# X-ray and neutron diffraction of Er-hydride films

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# Outline

- Structures of hexagonal Er metal, $ErH_2$ fluorite, Molybdenum
- Texture issues and processing effects
- Idea of pole figure integration
- Promising neutron diffraction work

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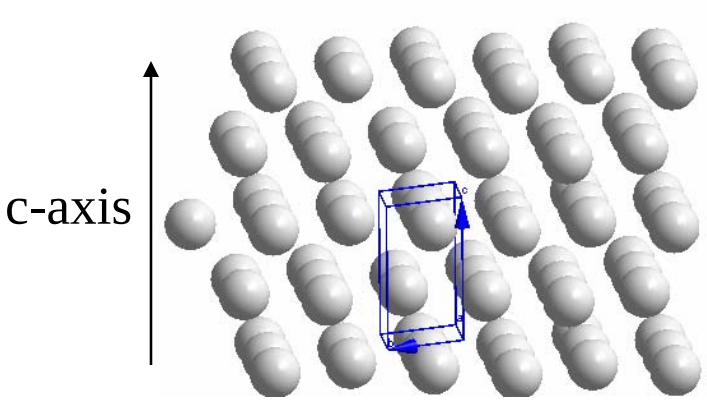
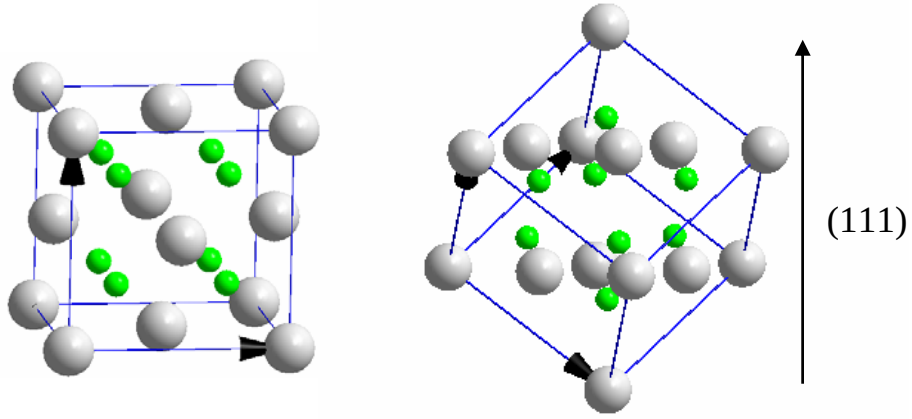
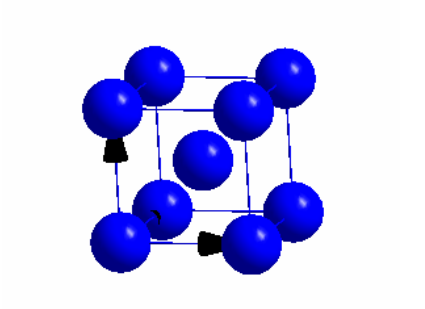
# Structures of target and substrate have high symmetries




Er metal (HCP)




$ErH_2$ Fluorite (FCC)



Moly metal (BCC)

- Er layers shift from HCP to FCC during loading
- Large void in center of fluorite lattice

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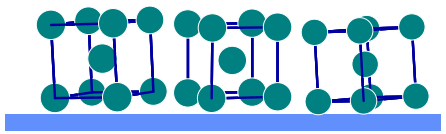
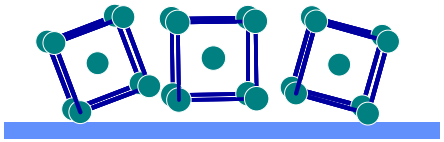
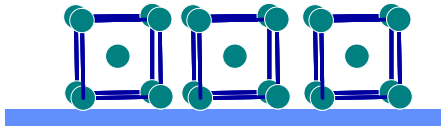
# Texture definitions

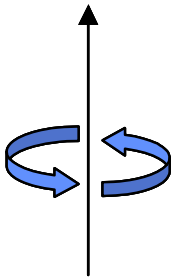
Random grain orientation = no texture

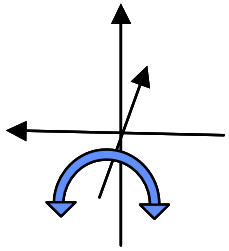
| Fiber | Rolling Texture | Bi-Axial |
|---|---|---|
| out-of-plane (YES)<br>in-plane (NO) | out-of-plane (YES)<br>in-plane: 1-dimension of freedom, other fixed | out-of-plane (YES)<br>in-plane (YES) |

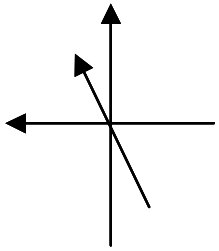












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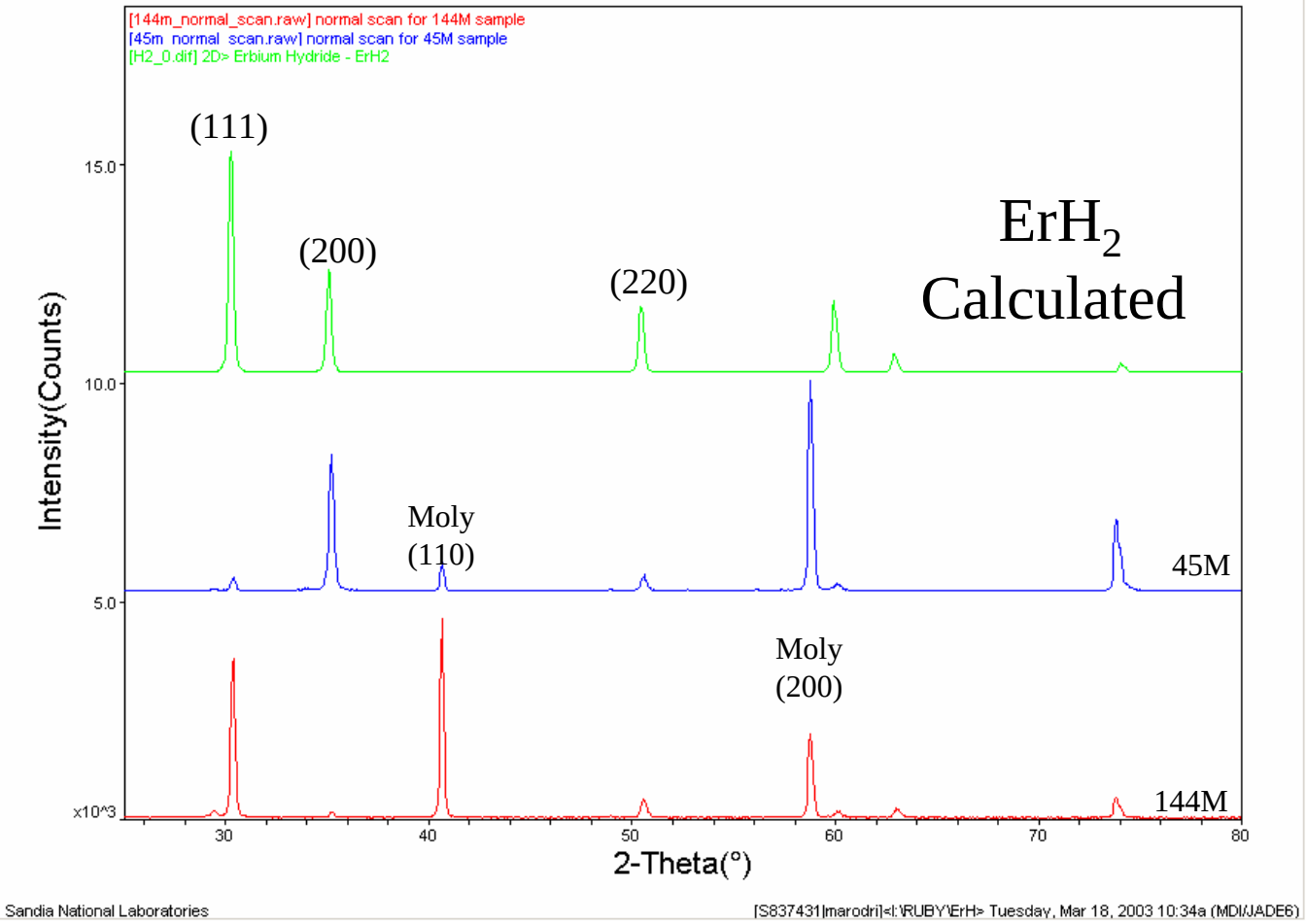
# Typical θ–2θ x-ray diffraction patterns reveal out-of-plane texture effects

