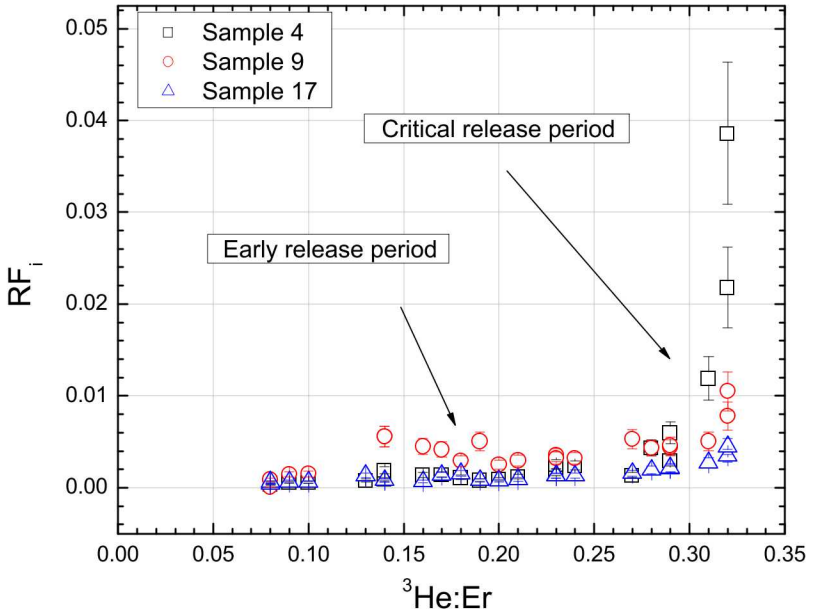
Immediately after tritium decays 2 things happen:

1) Helium begins to be emitted from the metal tritide – we term this "Early Release"

2) Helium bubbles begin to form which store the helium gas

Later a point is reached called "Critical Release" or "Catastrophic Release" where the Release Fraction = 1

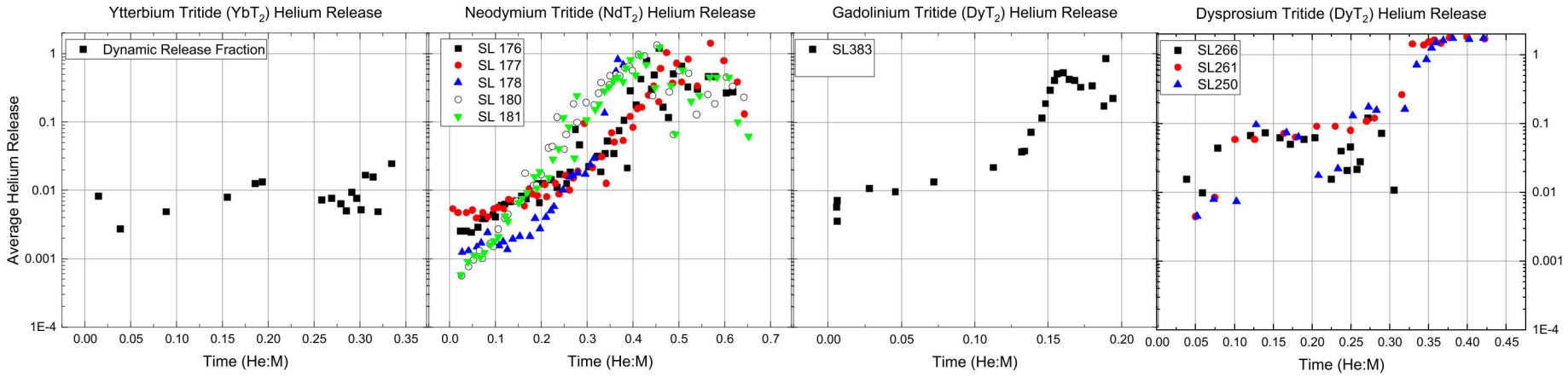


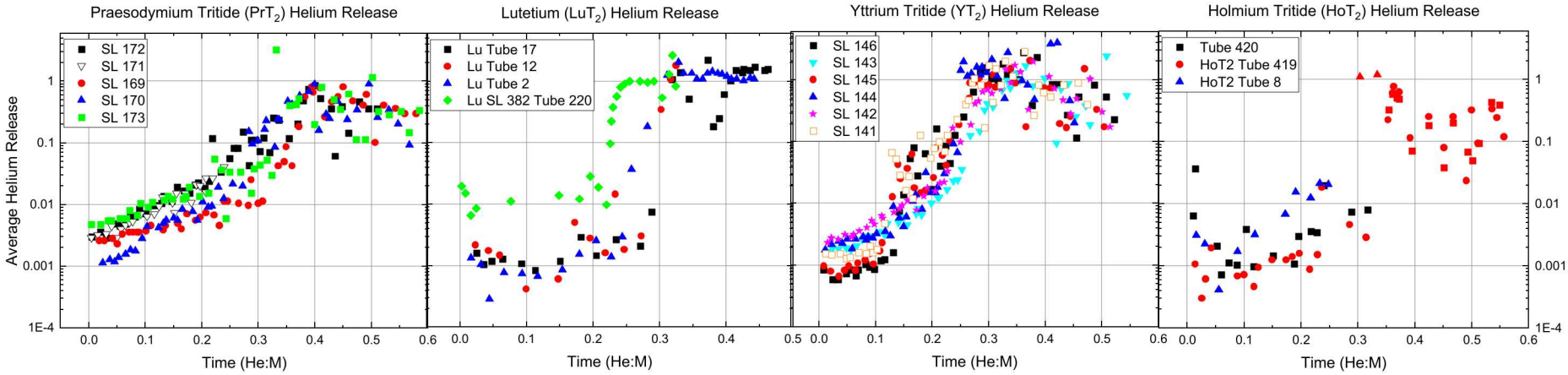


$$ARF = \frac{Released\ Helium}{Generated\ Helium}$$

$$ARF = \frac{\int_{t_1}^{t_2} (AccumulatedHelium)dt}{TotalTritium\left(e^{-\lambda t_1} - e^{-\lambda t_2}\right)}$$

Helium release from the rare-earth metal tritides



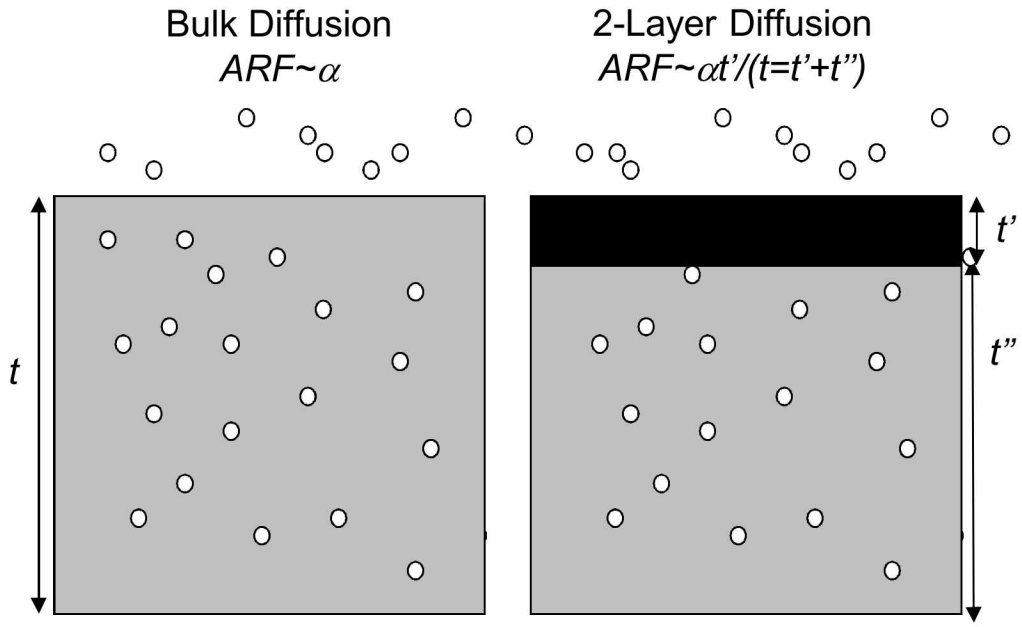


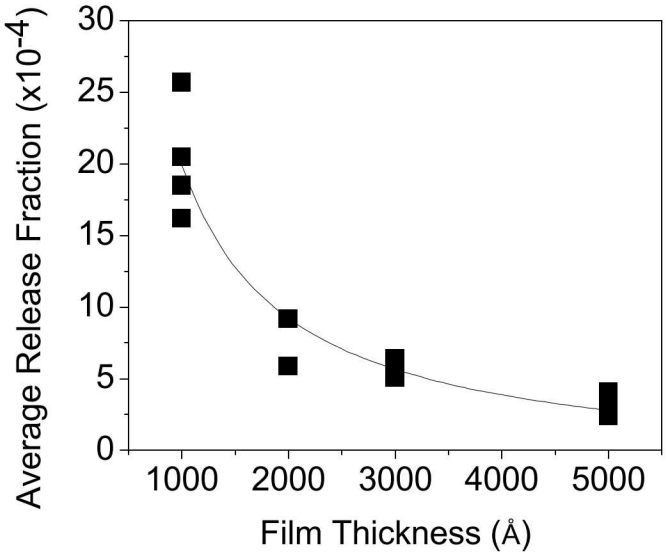
Where does the early release portion of helium come from?

