

Metastable Erbium Trihydrides Supported Films and Powders

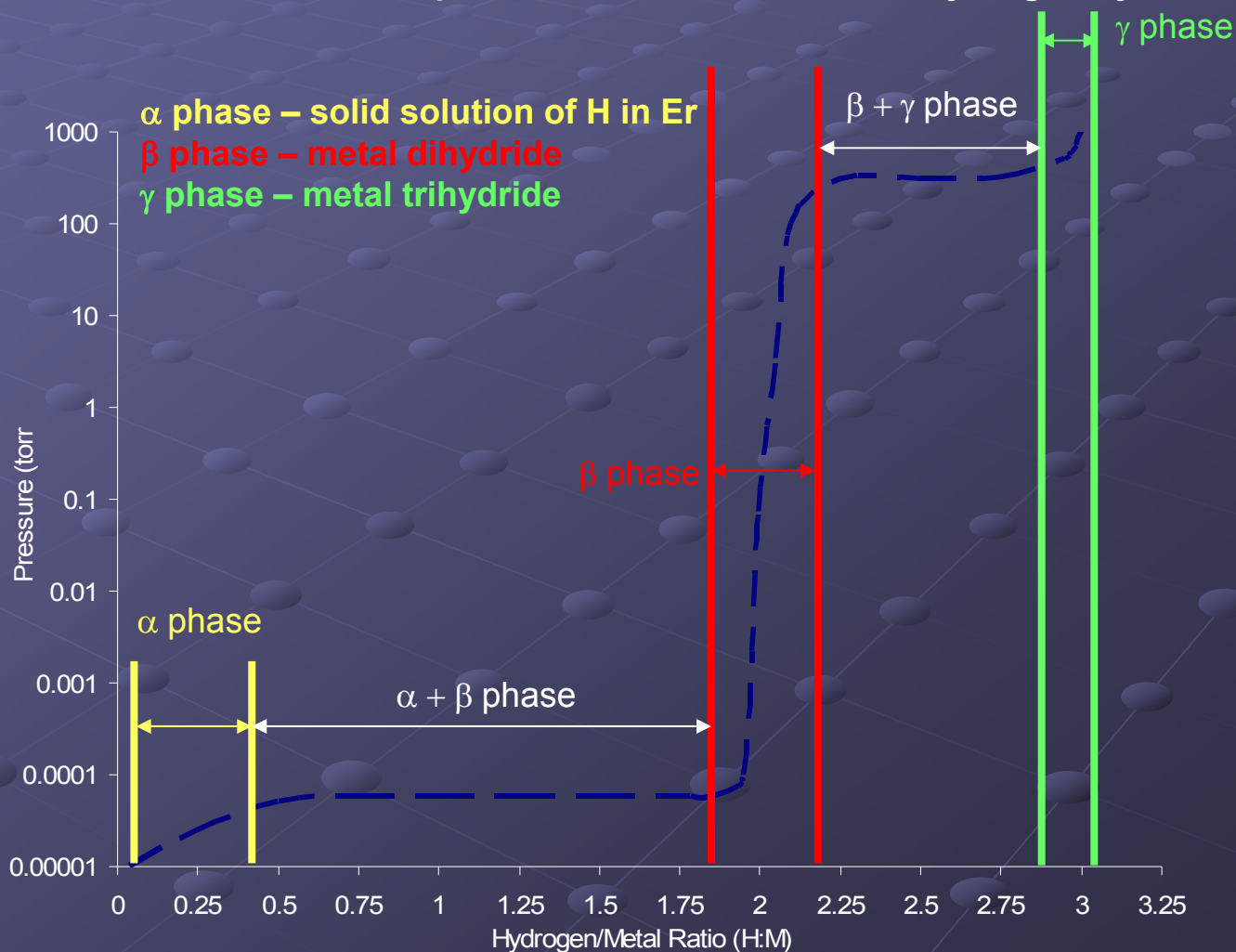
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Introduction

The γ phase of the erbium-hydrogen system is a hexagonal trihydride that is not predicted to be stable at room temperature without an overpressure of hydrogen gas. Here, we report the creation and preliminary physical studies of both thin films and powders of erbium trideuteride that are metastable at ambient conditions.

Generalized Pressure-Composition Isotherm for Erbium-Hydrogen System



PCT Apparatus

Capabilities:

