Hydrogen Site-Occupancy Studies in the $Er(H,D)_2$ System

Hydrogen and Helium Isotopes in Materials

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SNL/NM

Dept. 2564

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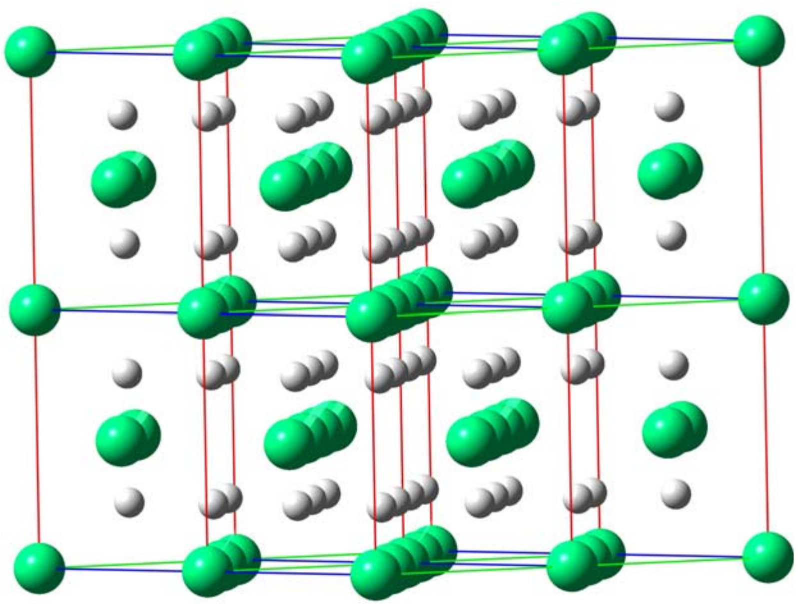
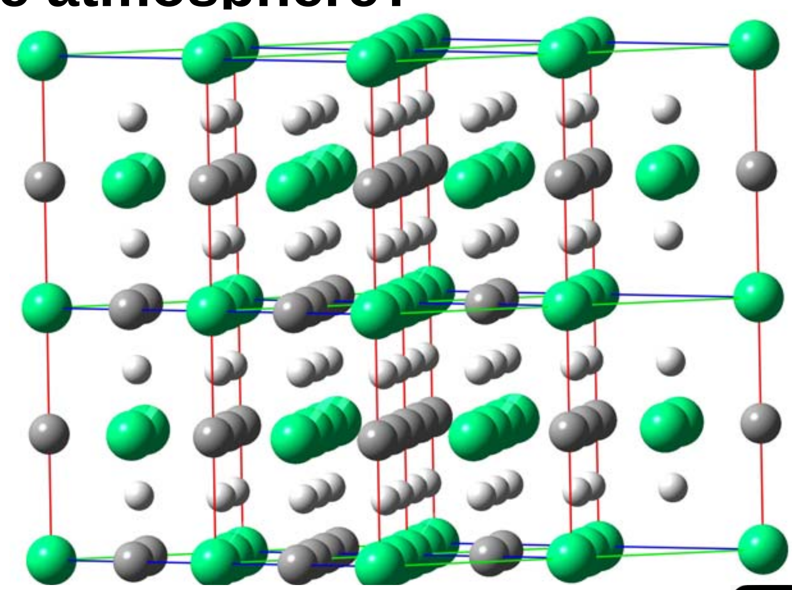
Why is the Hydrogen Site-Occupancy of Interest to Us?

- Primary interest in $ErT_{2-x}He_x$
  - How does the site-occupancy effect helium bubble nucleation and growth?
  - How does the site-occupancy effect the amount of helium released into the atmosphere?