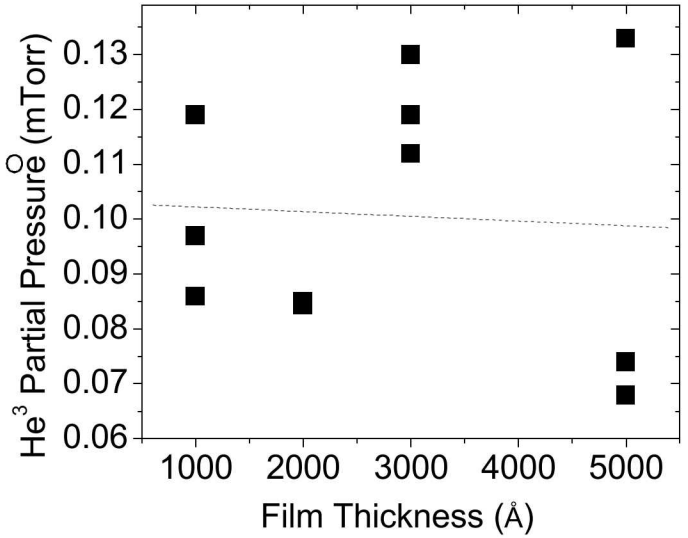
ErT_2 films of various thickness

Total amount of helium release is constant

Release Fraction varies inversely with thickness can be modeled as having 2-Layer Diffusion





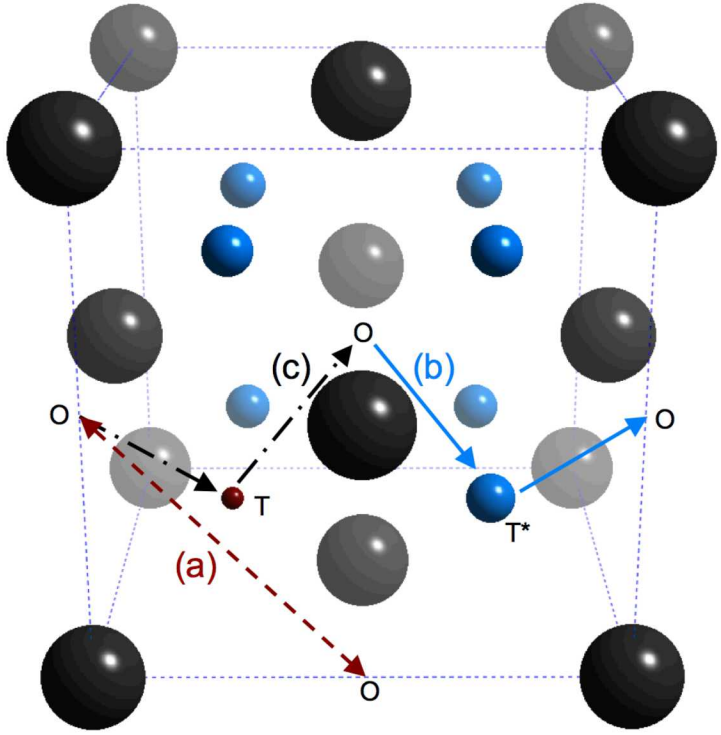


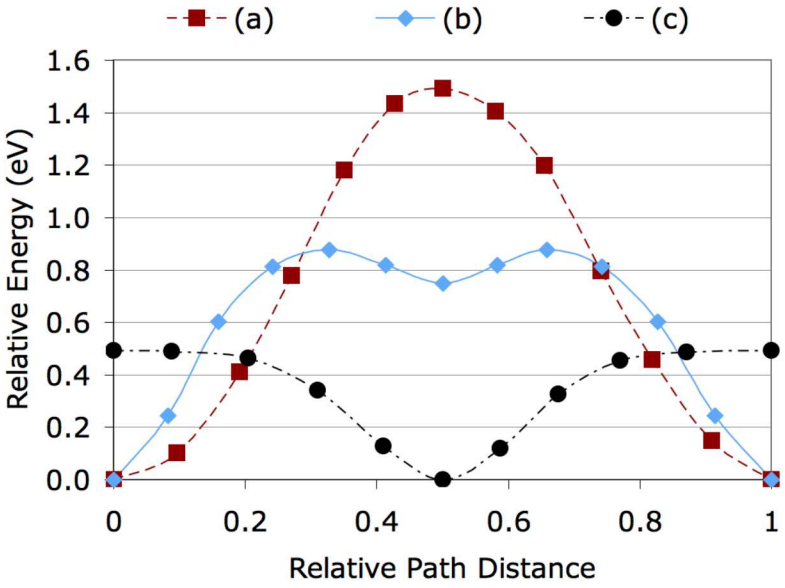
Snow et al., "3He bubble evolution in ErT_2: A survey of experimental results" in JNM 453 (2014) pp. 296-306

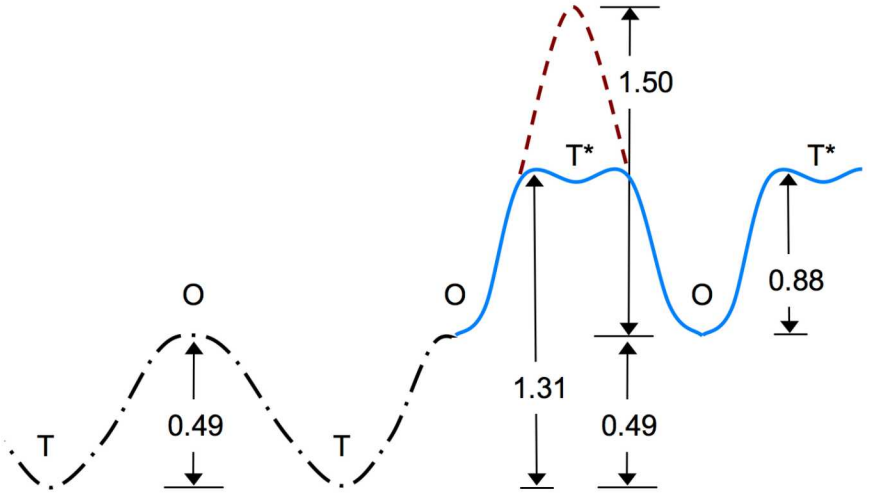
Can helium migrate in metal tritides? An example from ErT_2

Helium born in octahedral sites will stay in octahedral sites bound to empty tetrahedral site by 0.49 eV with a 1.31 eV dissociation energy.

Helium will move freely between two octahedral sites unoccupied by hydrogen, barrier 0.49eV.





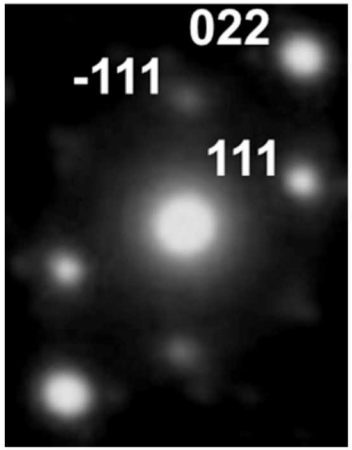


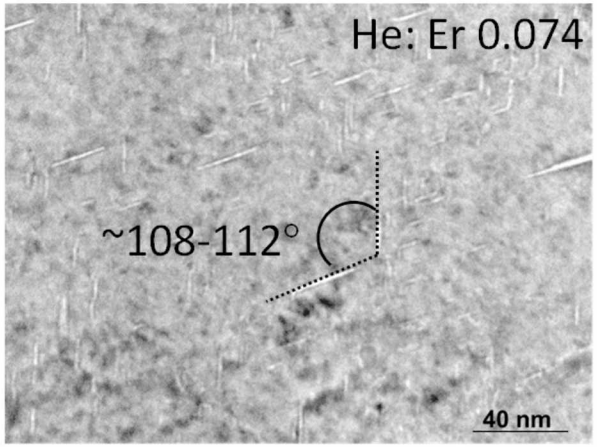
Wixom et al. "First principles site occupation and migration of hydrogen, helium, and oxygen in ß-phase erbium hydride" in JAP 103, 123708 (2008)

Helium bubble shapes

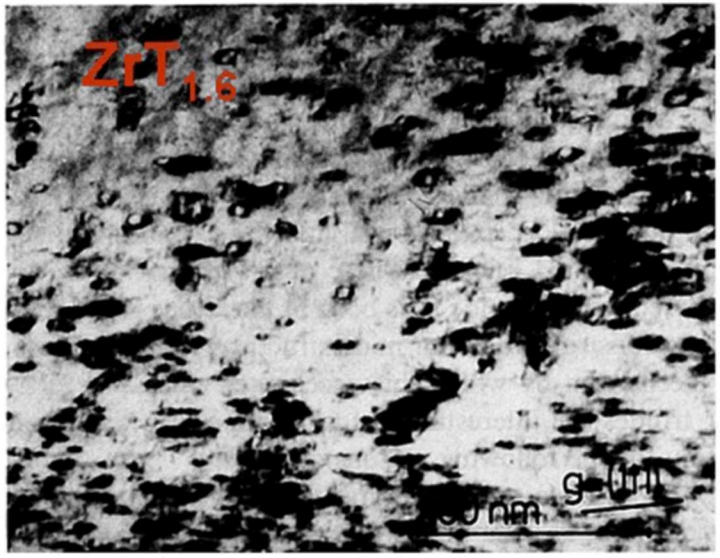
Helium Bubble Shape Ratios

	γ (GPa-nm)	μ (GPa)	b (nm)	Ratio
Pr	0.69	25	0.390182	0.070736
Nd	0.685	26.7	0.386363	0.066402
Sm	0.431	29.8	0.379999	0.038061
Gd	0.664	31.8	0.374979	0.055685
Tb	0.669	33.8	0.370948	0.053358
Dy	0.648	34.8	0.367766	0.050632
Ho	0.65	35.6	0.365221	0.049993
Er	0.637	36.9	0.362251	0.047654
Lu	0.94	40	0.355887	0.066032





γ (GPa-nm)	Surface Energy
μ (GPa)	shear modulus
b (nm)	Burger's vector



$$\text{Ratio of } \frac{Surface\ Energy}{Strain\ Energy} = \frac{\gamma}{\mu b}$$