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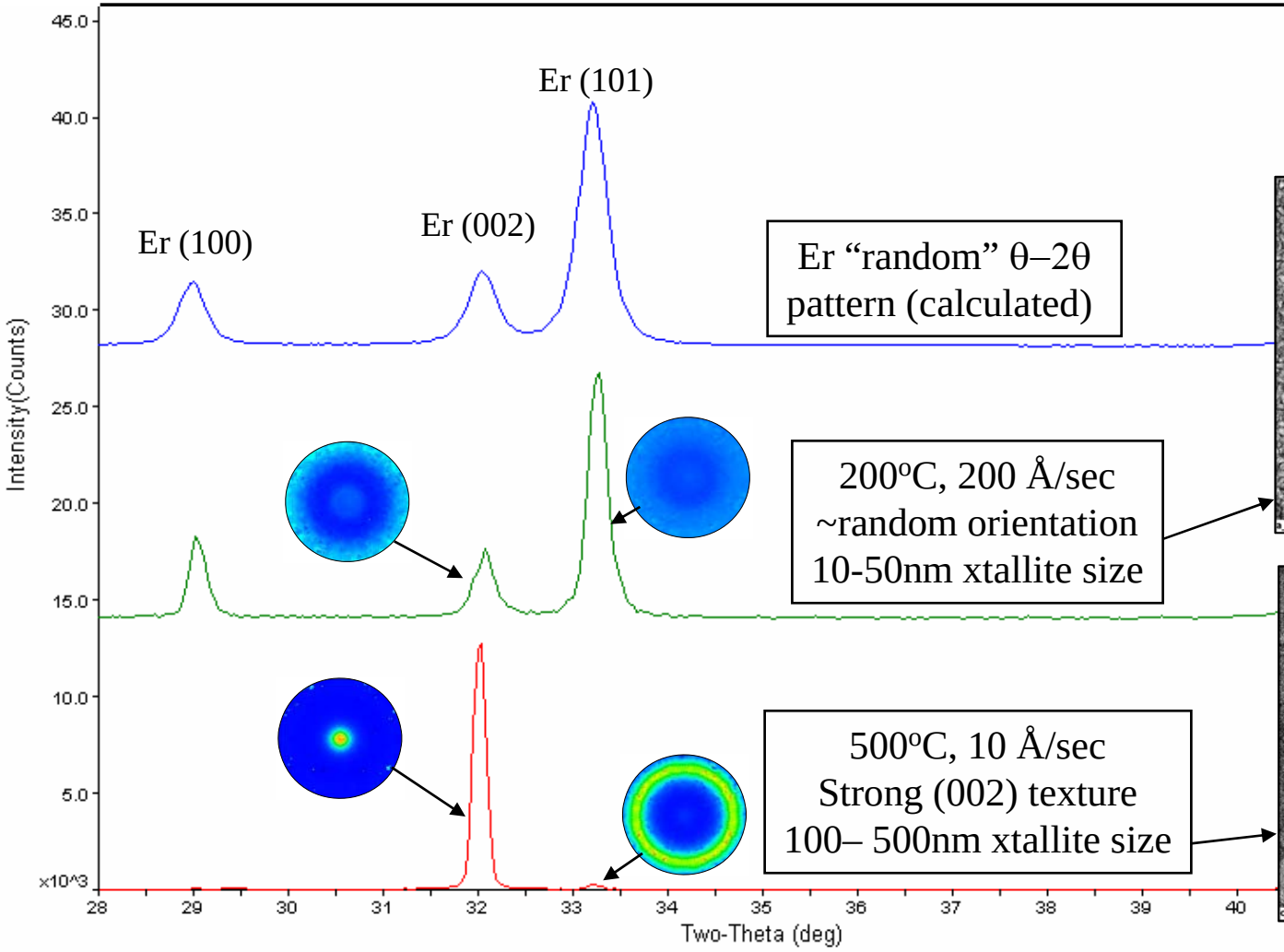
# Several processing issues control texture of Er and $ErH_2$ films

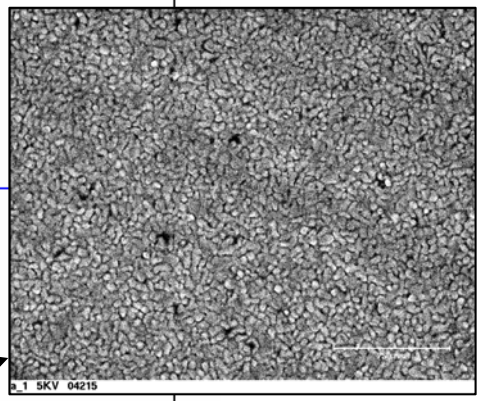
- Er deposition rate and/or temperature
  - Faster deposition rates encourage randomization
  - High deposition temperatures encourage grain growth
- Presence of oxygen
  - $O_2$ encourages Er (002) out-of-plane texture
- Texture of underlying Moly
  - Can dictate Er and $ErD_2$ texture via substrate templating