Without octahedral site occupancy



With octahedral site occupancy

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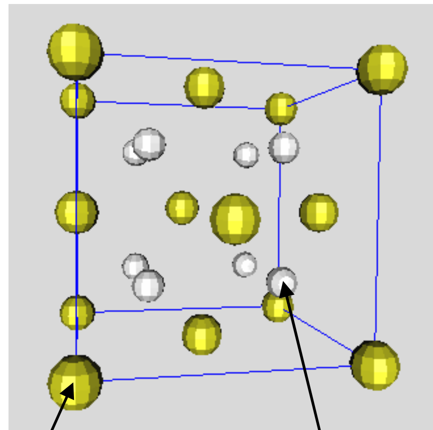
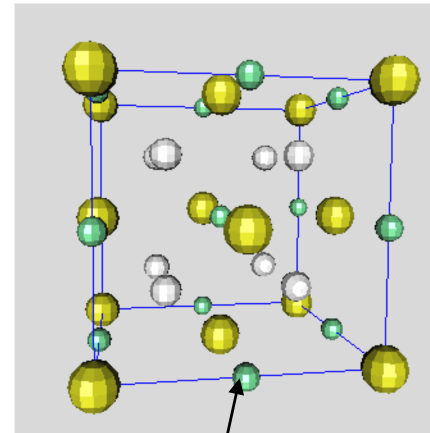
The Two Main Features of the ErH_2 System

- **Crystal Structure**
  - **CaF_2 Structure**



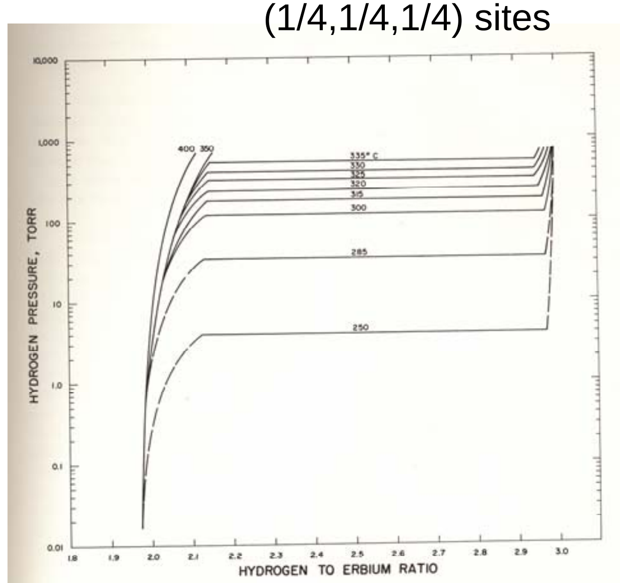
Erbium fcc lattice

H on tetrahedral (1/4,1/4,1/4) sites



Octahedral (1/2,1/2,1/2) sites may also be occupied

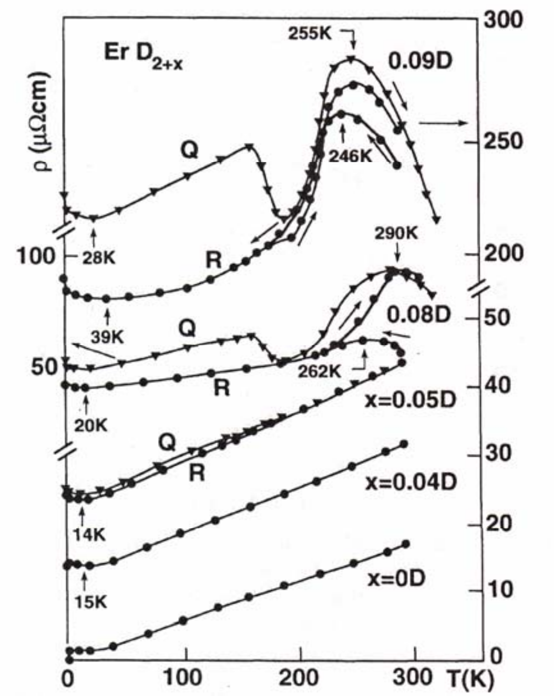
- **PCT Diagram**



C. E. Lundin "The Erbium-Hydrogen System" (1965)

Several different methods to measure the site-occupancy

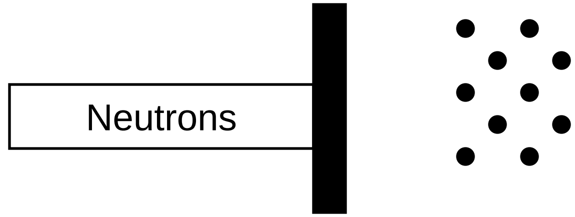
- Vibrational Spectroscopy's
  - FTIR/Raman
  - Inelastic Neutron Scattering Spectroscopy
- Direct measures
  - Neutron Diffraction
- Indirect Measures
  - Resistivity
  - Optical Properties
  - Many others…