$1 \times 10^{-8} \rightarrow 760^+$ torr

25 to 1000°C

Variable Cooling
Conditions

H, D and HD gas
mixtures available

Pressure and
Temperature to be
controlled to within
1%

Manual and
Automatic Modes

Temperature controlled gas
manifold

Supplemental gas manifold

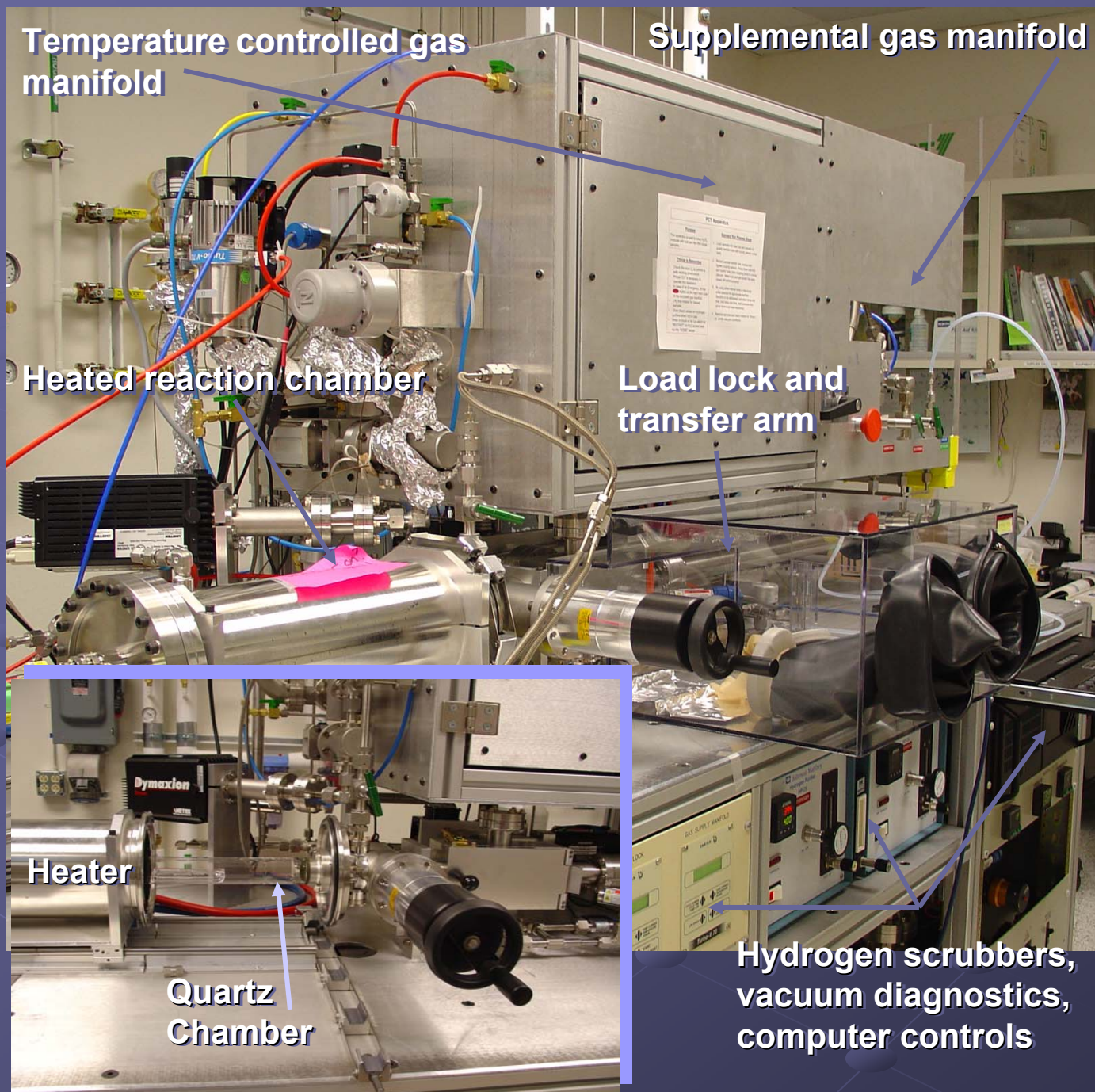
Heated reaction chamber

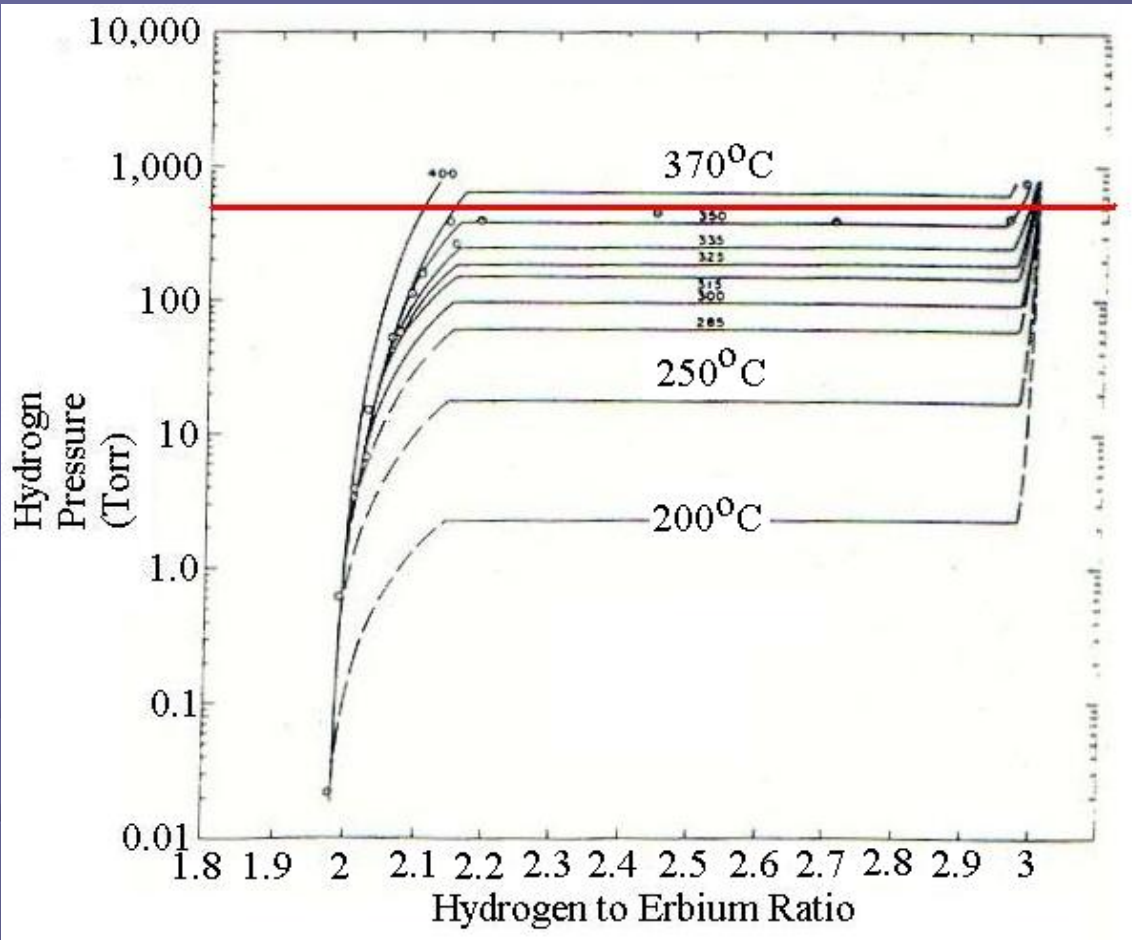
Load lock and
transfer arm

Heater

Quartz
Chamber

Hydrogen scrubbers,
vacuum diagnostics,
computer controls



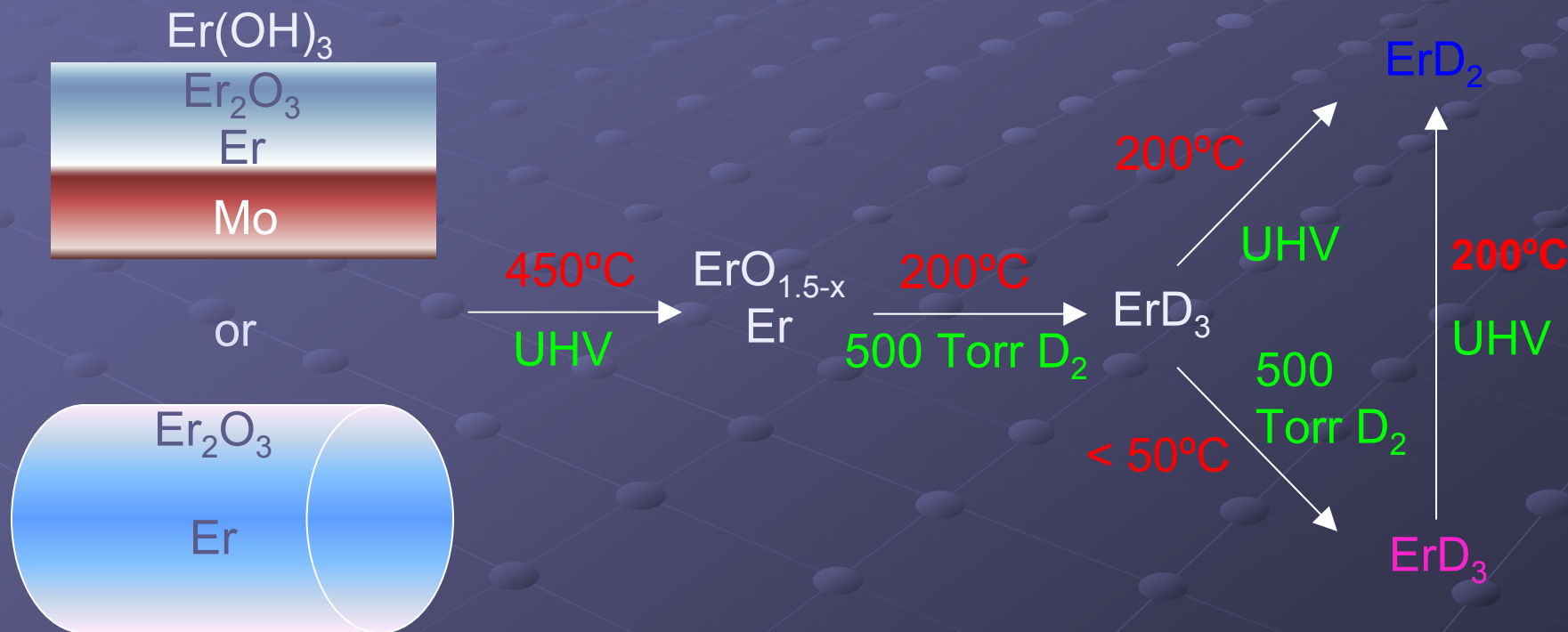


Past PCT curves developed for the erbium-hydrogen system^[1] indicate that by loading at temperature less than 370°C and above 1 torr the γ phase is thermodynamically favored.