# Deposition temperature/rate can dramatically alter resulting Er microstructure

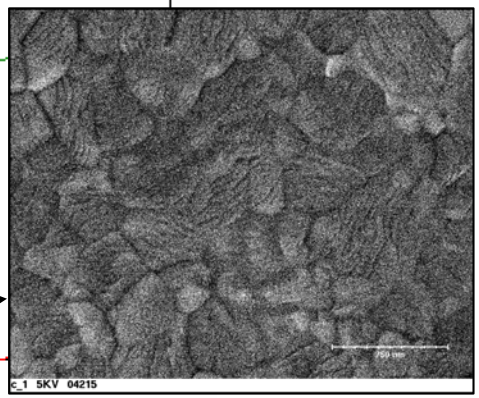



Er "random" θ–2θ pattern (calculated)

200°C, 200 Å/sec
~random orientation
10-50nm xtallite size



500°C, 10 Å/sec
Strong (002) texture
100– 500nm xtallite size



Note: underlying Moly was not strongly textured

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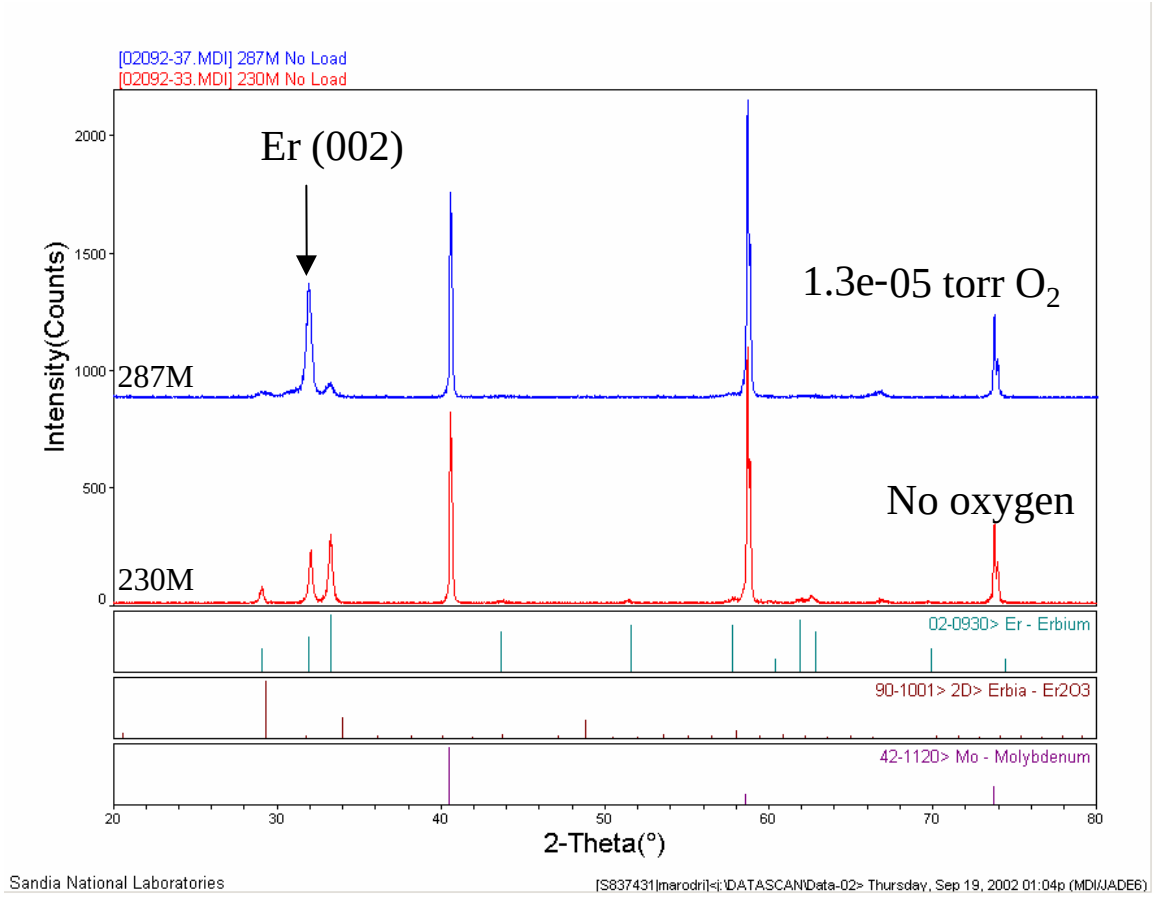
# Presence of oxygen strongly affects texture of deposited Er film




200°C
10 Å/sec

Sample with oxygen shows strong (002) out-of-plane texture

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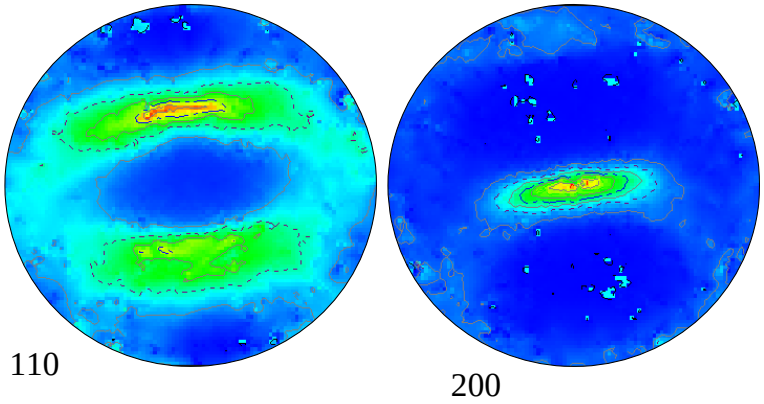
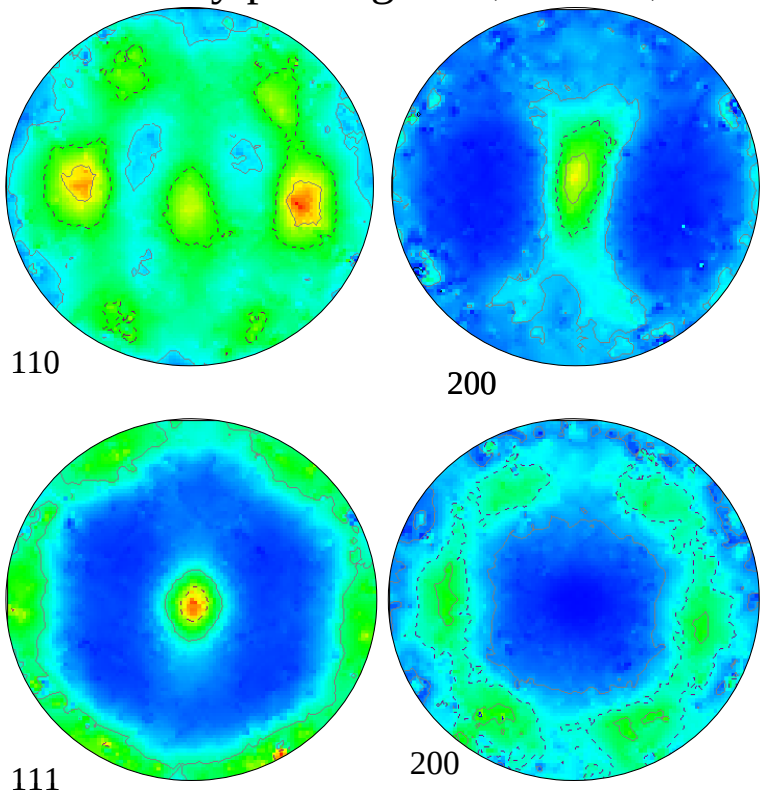
# Substrate etching changes Moly texture - dictates $ErD_2$ grain orientation