> 0.1 Sphere
< 0.1 Platelet

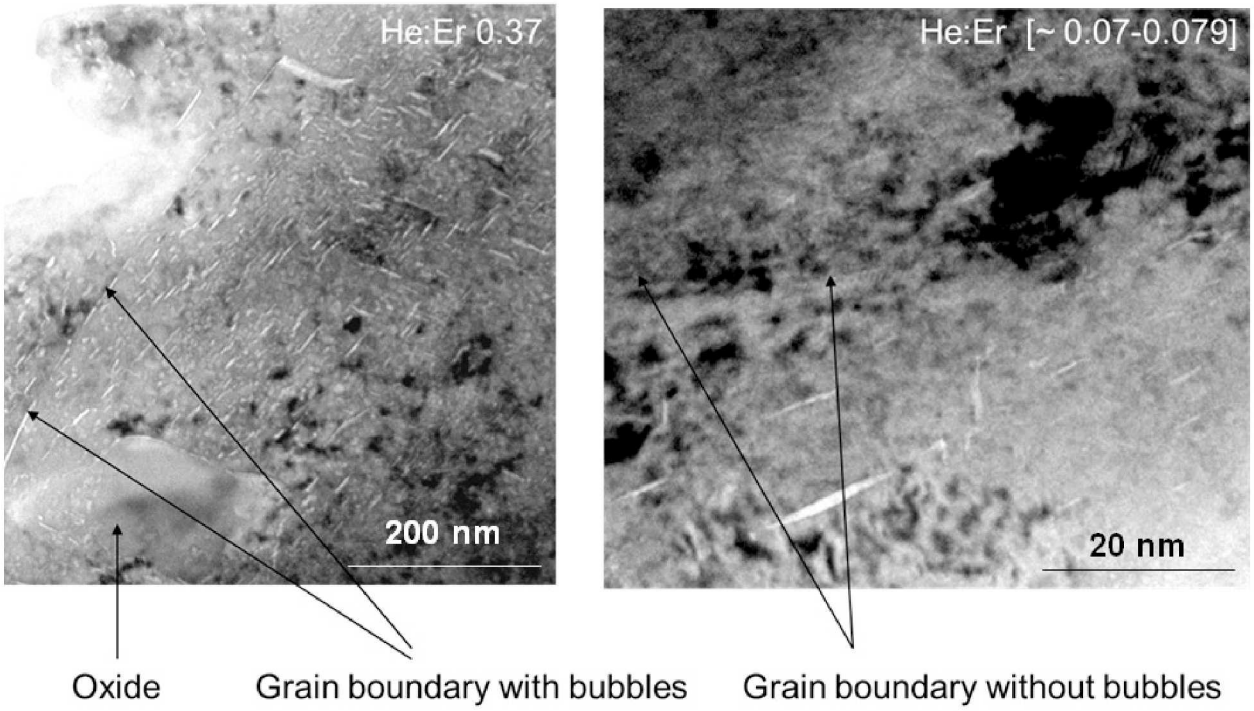
D. Cowgill "Helium nano-bubble evolution in aging metal tritides" in Fusion Science and Technology 48, 539

Helium bubble spatial distribution

Bubbles observed evenly distributed throughout film.

Grain boundary decoration only when GB aligns along (111) plane

Bubbles observed around Er_2O_3 pieces.



Helium bubble growth and interactions I

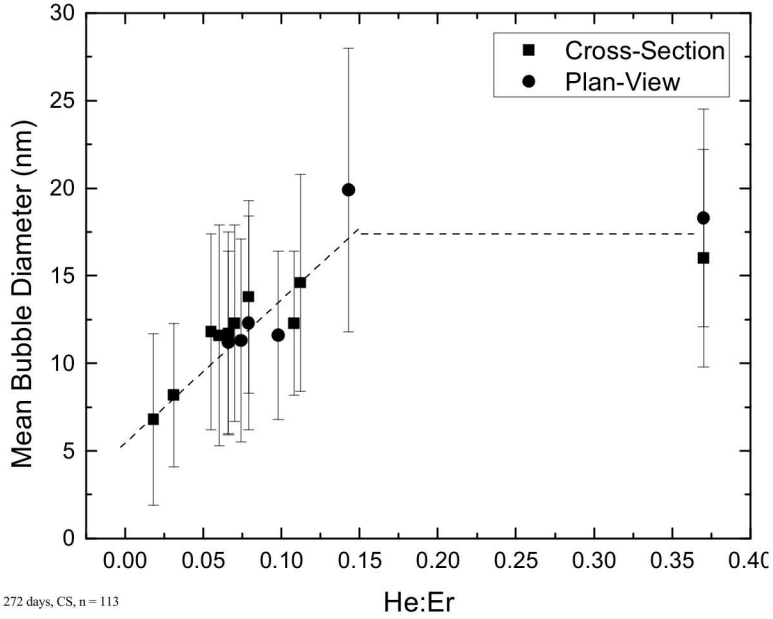
ErT_2 samples tracked and studied with TEM

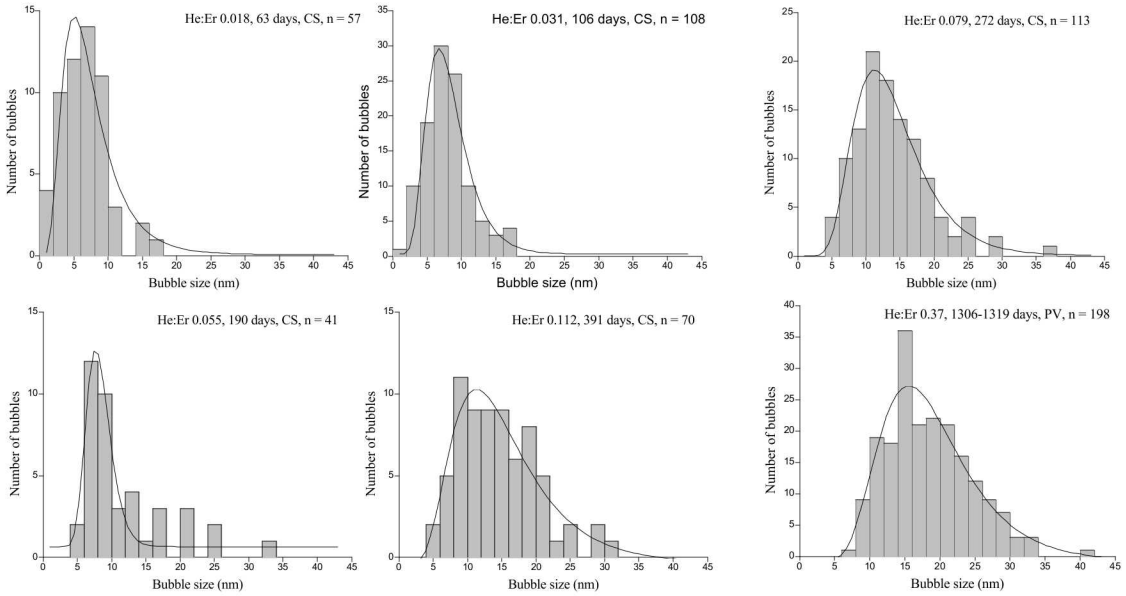
Length increases with time up to He:Er ~ 0.15.

Width doesn't change until He:Er ~0.15.

Size distribution log-normal throughout life.

- Tight distribution early
- Larger distribution later





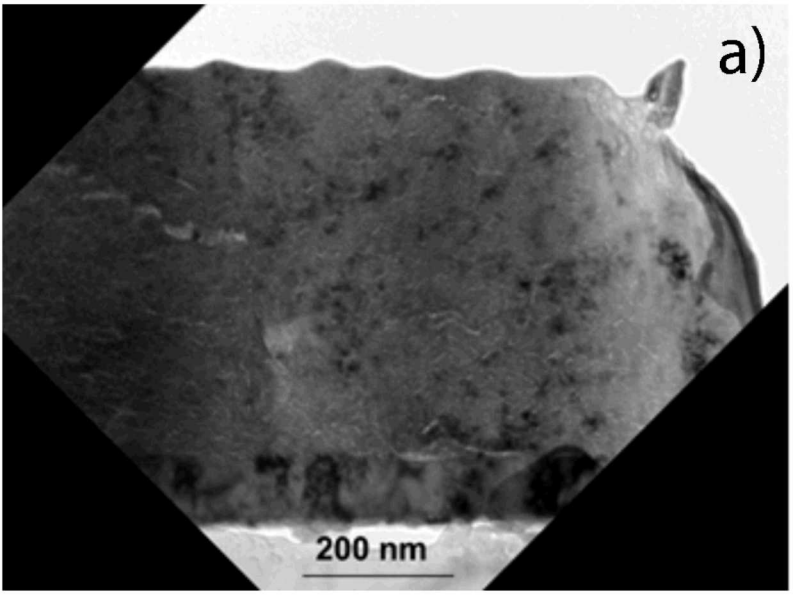
Bond et al., J. Appl. Phys. 107, 083514 (2010)

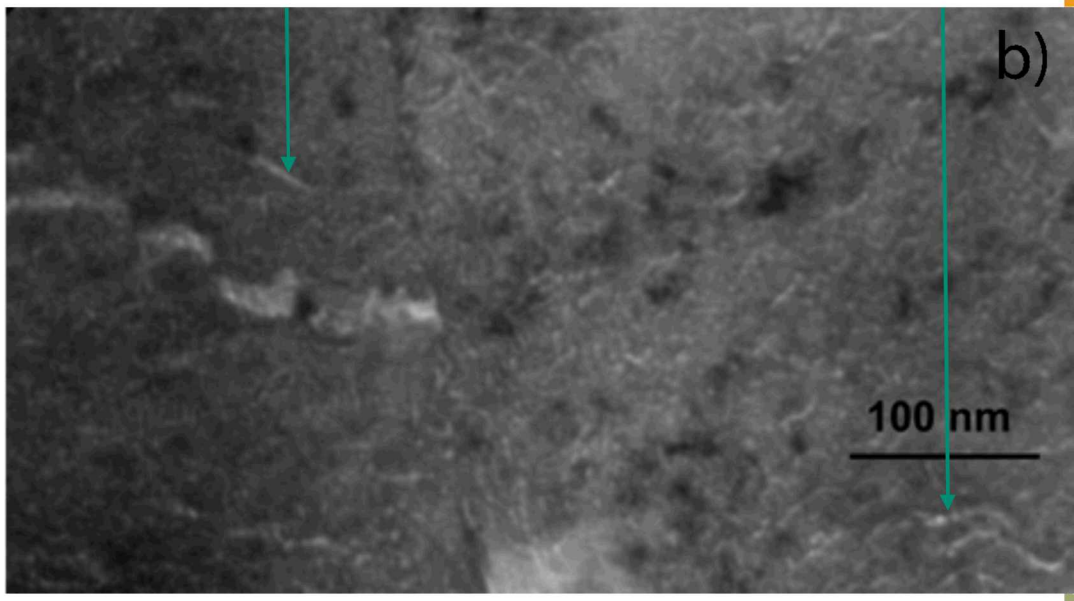
Helium bubble growth and interactions II

Bubbles begin to link later in life.