Extrapolating these curves to 25°C would suggest that as the γ phase is cooled down in vacuum it should decompose to the β phase.

Experimental Details

Before hydriding an Erbium film or ingot, the erbia layer needs to be activated at elevated temperature. XPS spectra taken of erbium films at elevated temperatures indicate a substoichiometric erbium oxide forms during the activation step. This reduced oxide likely increases the sticking coefficient of the incoming H_2 and may also play an important role in its dissociation.



Sample Preparation

Er ingots

99.9% Er

1 to 10 grams

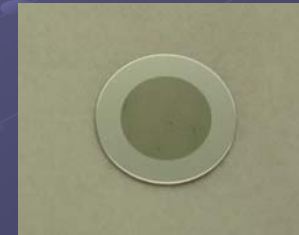
<1000 ppm O₂

<300 ppm N₂

<100ppm H₂

Other rare earths <1000ppm

Other metals <1000ppm



Er Films

5000 Å Er (evaporated from Er ingots)

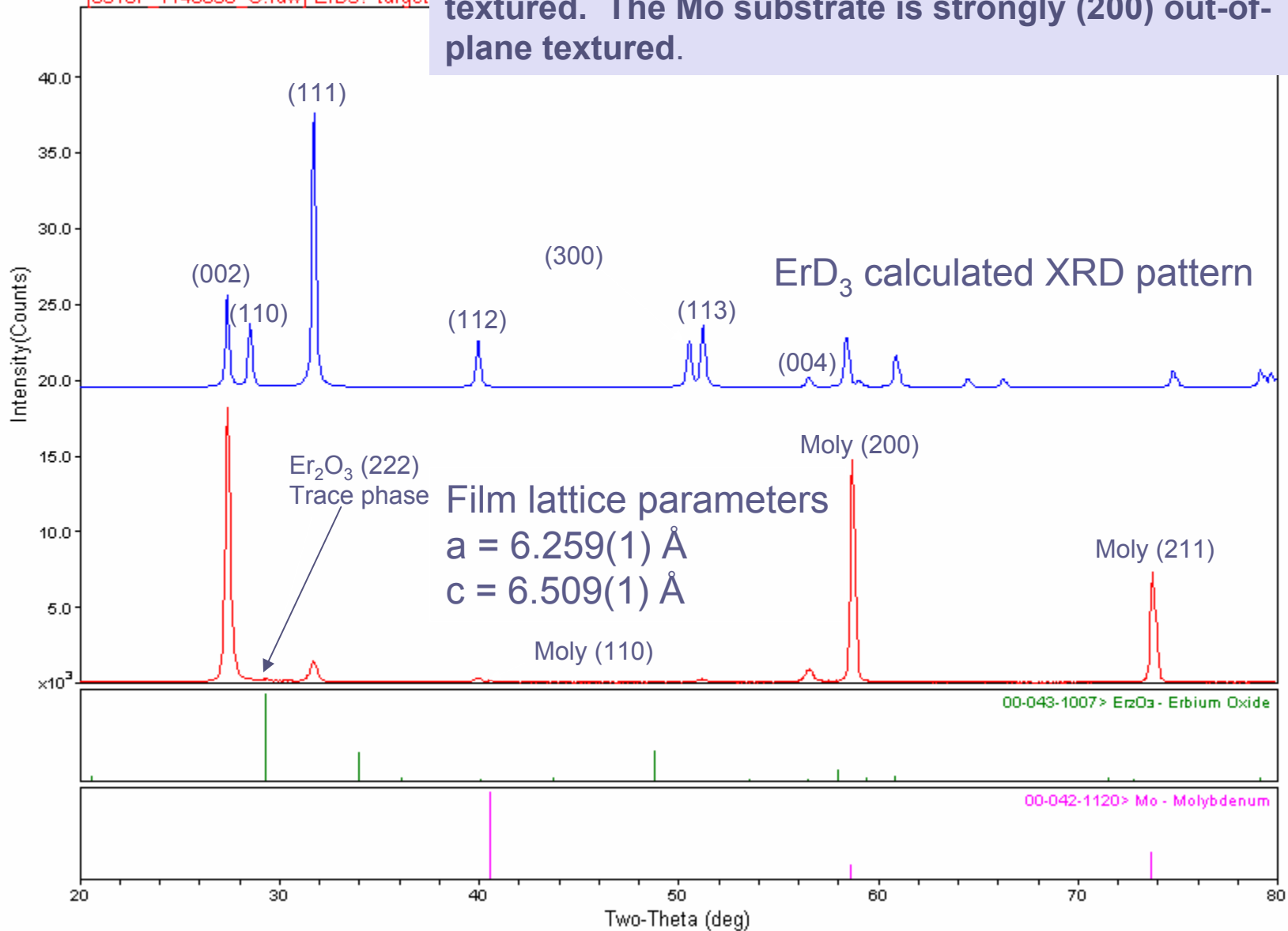
Evaporation rate 20 Å/sec

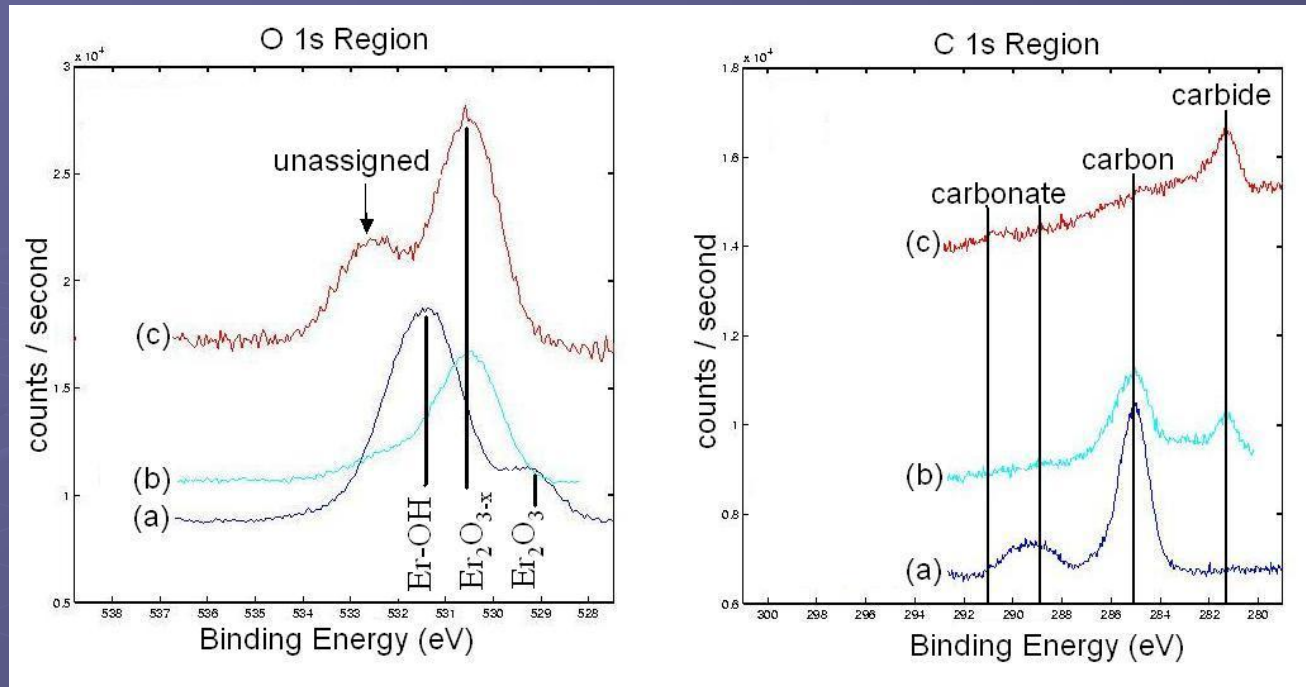
Evaporation temperature 450°C

Mo substrate chemically etched and vacuum fired

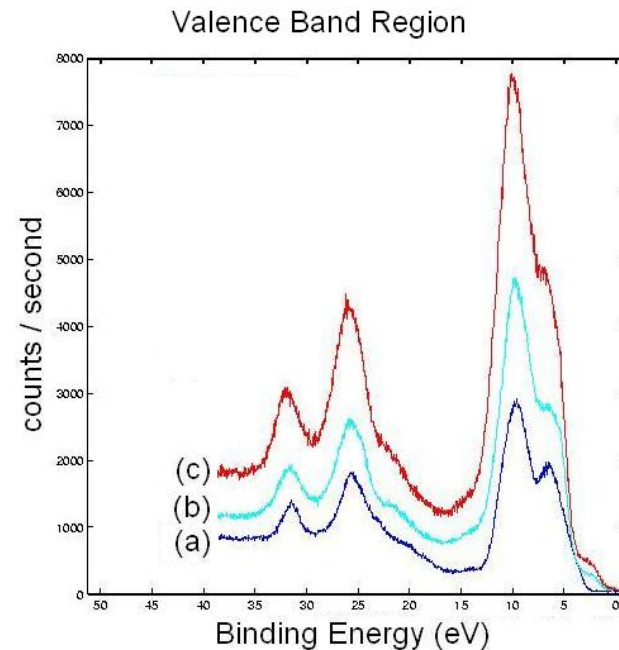
[ErD3A.raw] PowderCell 2.2
[05107_1146030_G.raw] ErD3? target

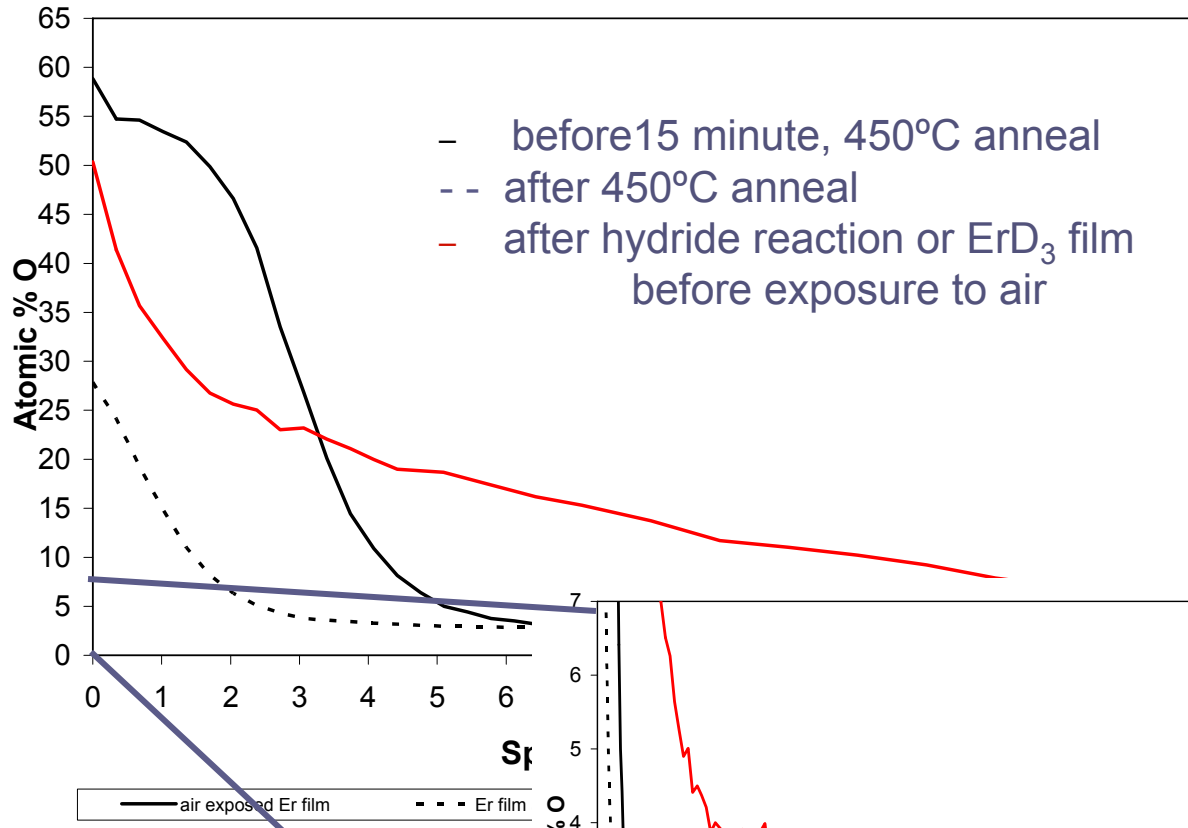
ErD₃ film is strongly (002) or c-axis out-of-plane textured. The Mo substrate is strongly (200) out-of-plane textured.



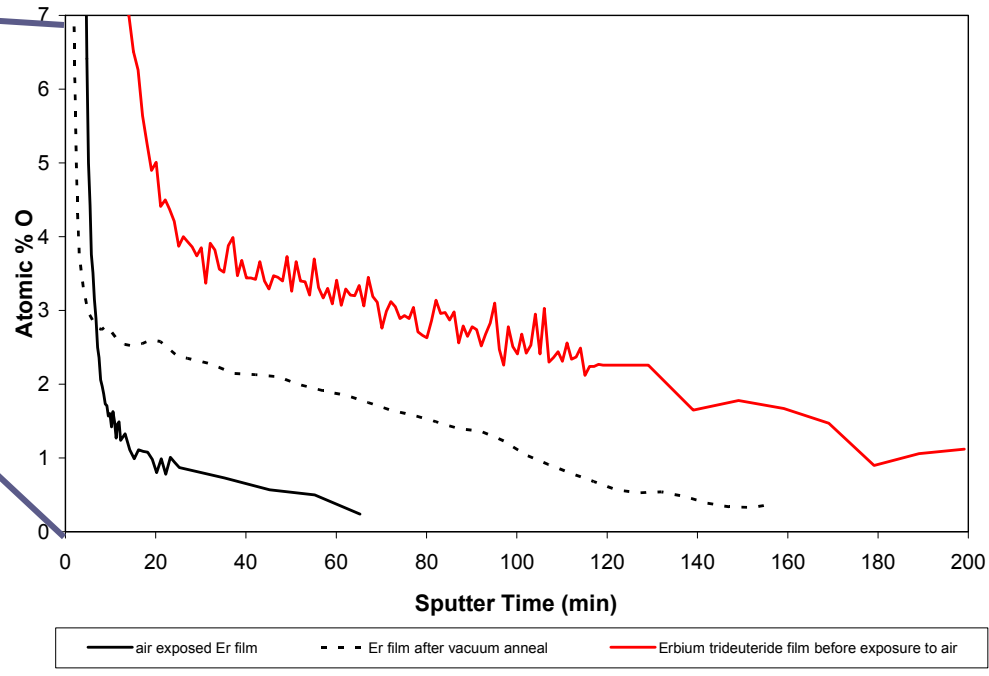


XPS spectra of the O 1s, C 1s, and valence band regions of the erbium film surface (a) before the vacuum anneal at 450°C, (b) after the vacuum anneal at 450°C, and (c) after the vacuum anneal, trihydriding reaction at 200°C and 500 Torr D₂, and before air exposure.