**Etched** | 450°C, 200 Å/sec | **No Etch**

Moly pole figures (15x random)




Moly pole figures (10x random)




$ErD_2$ pole figures (5x random)

$ErD_2$ pole figures (5x random)

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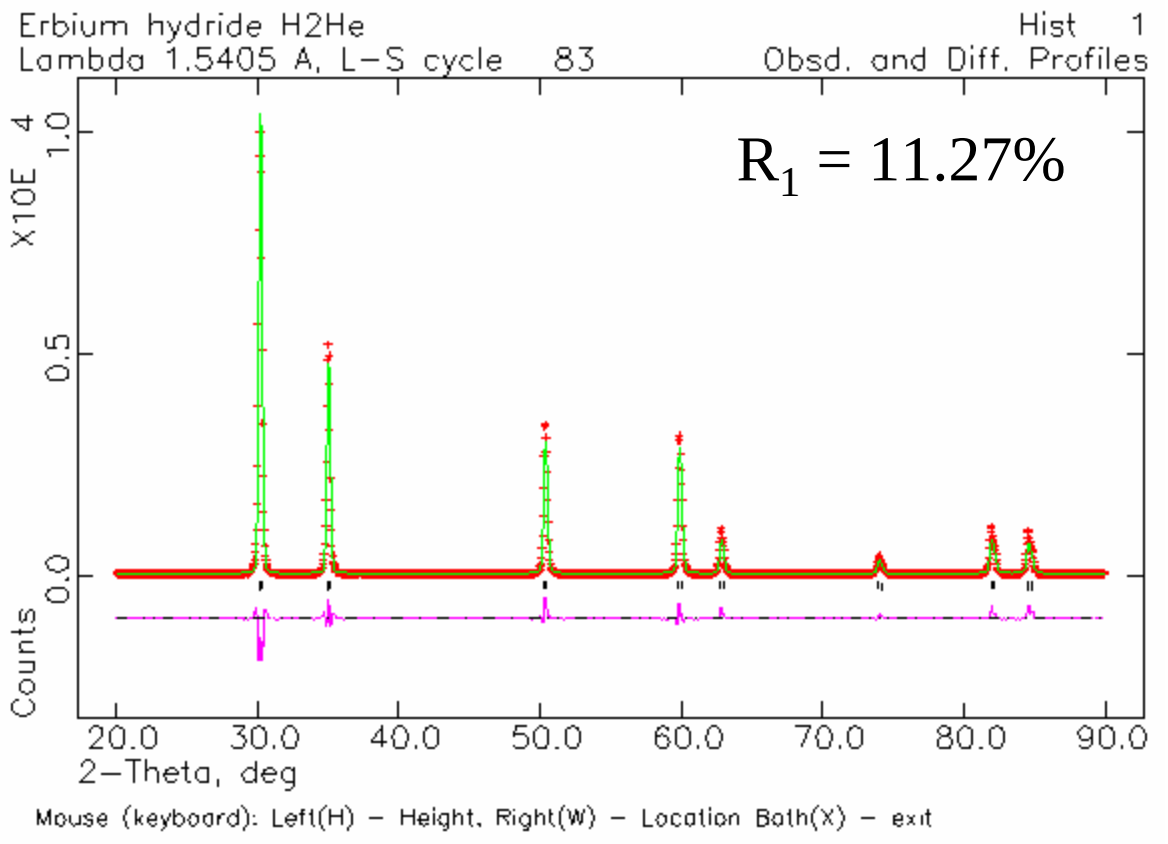
# Can we use XRD data to model Helium in $ErT_2$ lattice?

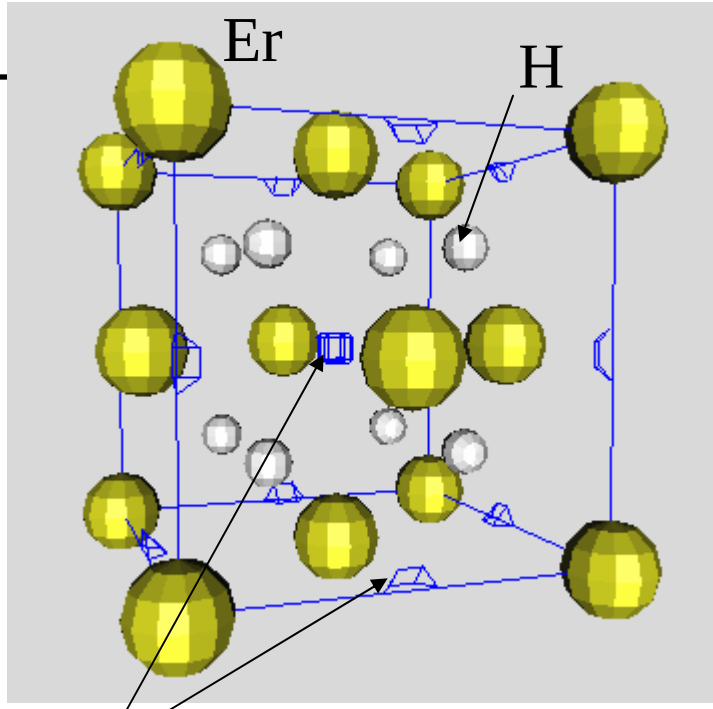
- Generate calculated pattern with Helium atom present in octahedral (oct) site.
- Perform Rietveld structural-refinement on calculated pattern using fluorite structure (without He addition).
- Perform difference-Fourier analysis to see if He electron density is detectable.

- Correct peak intensities are crucial.