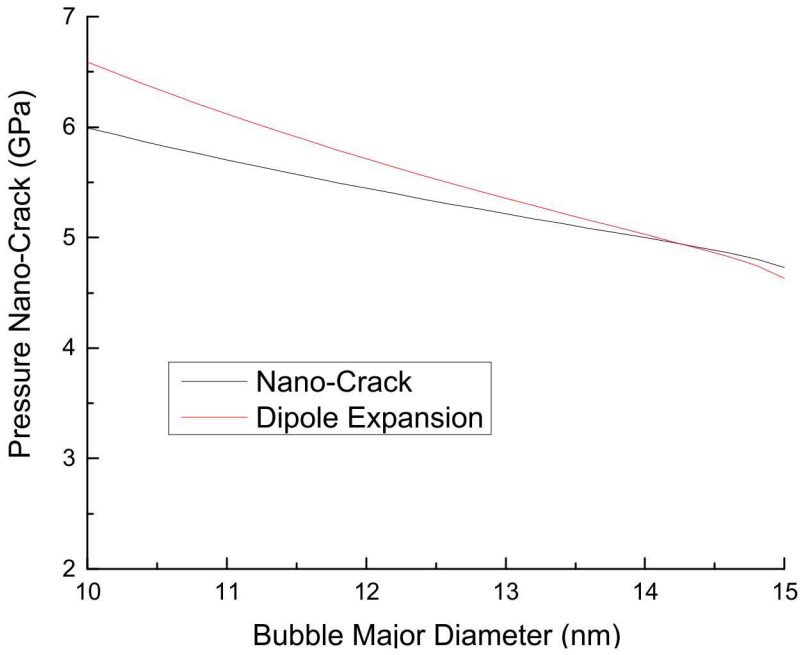
Length stops growing, width begins to increase.

Becomes very difficult to even define what is a bubble.





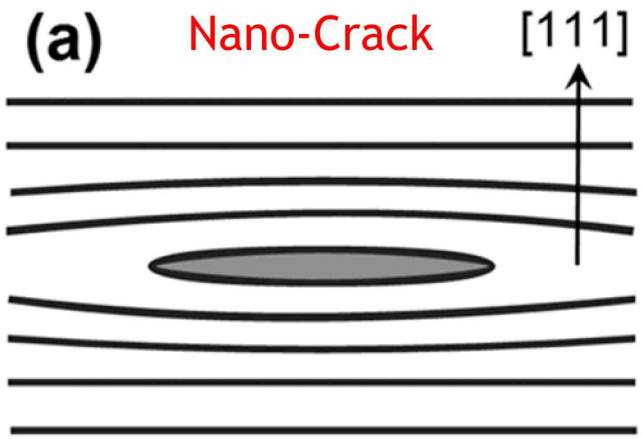
Helium bubble transition point

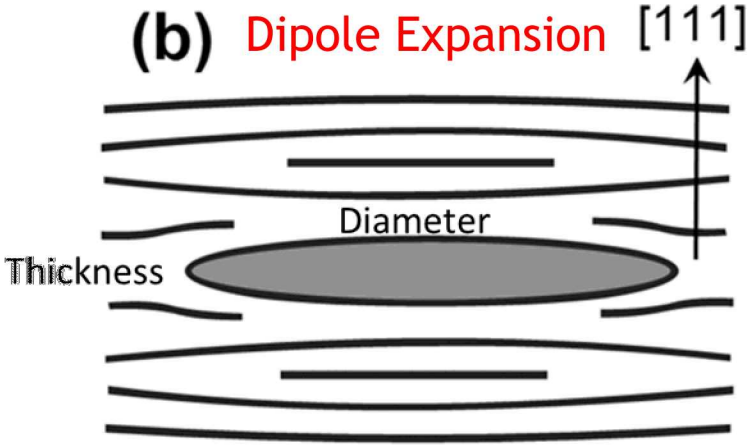


$$P_{Nano\_Crack} = \frac{\pi G m}{2(1-\nu)}\frac{s}{d}$$

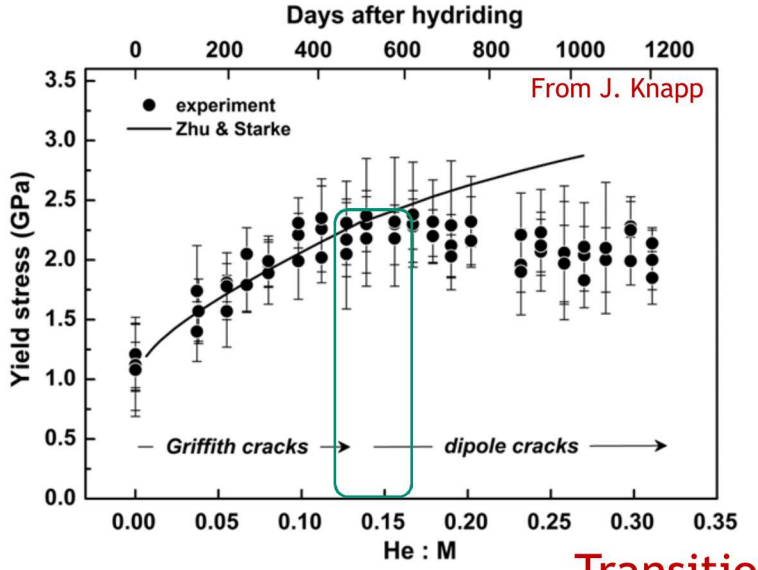
$$P_{dipole} = \frac{2\gamma}{s}\frac{(d+b+s)}{(d+b)} + \frac{G_m d_{111}}{(d+b)}$$

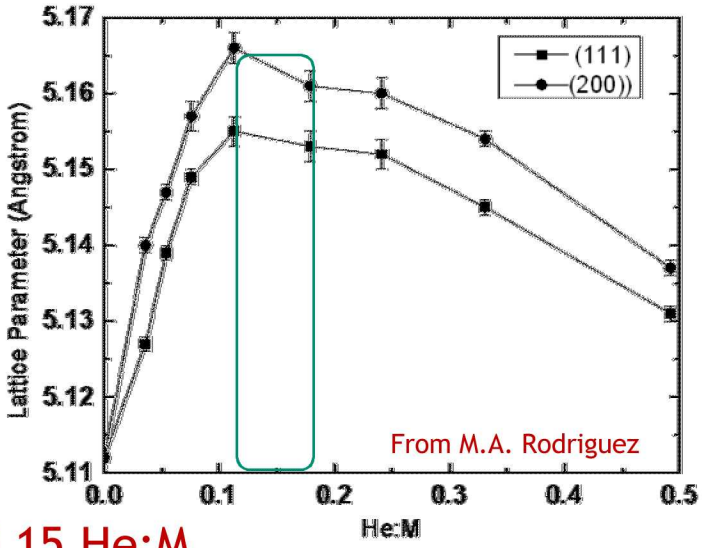
γ	= Surface Energy
ν	= Poisson's ratio
d	= platelet diameter
s	= platelet thickness
b	= Burger's vector
d_{111}	= 111 plane spacing
G_m	= effective Shear modulus