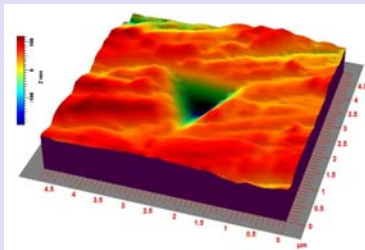
Auger depth profile of O content in Er films show that with both annealing and hydriding, O levels increase throughout the bulk of the film.



Nano-indentation of ErD_3 Film Supported on Mo

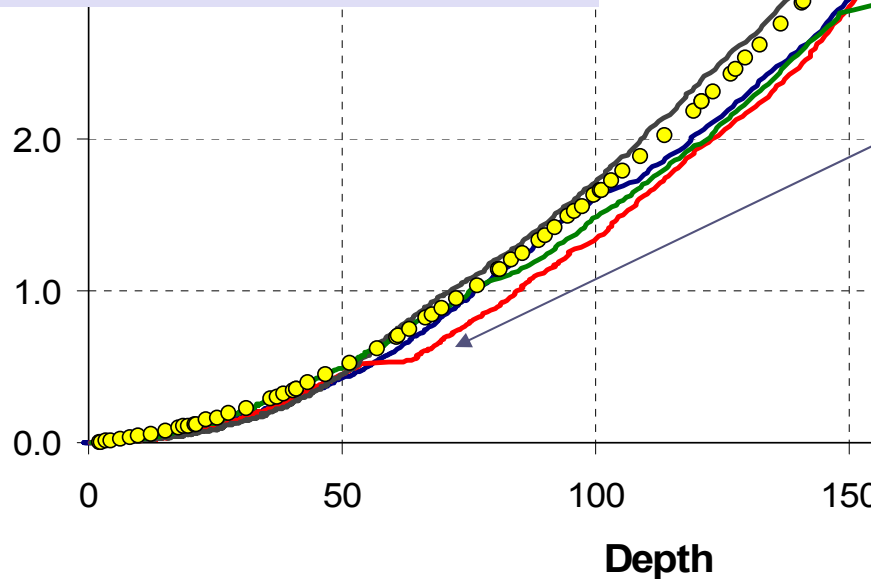
ErD_3 Data fit to lower part of three indents
(to avoid step-ins)

$H = 7.3 \pm 0.6 \text{ Gpa}$
 $E = 162 \pm 9 \text{ Gpa}$



These are deduced assuming isotropic behavior, a Poisson's ratio of 0.25 and a work hardening coefficient of 0.25.

Similar H and E found for comparable ErD_2 films.

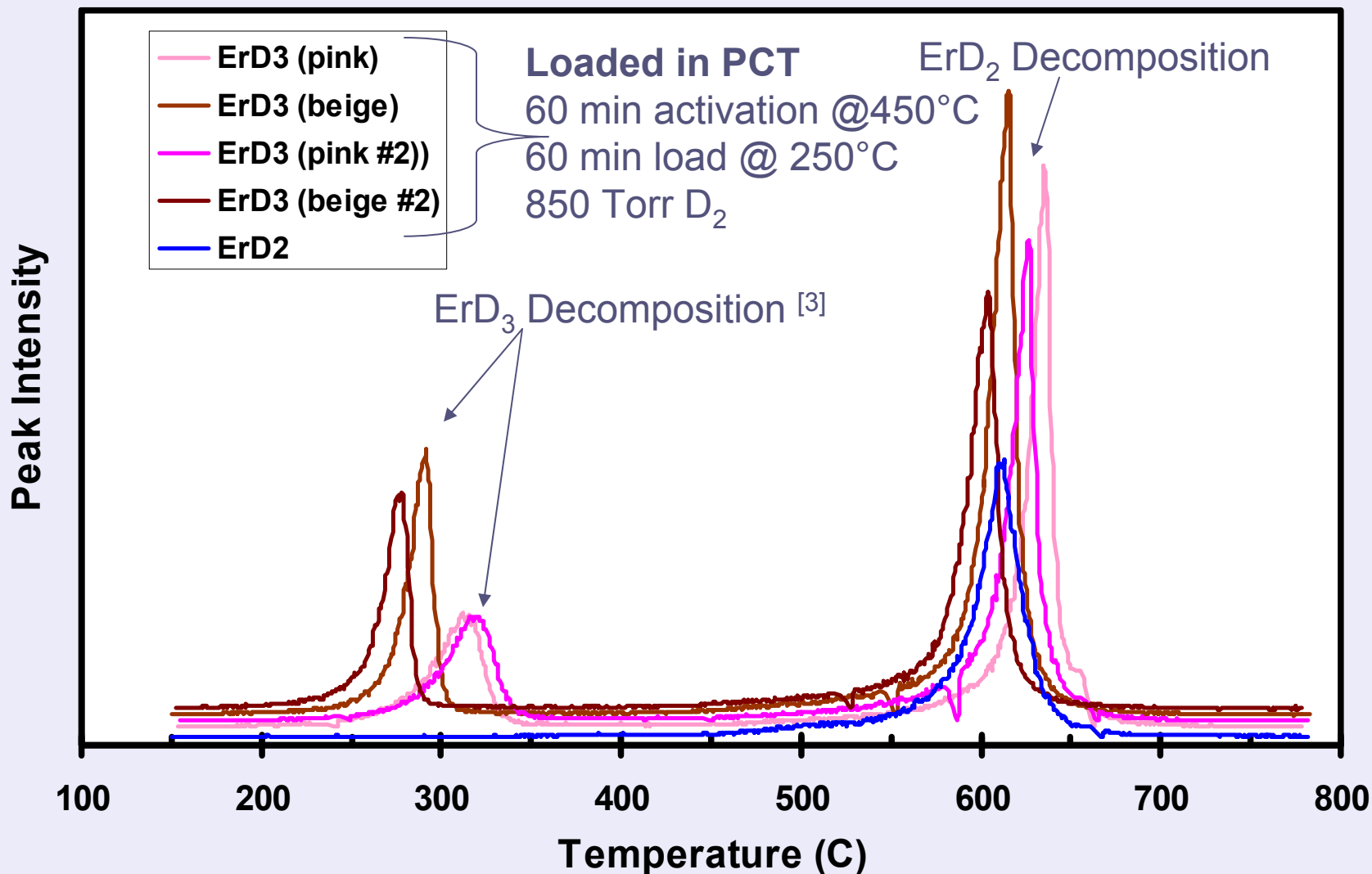


Steps seen in Load vs Depth curves could be:

- Phase transformation under pressure
- Microcrack formation

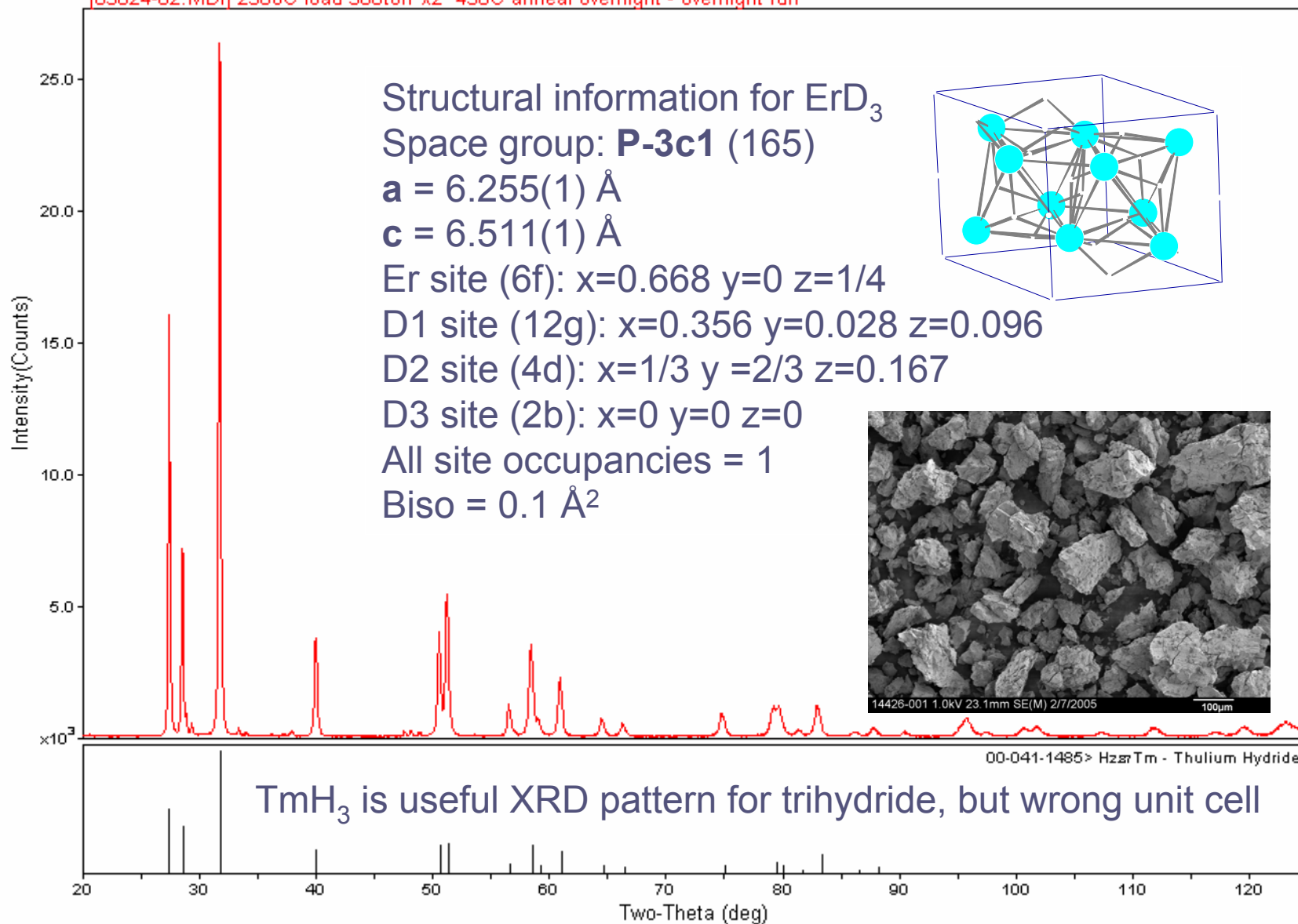
These steps are not seen in comparable ErD_2 films