# Calculated data for $ErH_2$ with He added at (½ ½ ½) site shows electron density in difference-Fourier mapping




Rietveld refinement of calculated pattern




He detected in oct site via diff-Fourier

Contour plotted at 1.7

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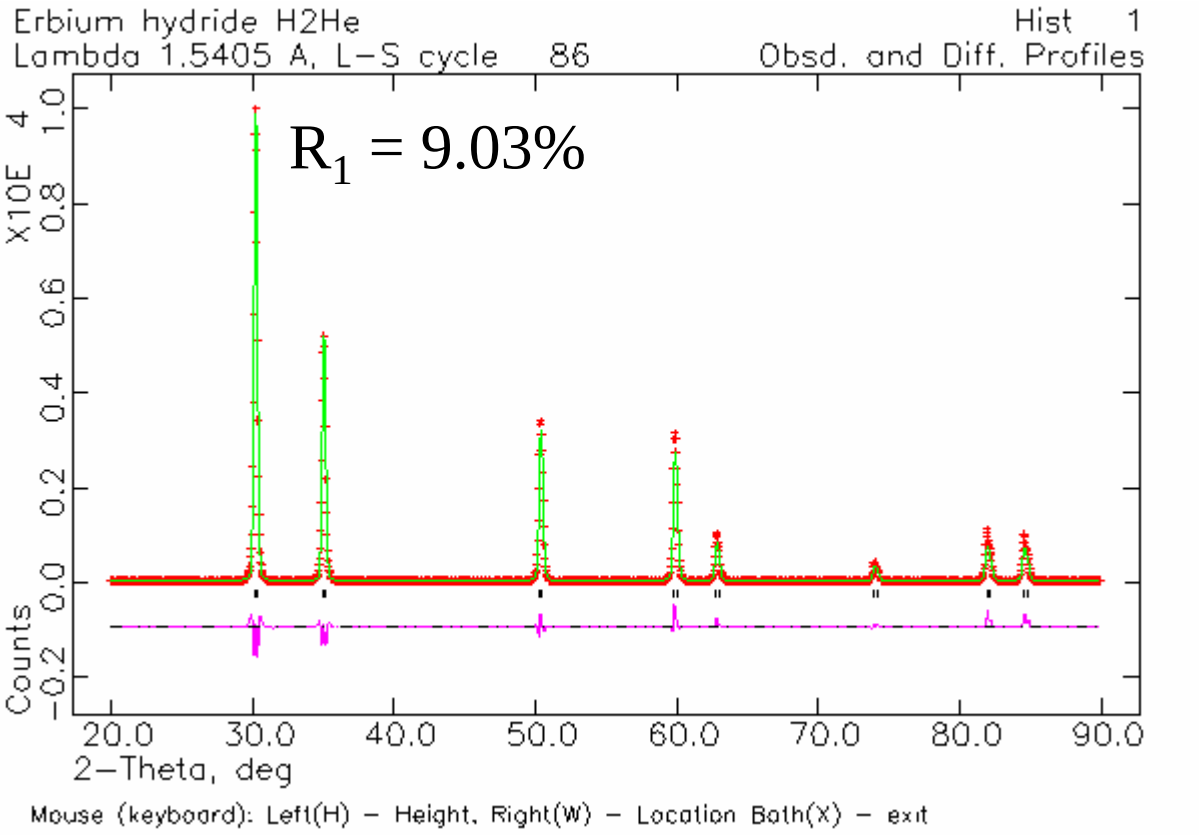
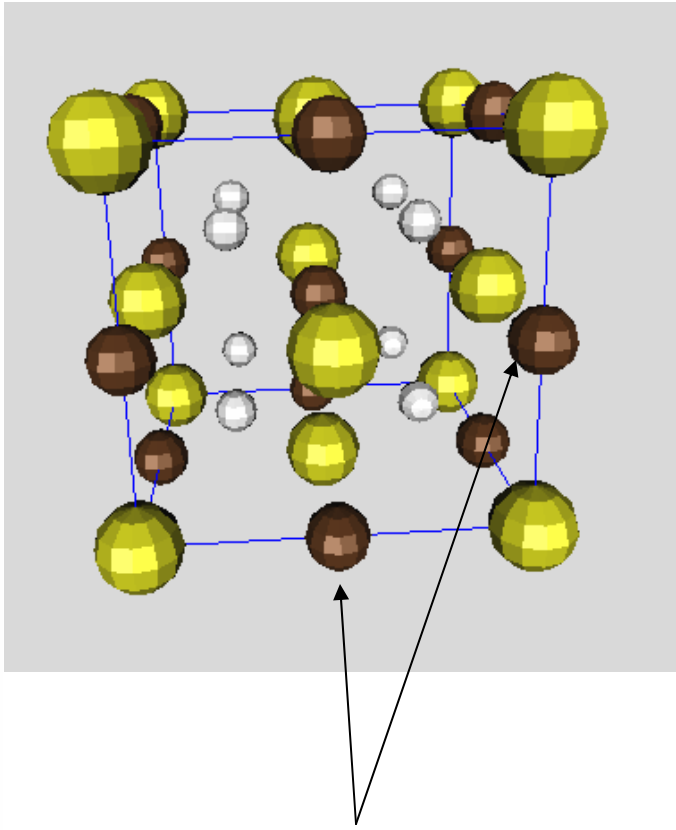
# He was inserted into the model and refined To ~1 or full occupancy (as expected)



He on oct site

Significant drop in R value (-1.72%)

Final difference Fourier map just shows background noise

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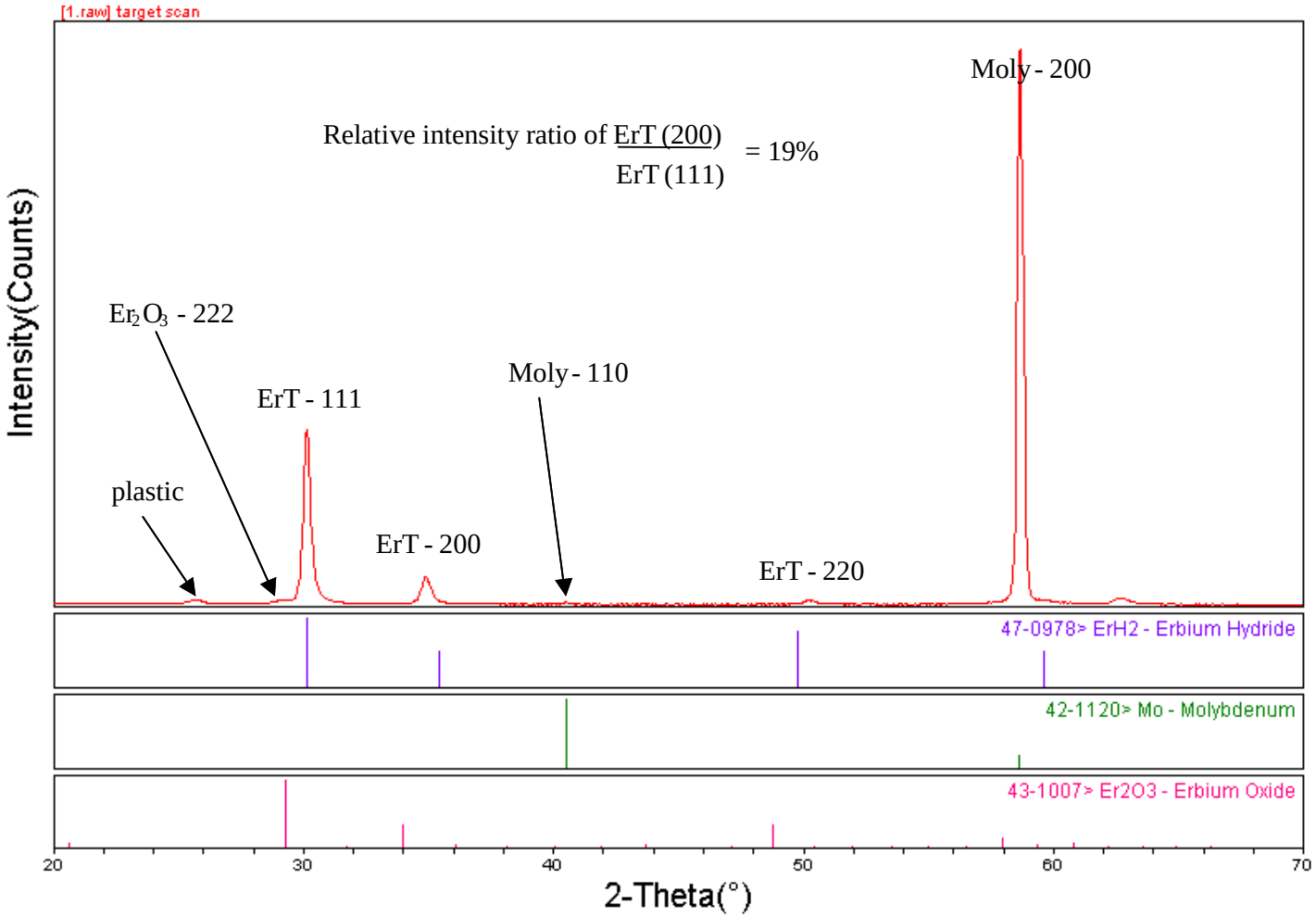
# Accurate integrated intensities are crucial for He site occupancy measurements with XRD