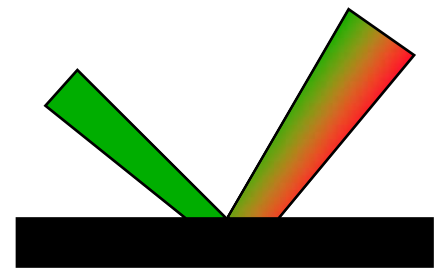
Vajda and Daou, Phys. Rev. B, Vol. 49, 3275 (1994)

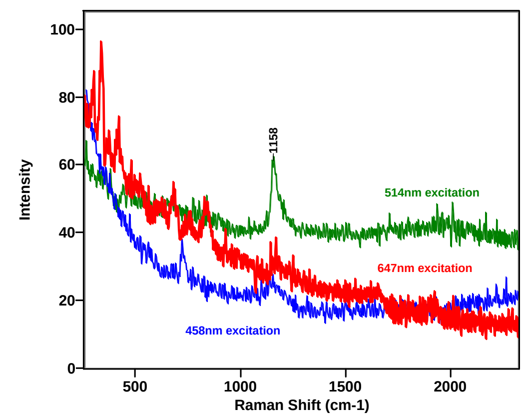
How this talk will proceed.

- Neutron Diffraction



- Vibrational Spectroscopy's
  - FTIR
  - Raman
  - Inelastic Neutron Scattering Spectroscopy