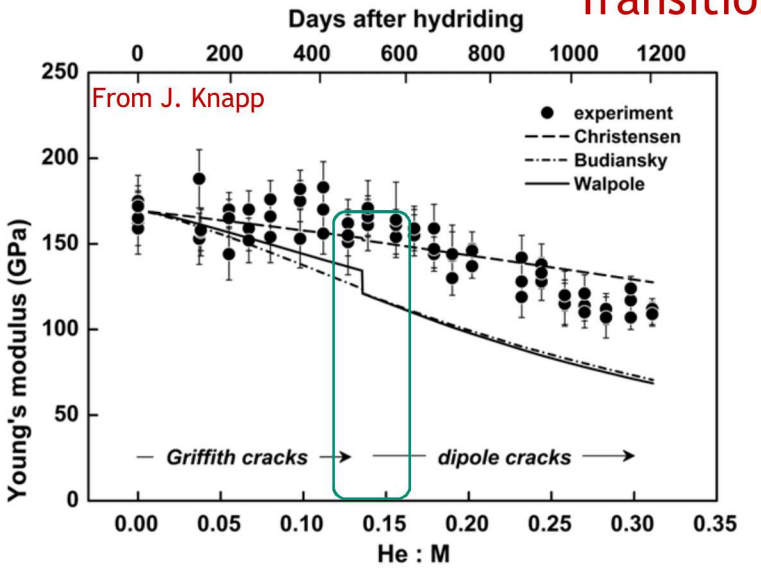


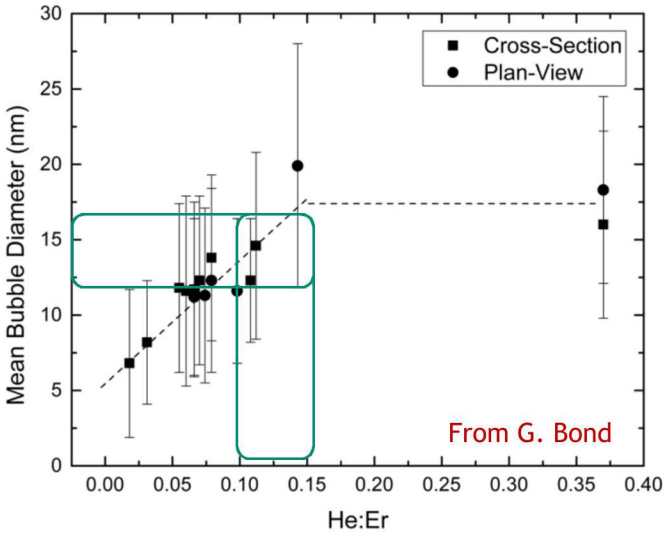
Evidence for the bubble growth model





Transition ~ 0.12-0.15 He:M





Helium bubble pressures

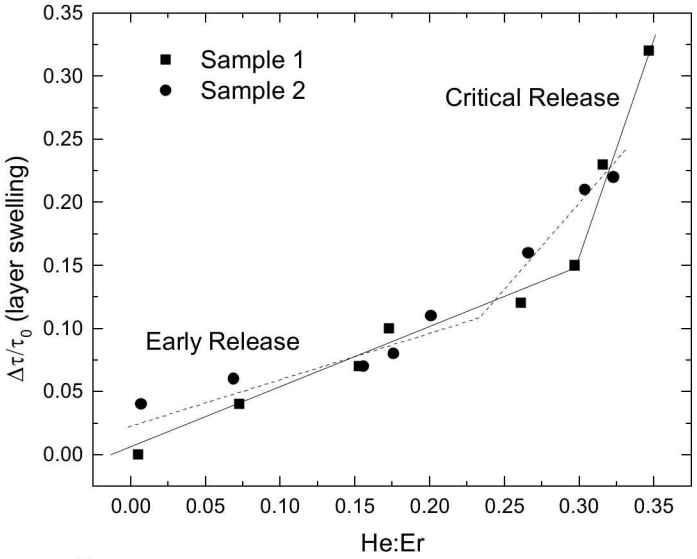
Pressure in bubble

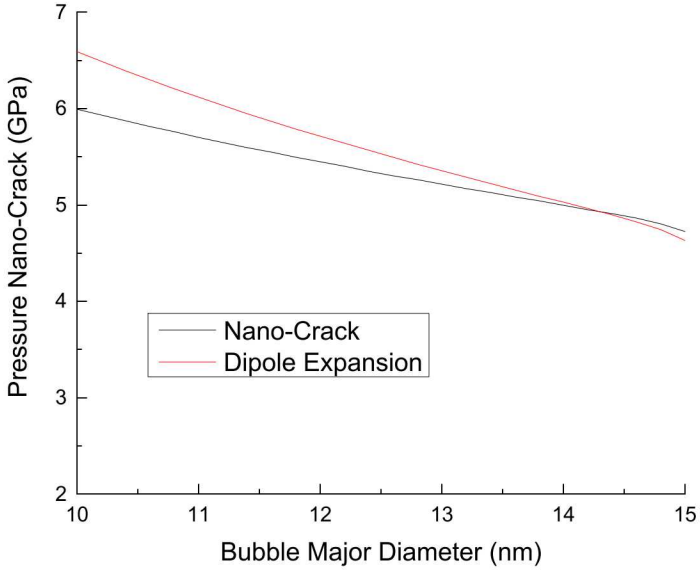
$$\frac{\Delta V}{V} = \frac{c_{T0} t \lambda \Delta v THe}{\Omega}$$

- $\sim c T_0 \lambda t \left[\left(\frac{v_{He}}{\Omega}\right) * \left(\frac{\Delta vI}{\Omega}\right) - \left(\frac{\Delta vT}{\Omega}\right)\right]$
- Ω = atomic volume (volume of the tritide per metal atom)
- v_{He} =volume required by 3-He in the high pressure bubbles
- $\Omega = \Omega_0[1 + cT(^{\Delta v}/_{\Omega_0})_T]$
- Using EOS for 3-He can extract bubble pressure

Using Neutron Reflectivity to measure swelling P ~1-3 GPa

Models predict 5 GPa





Summary, Conclusions, and Future Work

- Lots of great physics and still more to learn
- What is the helium bubble nucleation mechanism?
  - Why do they start where they do?
  - Oxide inclusions?
  - A defect?
  - Self-trapping?
- Verify some of these predictions on other materials, study as in-depth as ErT_2
- Develop a GUT (Grand Unified Theory) of Helium bubbles in metals

Back-Up Slides

Thermodynamics of the metal hydrides

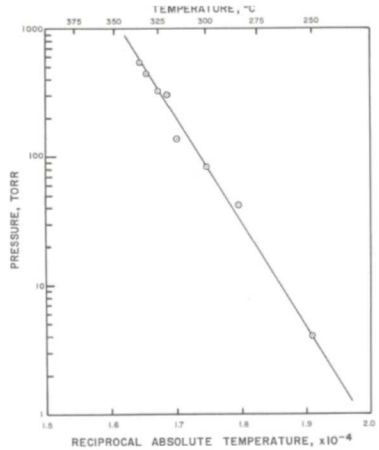


Figure 4. Van't Hoff Plot of the Plateau Data in the Dihydride-Trihydride Region of the Erbium-Hydrogen System

$$\Delta H^{\alpha\to\beta} - T\left(\Delta S^{\alpha\to\beta} + k\ln\frac{P}{P_0}\right) = 0$$

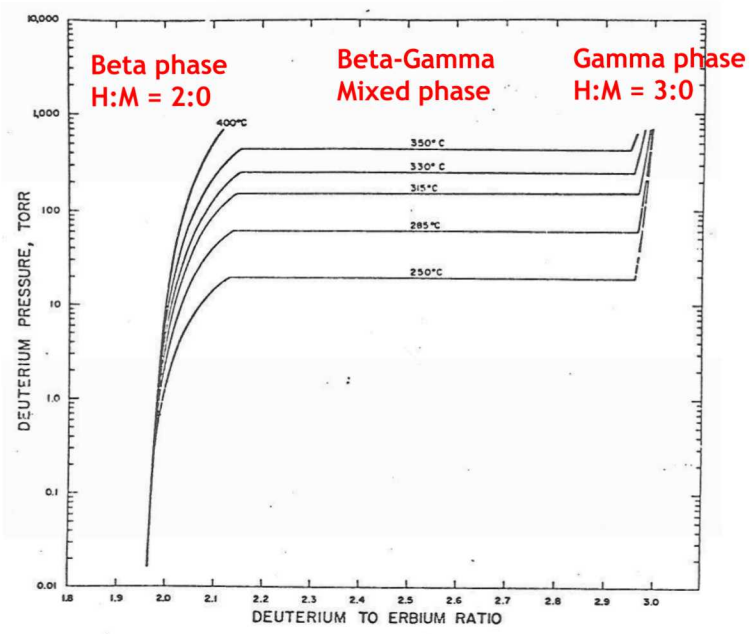


Figure 2. Family of Isotherms in the Dideuteride - Trideuteride Region

Er-D Isotherms

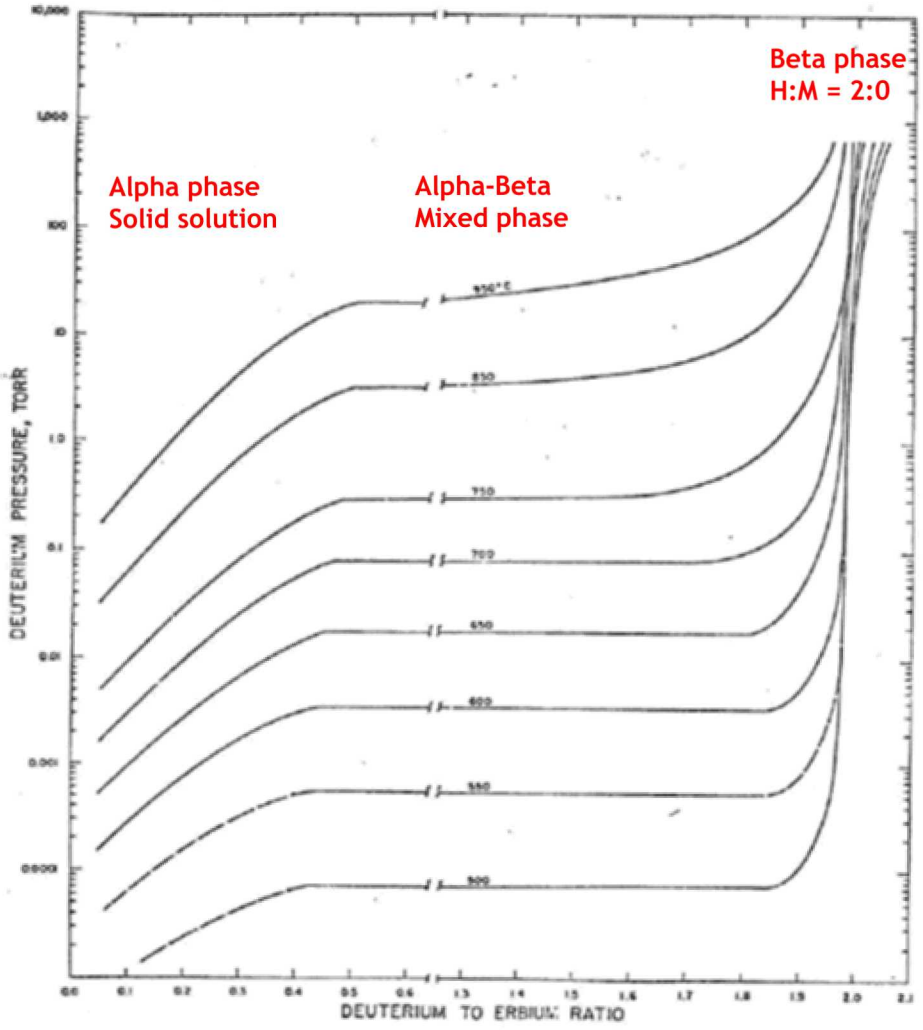


Figure 1. Family of Isotherms in the Erbium Solid Solution-Dideuteride Region

Lundin DRI

Dissociation pressures of the rare-earth hydrides

Dissociation Pressure peaks at Ho

Er still very high and makes for a very stable beta phase di-hydride.