| | (111) | (200) |
|---|---|---|
| $ErH_2$ | 100% | 48% |
| $ErH_2He$ | 100% | 54% |

Biggest change of intensity:
6% increase in (200) with He addition at octahedral site

Challenge for this type of analysis – Texture

# $ErT_2$ films on Moly show texture effects that bias intensities in standard θ–2θ scans

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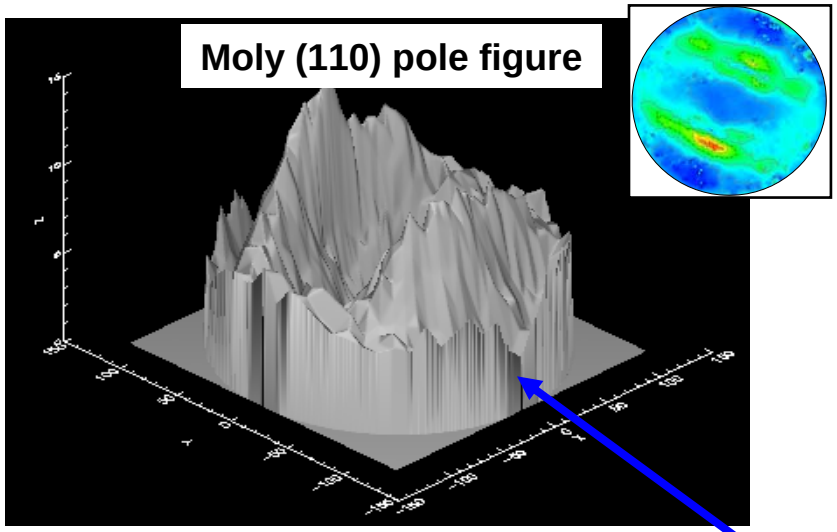
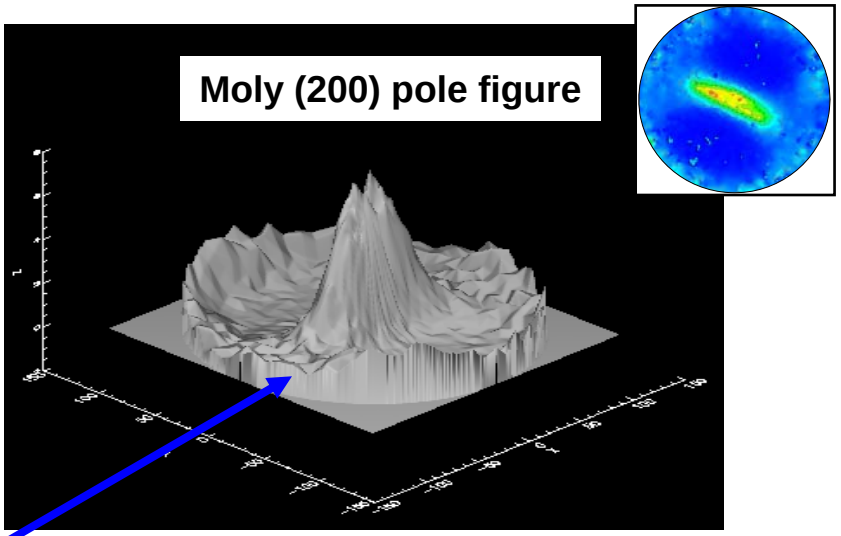
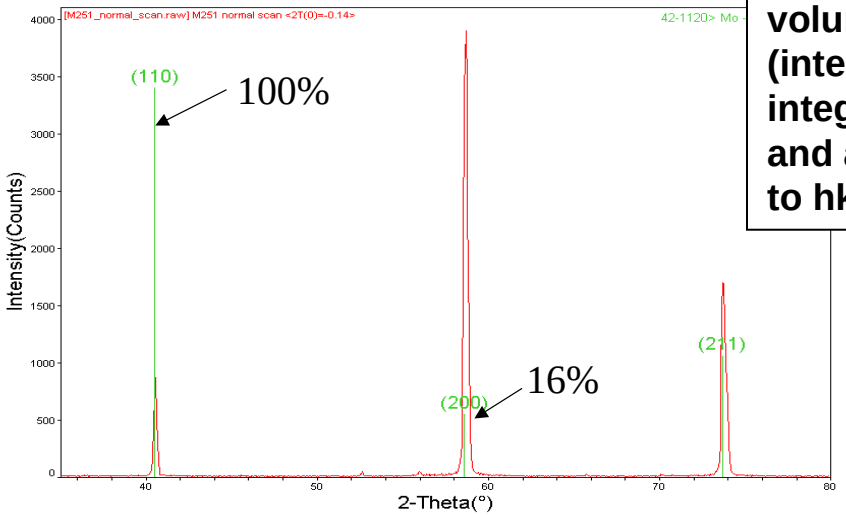
**Approach**: Collect intensity of hkl in many different orientations (pole figure) to un-bias observed intensities due to texturing.