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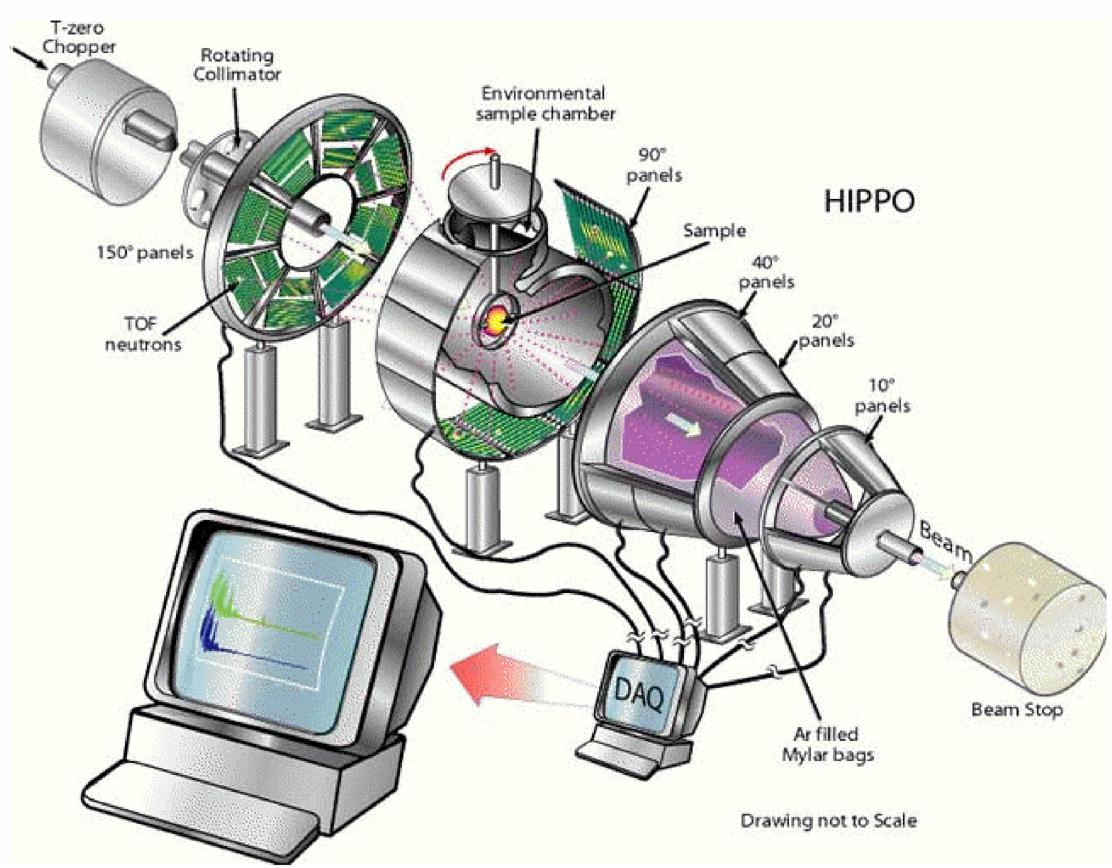
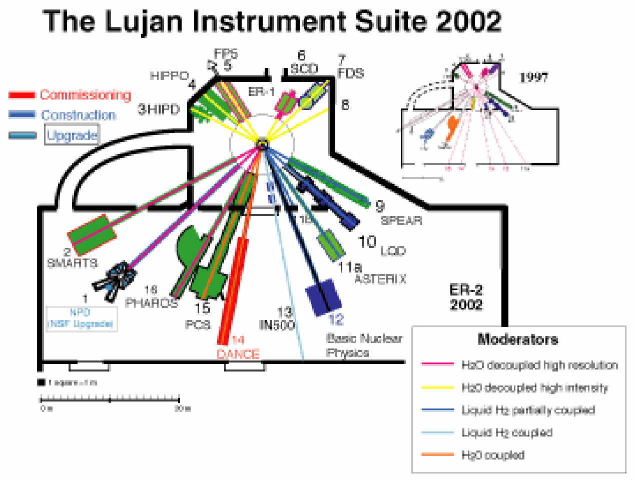
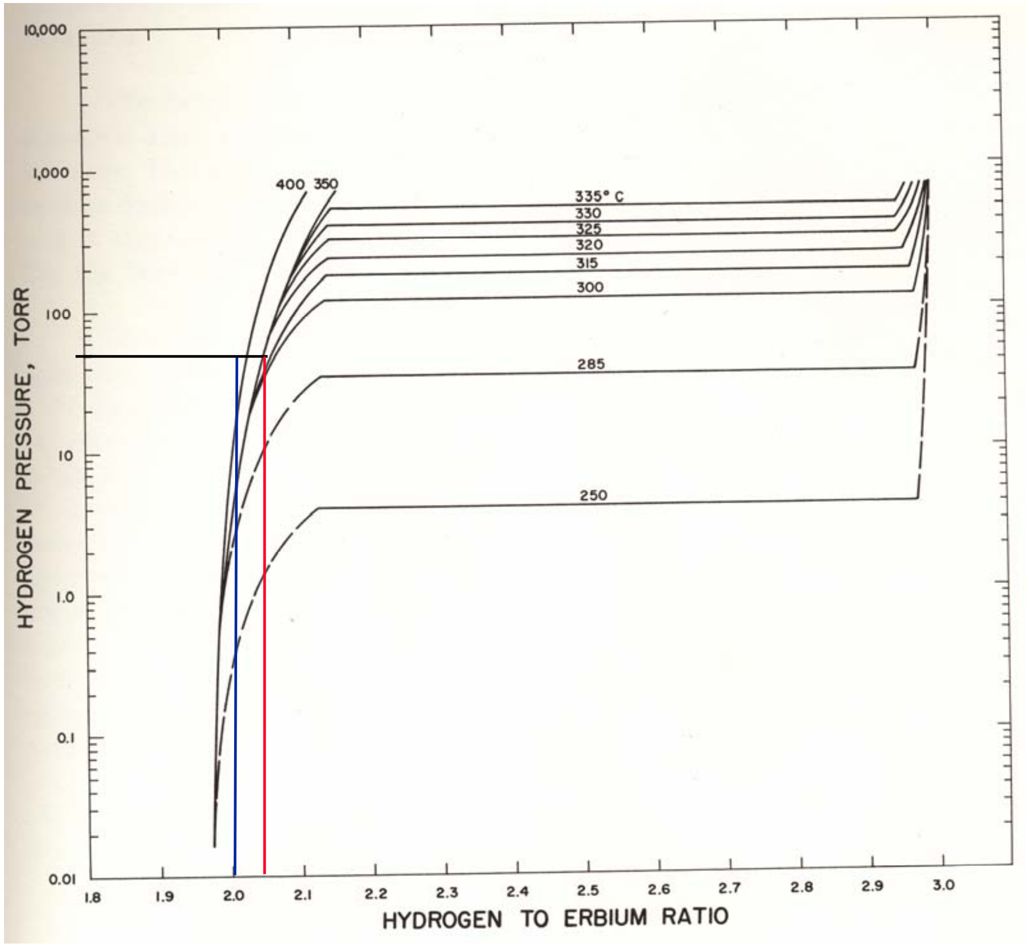
The Neutron Powder Diffraction measurements were performed on the HIPPO spectrometer at the Lujan Center at LANL