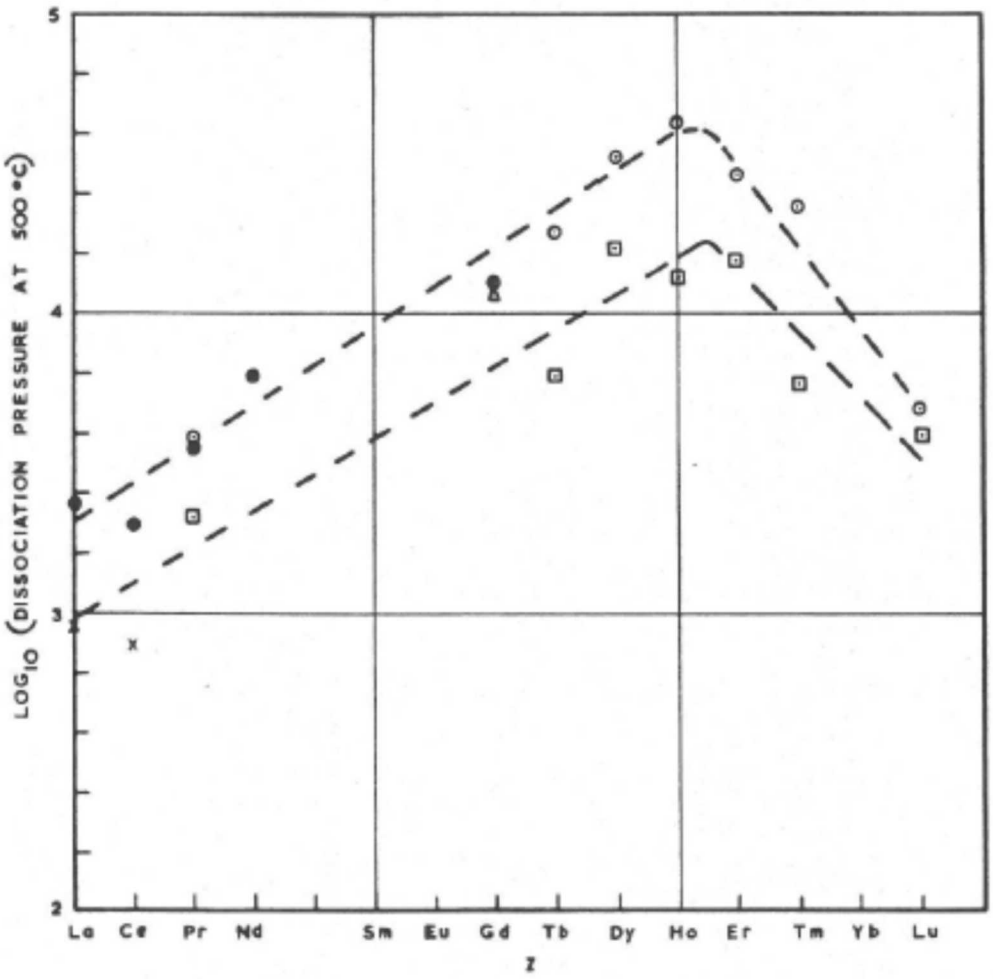


FIGURE 9. DISSOCIATION PRESSURE AT 500°C

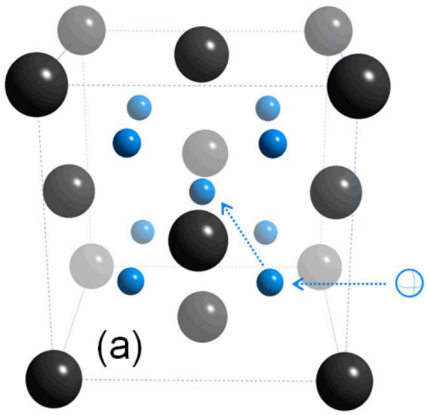
AWRE Report No. O-22/64 Jones et al.

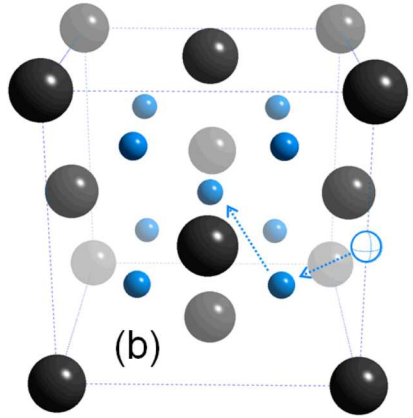
Computed site stabilities and hydrogen movement in rare-earth metals

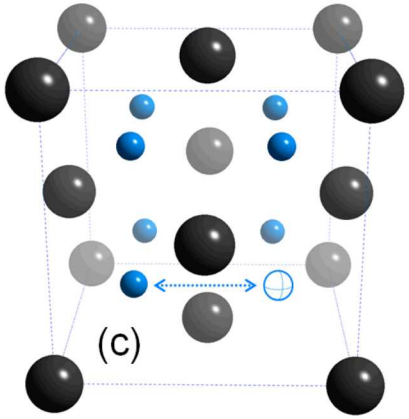
Results are for ErH_2 but should be similar for all rare earth metal hydrides

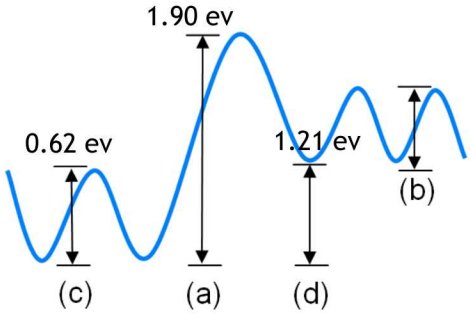
Dominant mechanism determined by stoichiometry

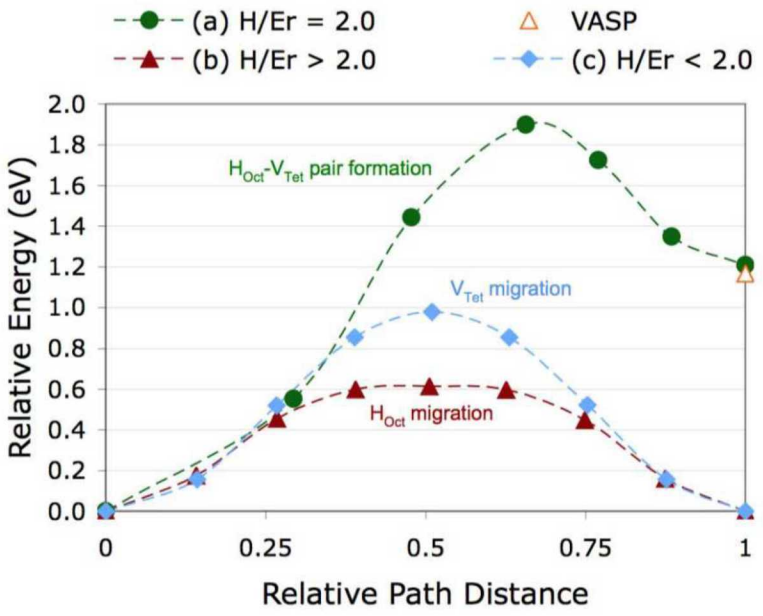
Movement of hydrogen will more likely result from nonstoichiometry









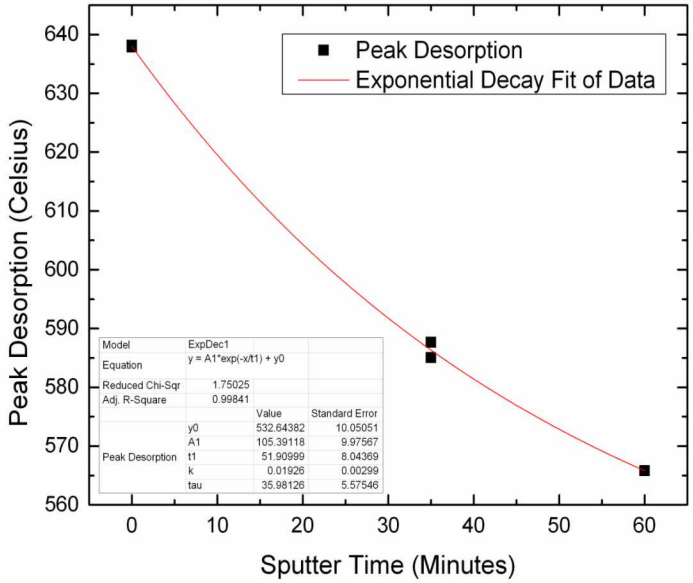


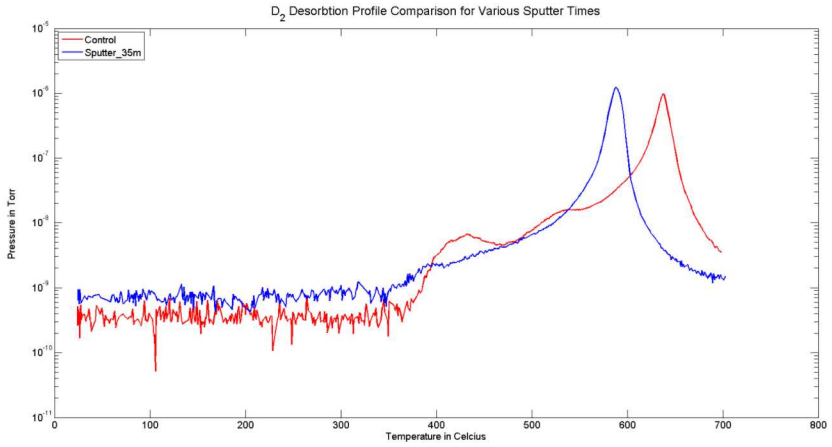
Wixom et al. "First principles site occupation and migration of hydrogen, helium, and oxygen in ß-phase erbium hydride" in JAP 103, 123708 (2008)