**Pole figure volume (intensity) integrated and assigned to hkl**




| hkl | Obs. RI (%) | Exp. RI (%) | Cor. RI (%) |
|---|---|---|---|
| 111 | 34 | 100 | 100 |
| 200 | 100 | 16 | 14 |

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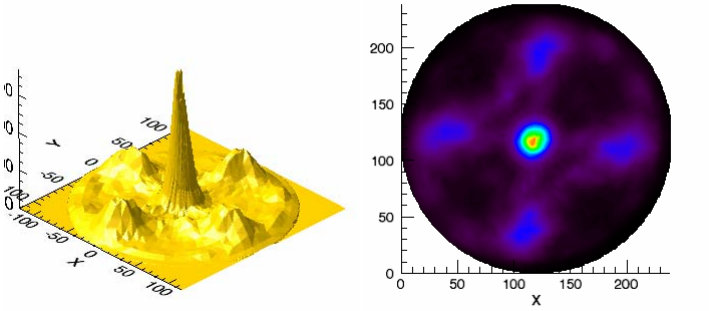
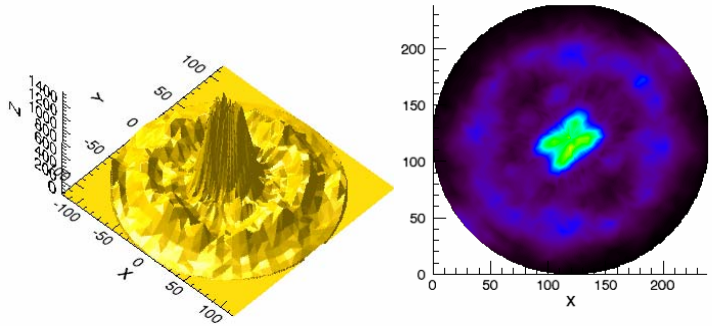
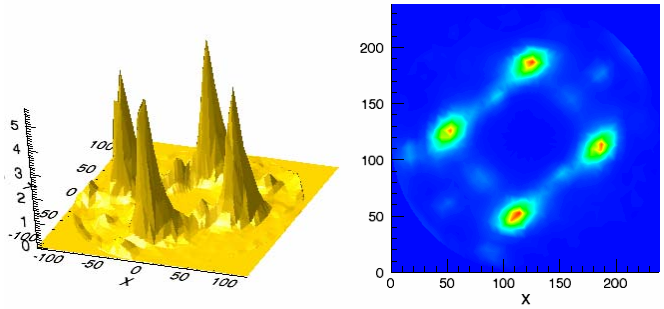
# Pole figures for $ErT_2$ films show texturing effects and influence of Moly substrate

$ErT_2$ (111)

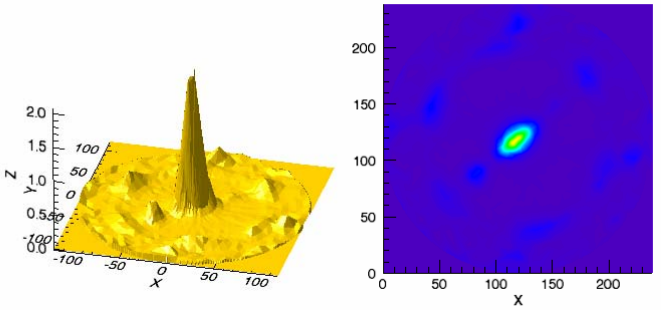


$ErT_2$ (200)





Moly (110)



Moly (200)

Bi-modal distribution of $ErT_2$ grain orientations

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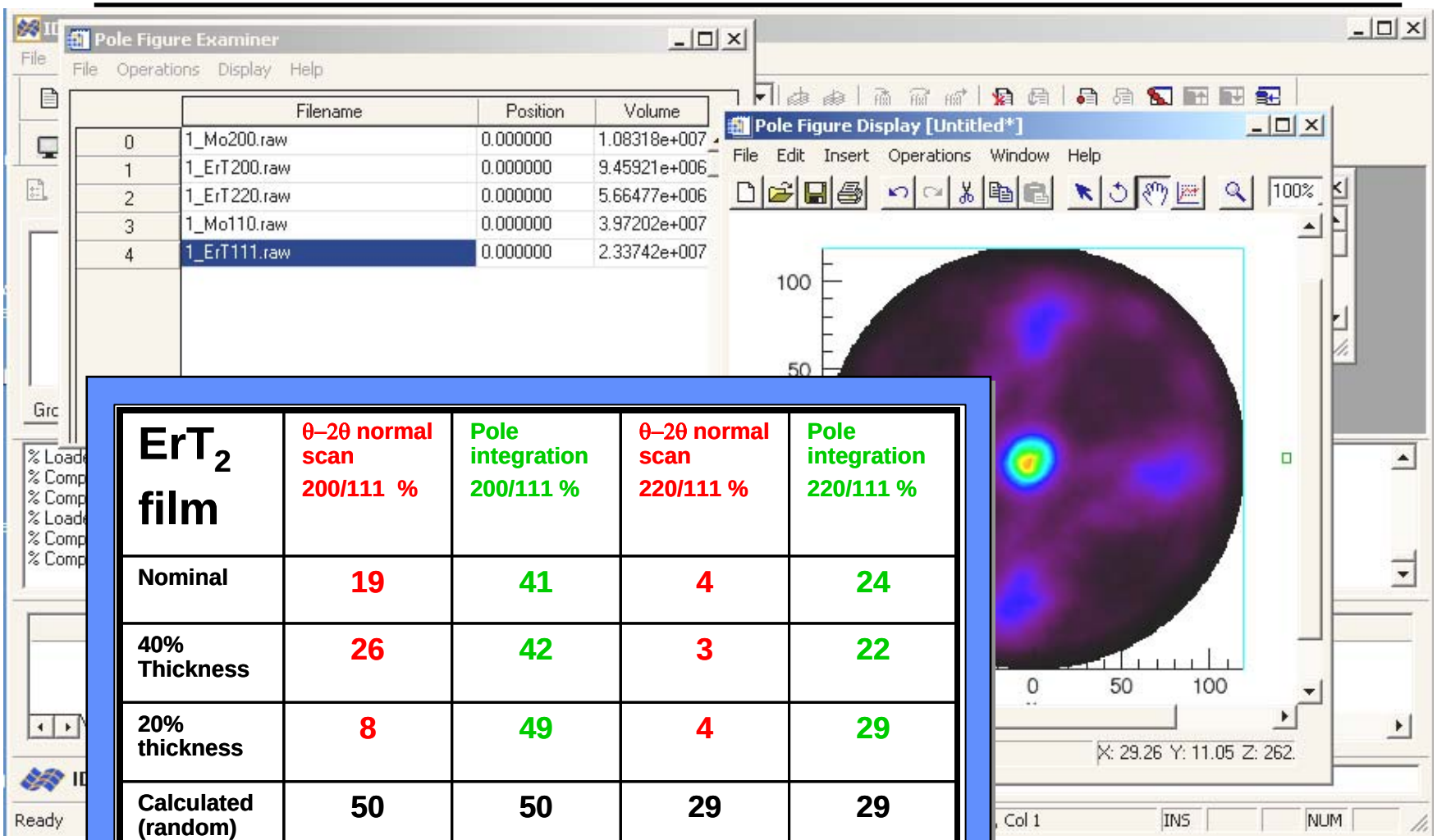
# Relative intensity ratios derived from $ErT_2$ pole figures are much better estimates than θ–2θ scans




| $ErT_2$ film | θ–2θ normal scan 200/111 % | Pole integration 200/111 % | θ–2θ normal scan 220/111 % | Pole integration 220/111 % |
|---|---|---|---|---|
| Nominal | 19 | 41 | 4 | 24 |
| 40% Thickness | 26 | 42 | 3 | 22 |
| 20% thickness | 8 | 49 | 4 | 29 |
| Calculated (random) | 50 | 50 | 29 | 29 |