We have studied two ErD_2 powders processed at ~50 Torr 450 and 350C

- **50 Torr**
  - **450 C (blue)**
  - **350 C (red)**



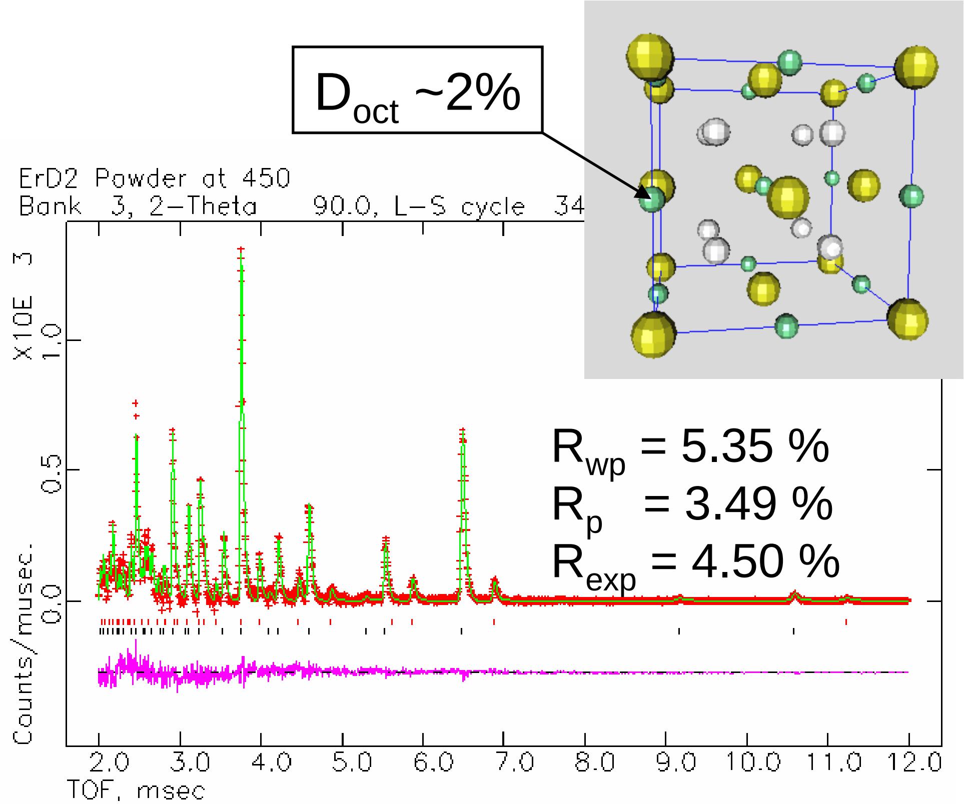
C. E. Lundin "The Erbium-Hydrogen System" (1965)