D₂ Desorption Spectra of ErD₃ Film Supported on Mo

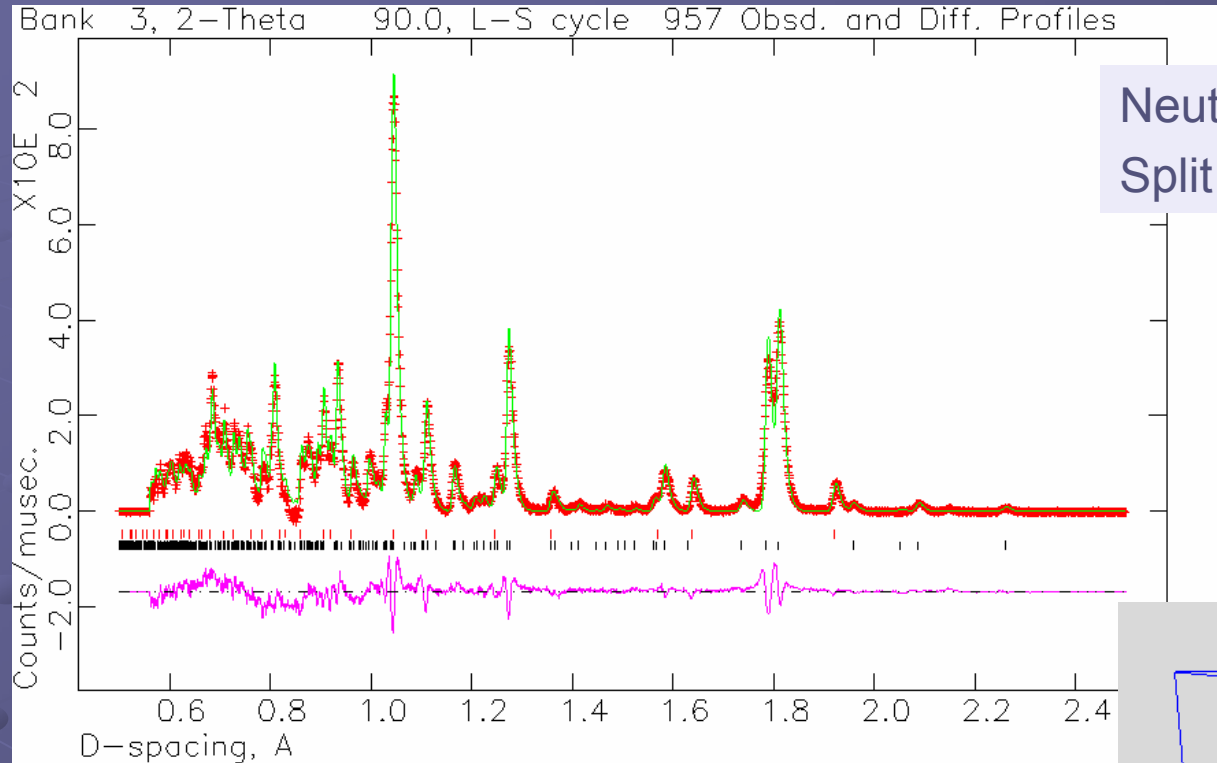


XRD Pattern for Hexagonal ErD_3 Powder - Hydrided at 250°C 300 torr D_2

[05024-02.MDI] 250oC load 300torr x2 450C anneal overnight - overnight run

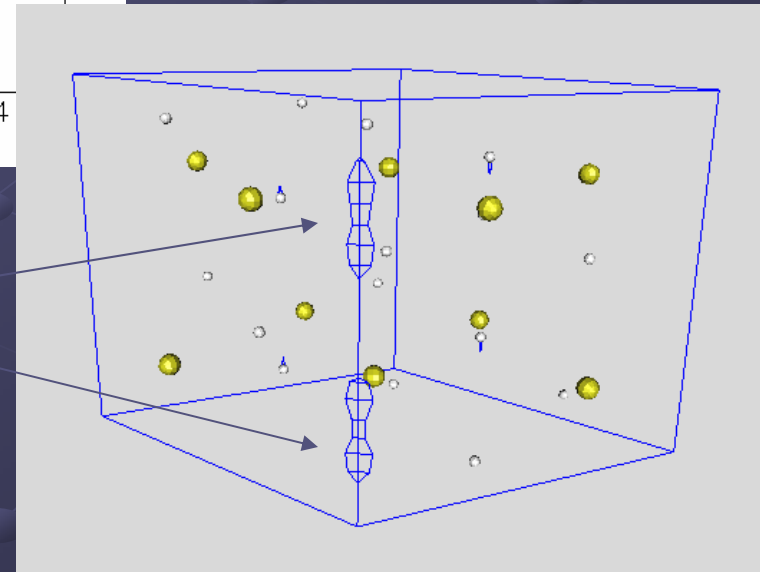


To learn about hydrogen site occupancy and isotopic effects in ErD_3 films and powders, neutron scattering and vibrational spectroscopy studies are under way on ErD_3 , ErH_3 and $\text{ErH}_{1.5}\text{D}_{1.5}$ samples.



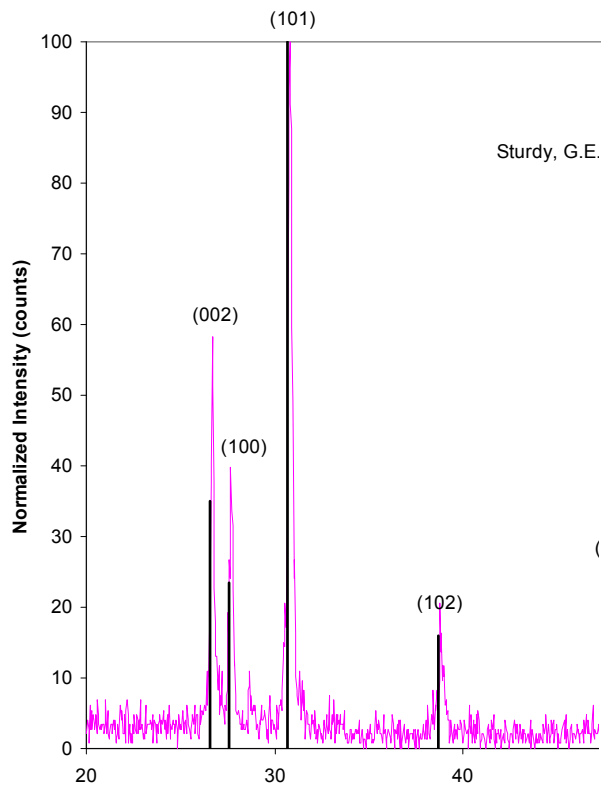
Neutron diffraction pattern of ErD_3
Split site: $R_p = 2.64\%$

Difference Fourier indicates
disordered site-occupancy
along the c-axis at 25°C .

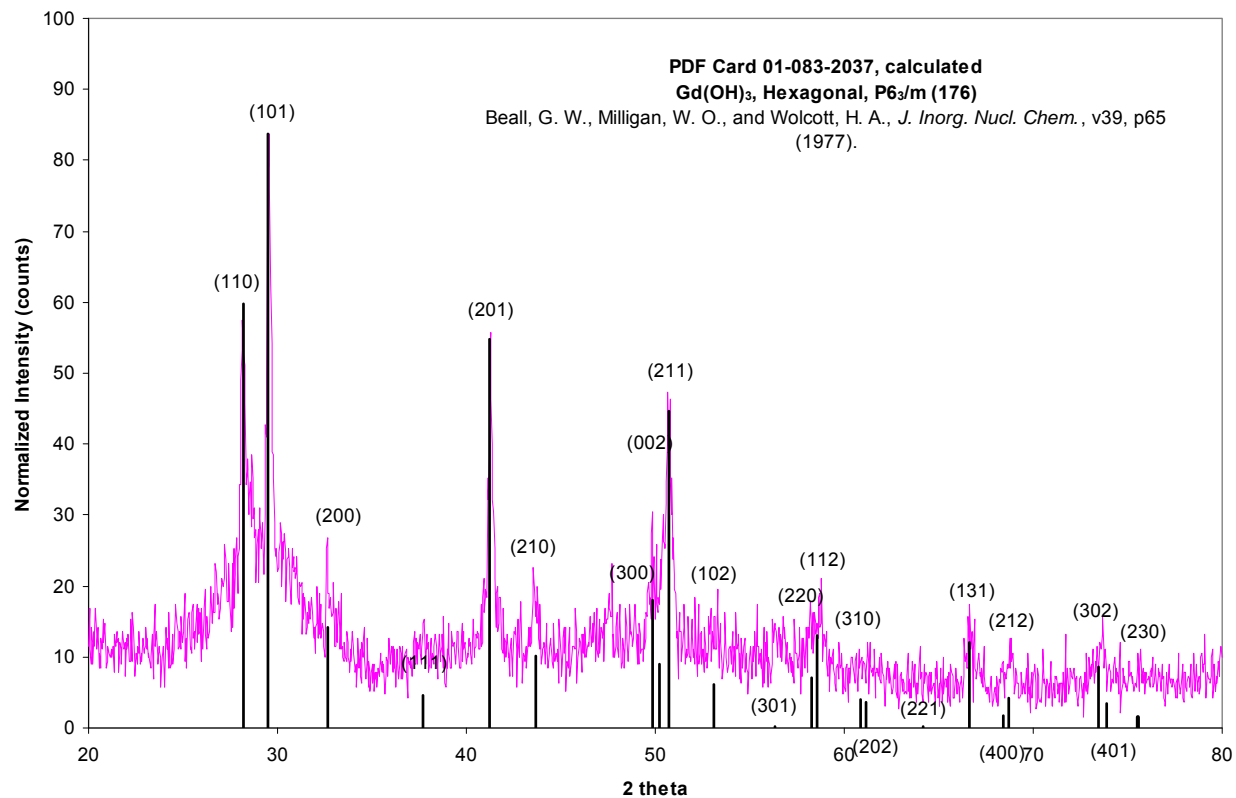


GdD₃ is unstable compared to ErD₃ system. After 60 days, the GdD₃ has decomposed completely to Gd(OH)₃. What makes ErD₃ so special...it's very stable oxide?