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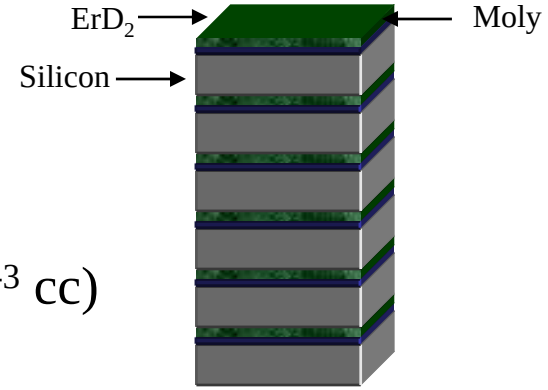
# Neutron diffraction is being investigated as a diagnostic tool for $ErD_2$ films

- Advantage
  - Unlike x-rays, neutrons scatter well from deuterium (and tritium)
- Disadvantages
  - Need large volume of sample
  - Difficulties for analysis of thin films
  - Limited facilities and beam-time
  - Samples may activate

# Recent neutron diffraction experiments at LANSCE /LANL show promise for structural analysis




- First attempt: HIPD (2002)
  - 6 $ErD_2$ films on moly-coated silicon ($ErD_2$ = $0.2x10^{-3}$ cc)
  - Result…
    - need more $ErD_2$ signal, patterns swamped by Si peaks

- Second attempt: HIPPO (2003)
  - 80 $ErD_2$ films deposited on 40 thin Moly foils ($ErD_2$ = $3x10^{-3}$ cc)
  - Result…

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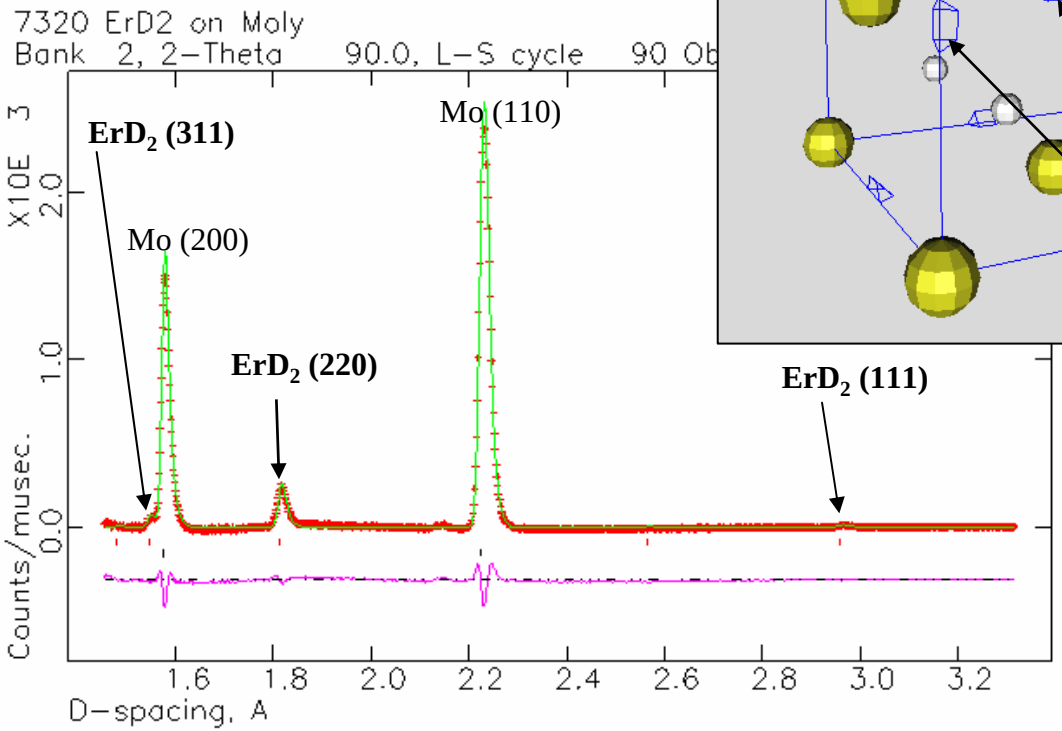
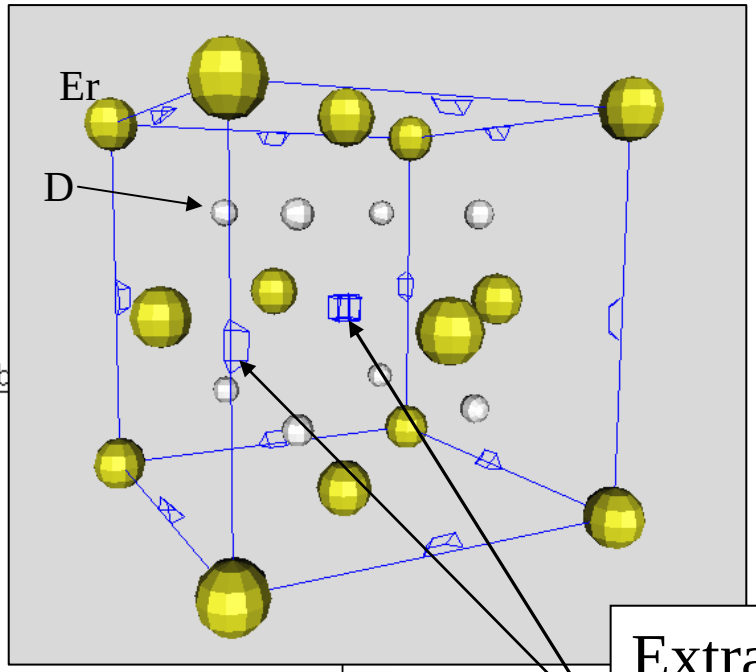
# $ErD_2$ phase detected in neutron diffraction measurement: possible sensitivity to oct. site

Refined weight % $ErD_2$ = **2.1(3)%**
Expected weight % $ErD_2$= 2.6 %

Refined $ErD_2$ lattice parameter, **a = 5.126(2) Å**




Density map at 60% of max scale

Extra density at the ½ ½ ½ site from diff-Fourier

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# Summary

- $ErD_2$ and $ErT_2$ film microstructures are strongly effected by processing conditions.
- Both X-ray and neutron diffraction are being pursued to help diagnose structure/property issues regarding $ErT_2$ films and these correlations to He retention/release.
- Texture issues are great challenge for determination of site occupancy.
- Work on pole-figure-integration looks to have promise addressing texture issues in $ErD_2$ and $ErT_2$ films.

# Acknowledgments


- I would like to thank Darrick Williams and Sven Vogel of LANL for their help with neutron data collection.
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- Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.


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