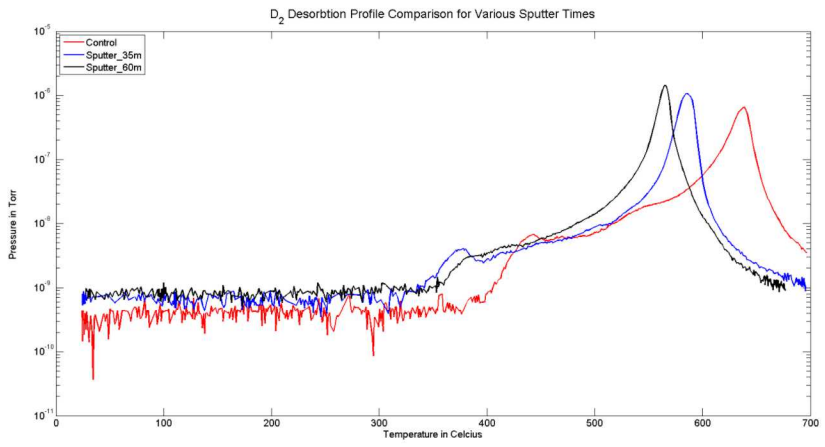
The role of the native oxide in inhibiting hydrogen desorption

Temperature Programmed Desorption with a ramp rate of 1 C/second

Removing the native oxide layer shifts the main tetrahedral desorption peak from 640C to 565C with one hour of sputtering





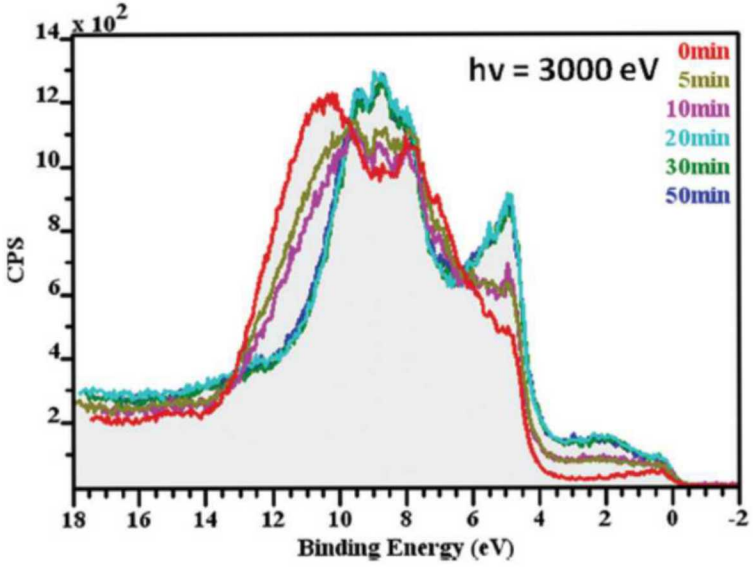


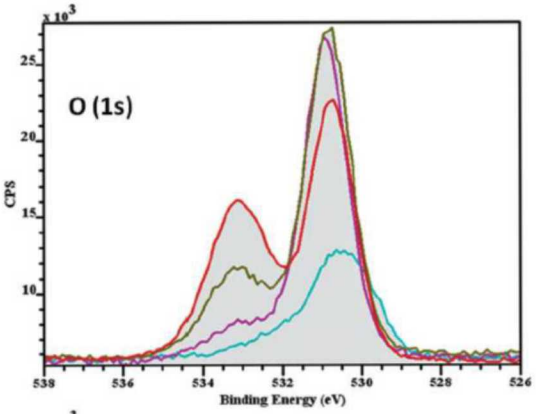
The role of the native oxide in inhibiting hydrogen uptake

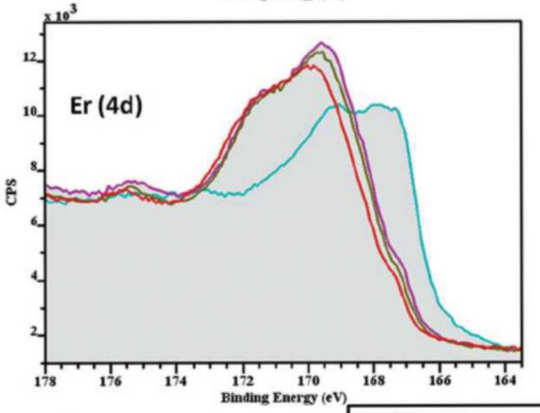
Before gaseous loading need to "activate" the surface of the sample.

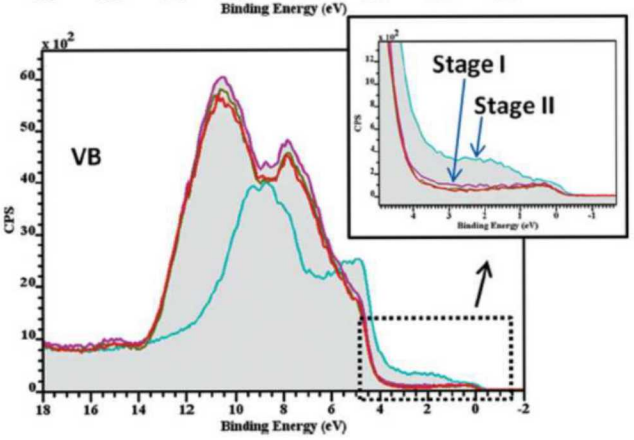
Activation breaks down the oxide layer, leaving a mostly metallic surface layer

Activation occurs very quickly, 5-10 minutes.

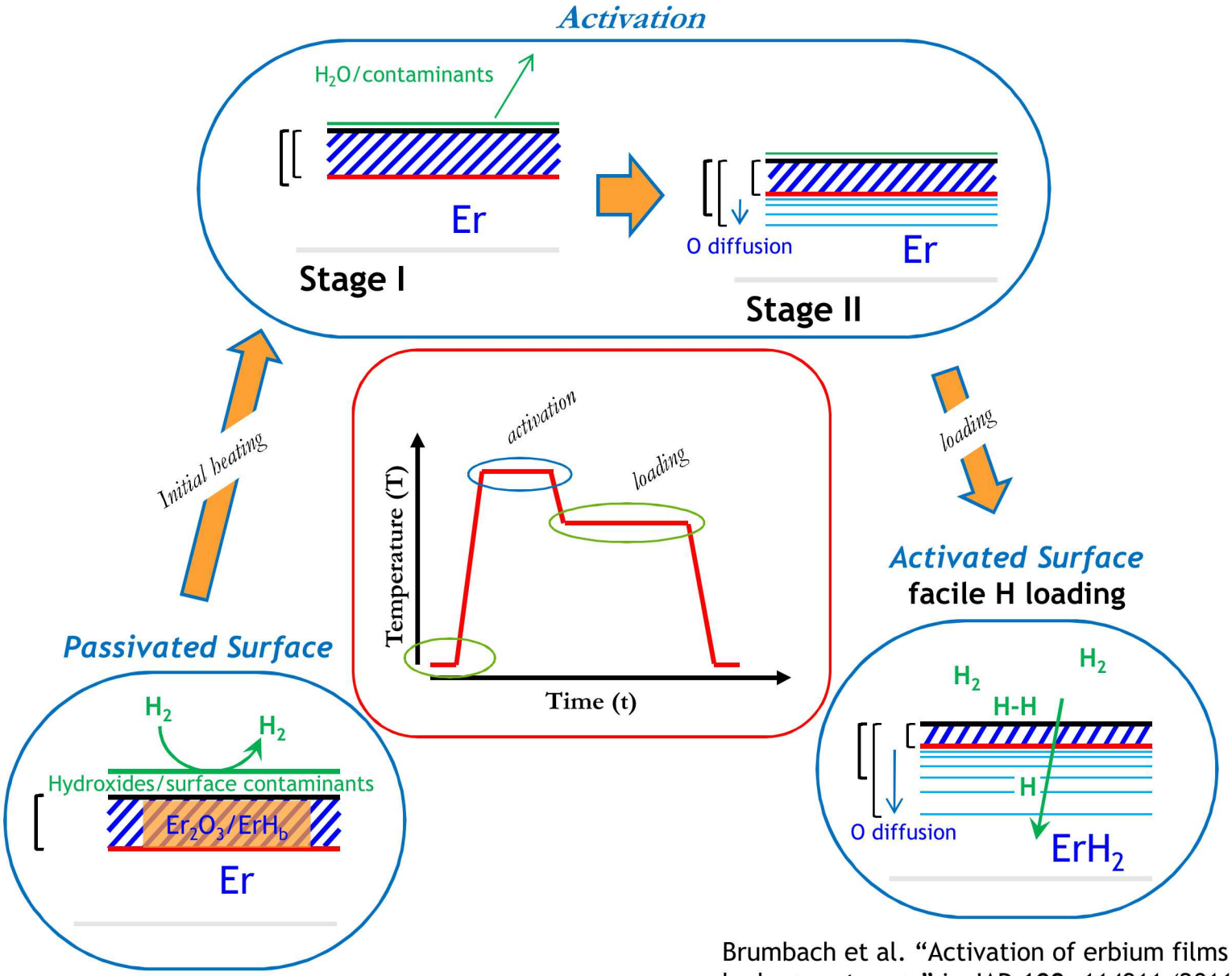








Summary of activation processes



Brumbach et al. "Activation of erbium films for hydrogen storage" in JAP **109**, 114911 (2011)

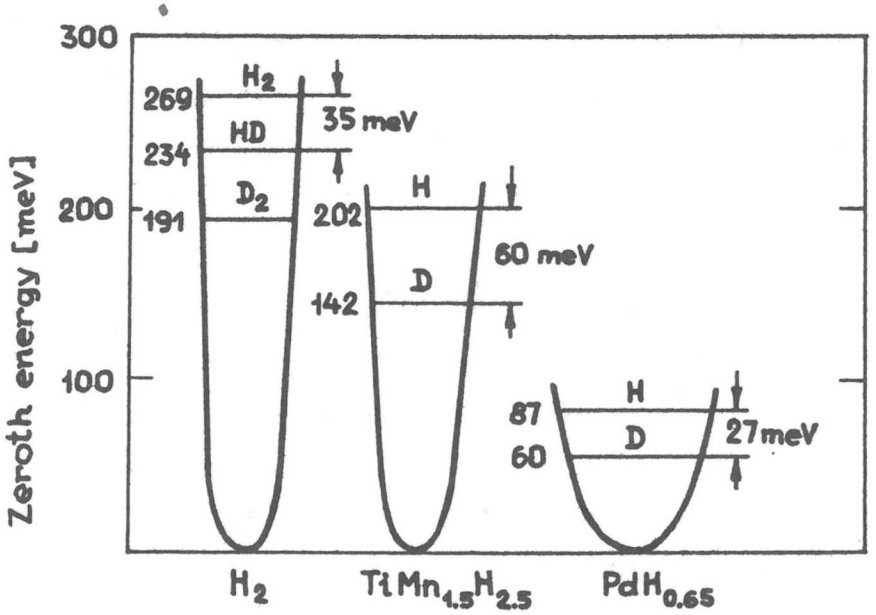
Isotopic enrichment of solid phases

Zero Point Energy (ZPE) is the difference between the lowest possible energy that a quantum mechanical system may have, and the classical minimum energy of the system.