XRD of GdD₃ with several hours air exposure



XRD of GdD₃ with two months air exposure



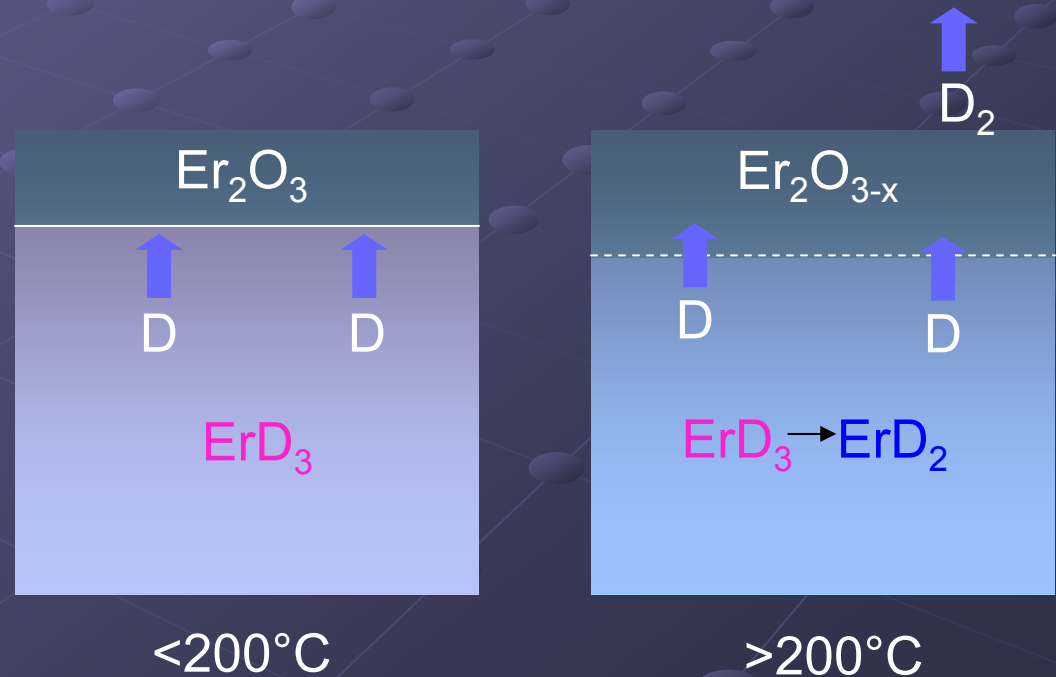
Conclusions



Sputtered area on a ErD_3 supported film. IBA of the blue, sputtered area has an $(\text{H} + \text{D}):\text{Er}$ ratio of 2.1 .

The extrapolated decomposition pressure for ErD_3 could be erroneous *OR* the observed surface **oxides** could be preventing D from diffusing to the surface and D_2 from desorbing. UHV sputter experiments on films, shown right, suggest the later is more likely.

The **oxide** layer (observed on the films and assumed to be also present on the powders) appears to serve as a diffusion barrier under ambient conditions. Diffusion of D through the activated, substoichiometric oxide and recombination to D_2 on the oxide surface begins to occur at 200°C .



Future Path



200°C

time

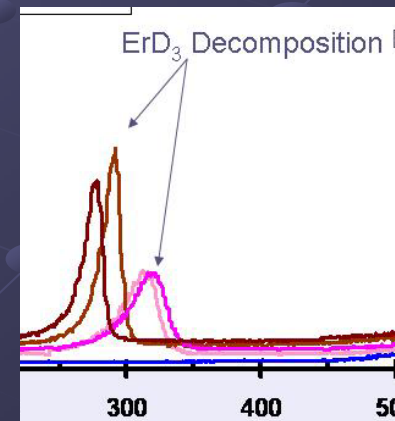
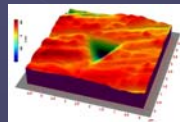
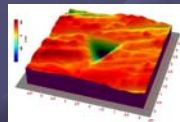
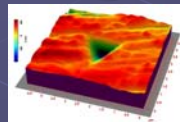
HV



Kinetic explanations (oxide thickness, surface area, etc.) for the observed hysteresis between the decomposition (ErD_3 to ErD_2) and the formation (ErD_2 to ErD_3) are being studied.

Film mechanical properties versus processing history.

Thermal decomposition kinetics versus ErD_3 concentration and film "color".



Acknowledgements

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Simplified Thin Film PCT Measurement

$$P_{equilibrium} = \frac{P_a}{V_{Tot} / V_a} - \frac{1}{2} \cdot \frac{(H : M) \cdot mass_{Er} \cdot RT}{V_{Tot} \cdot AW_{Er}}$$

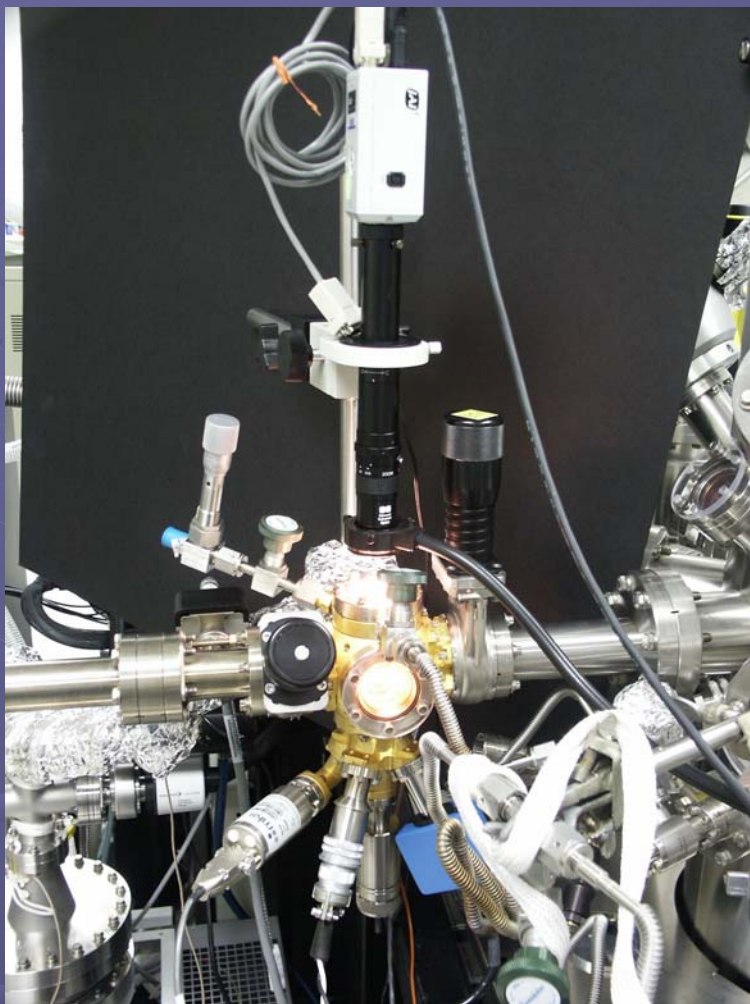
Boyle's Law
Expansion of
aliquot from V_a
into V_{Tot}

Pressure loss due to reaction of H_2 with erbium metal. To maximize the sensitivity of these measurements, this quantity should be *significant* otherwise $P_{equilibrium}$ will not be different than the expansion pressure of the aliquot.

To optimize this experiment for low total $mass_{Er}$, V_{Tot} must be *minimized*.

Calibration is critical to successful PCT measurements.

Hydrogen Reaction Cell/UHV Surface Analysis System



Capabilities:

Reaction Cell

3×10^{-9} → 1000 torr

25 to 550°C

H, D and HD gas mixtures available

Surface Analysis System

8×10^{-11} torr base pressure

-170 to 1000°C

AES

XPS (mono Al source)

UPS

Reflectance IR Spectra for ErD_3 and $\text{ErH}_{1.5}\text{D}_{1.5}$ Powders