ZPE leads to differences in isotopic enrichment of metals.

Pd H is preferred over D

Er D is preferred over H



"Interaction of Hydrogen Isotopes with Transition Metals and Intermetallic Compounds" by B. M. Andreev et al.

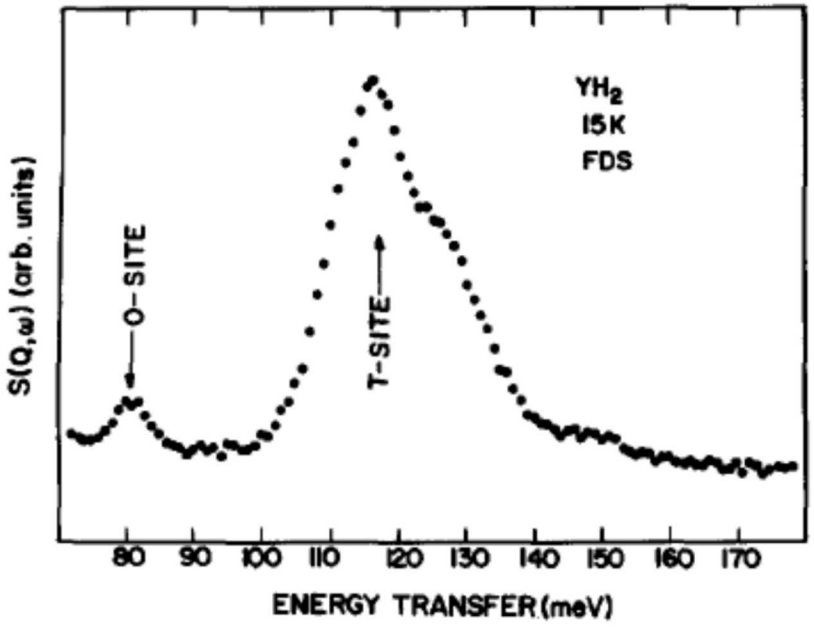
Hydrogen site stabilities

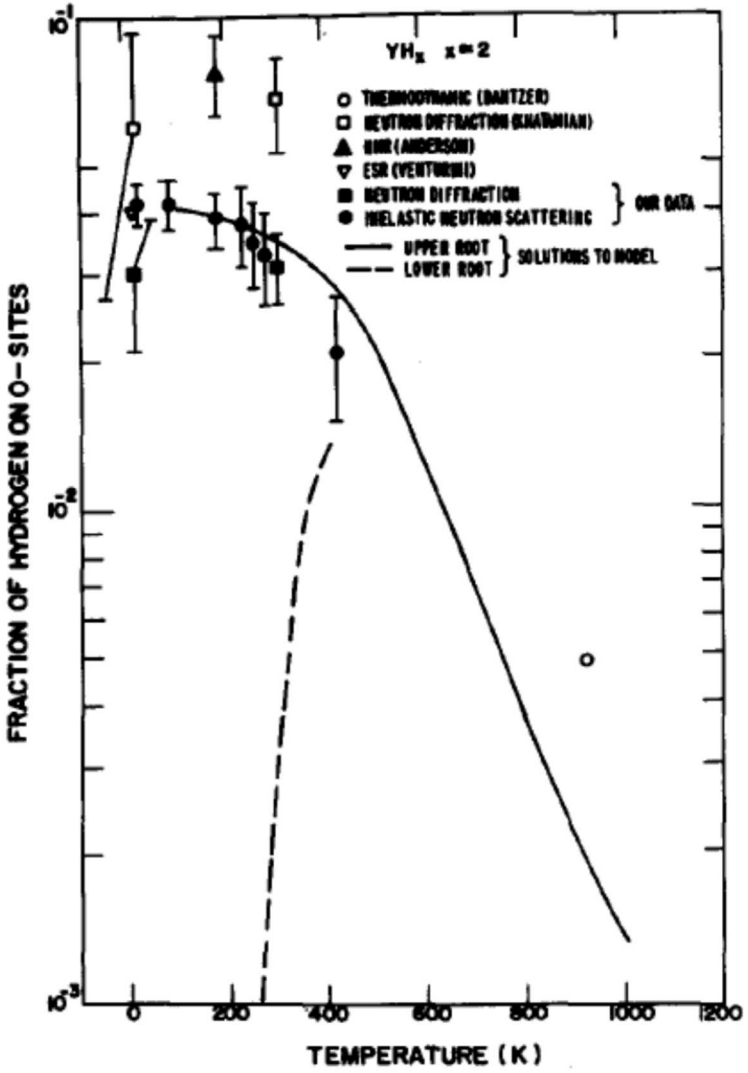
Yes!
Maybe?
Depends on purity of sample

Two important questions about site occupancy:

1) Is the Octahedral site occupied at 2.0?

2) In a mixed isotope system is there a site preference?





Goldstone et al., "Temperature Dependence of Hydrogen Site Occupancy in Yttrium Dihydride" in *Solid State Communications*, Vol 49, No. 5, pp. 475-478

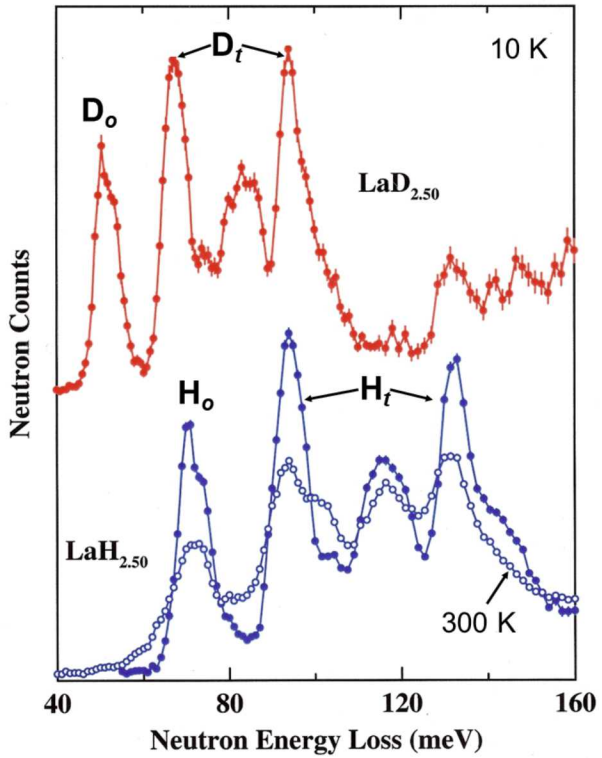
Hydrogen site stabilities

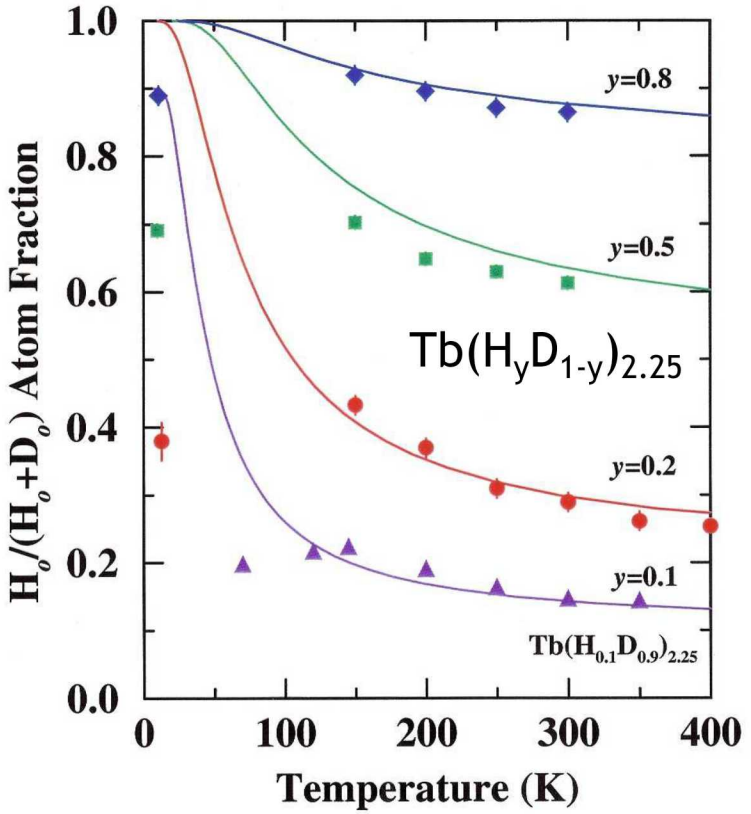
Two important questions about site occupancy:

1) Is the Octahedral site occupied at 2.0?

2) **In a mixed isotope system is there a site preference?**

YES! The heavier atoms prefer tetrahedral sites, lighter prefer octahedral sites





Udovic et al., "Hydrogen and deuterium site separation in fcc-based mixed-isotope rare-earth hydrides" in Physical Review B, Vol. 61, No. 10 March 2000 pp. 6611-6616