Neutron Powder Diffraction results for ErD_2 powder loaded at 450 °C, ~50 Torr

Crystal structure data

- **Atom**x,y,z occ. B(Å^2)
- Er 0,0,0 1.0 0.15(2)
- D_{tet} ¼,¼,¼ 1.00(1) 1.01(2)
- D_{oct} ½,½,½ 0.02(1) 1.01(2)
- a = 5.1187(2) Å
- Formula: $ErD_{tet(2.00)}D_{oct(0.02)}$
- Vol = 134.11 Å^3
- D_x = 8.48 g/cm^3

Silicon 640c used as internal standard



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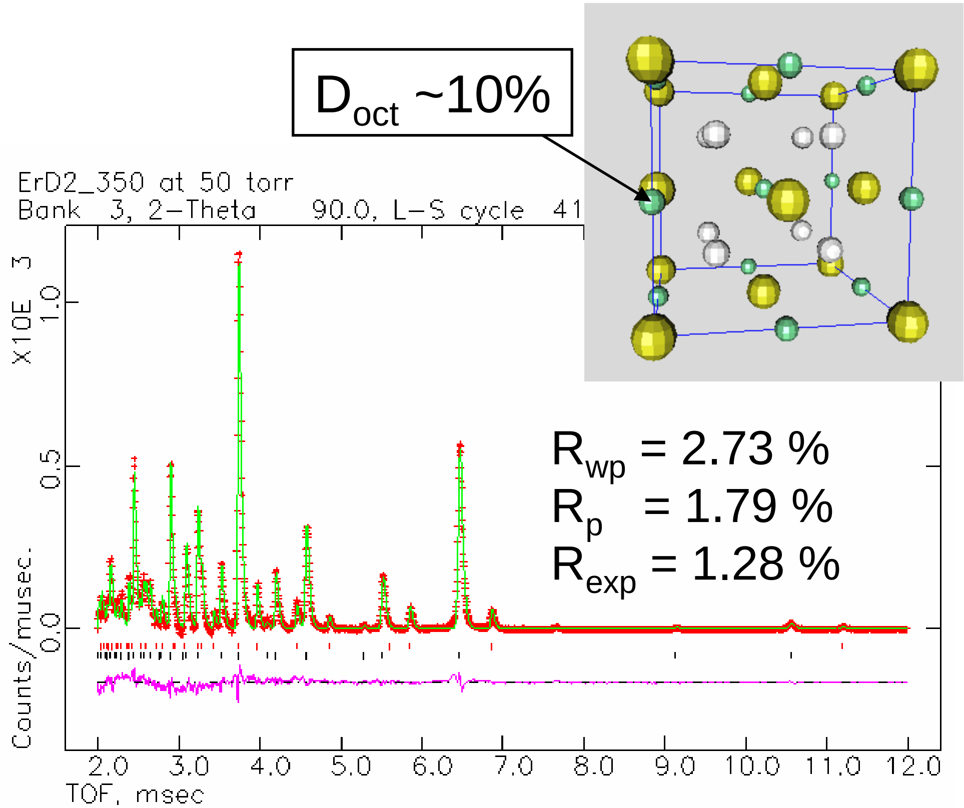
Neutron Powder Diffraction results for ErD_2 powder loaded at 350 ºC, ~50 Torr

Crystal structure data

- **atom** x,y,z — occ. — B(Å^2)
- Er — 0,0,0 — 1.0 — 0.28(2)
- D_{tet} — ¼,¼,¼ — 1.01(1) — 1.25(3)
- D_{oct} — ½,½,½ — 0.10(1) — 1.25(3)
- a = 5.1166(2) Å
- Formula: $ErD_{tet(2.00)}D_{oct(0.10)}$
- Vol = 133.95 Å^3
- Dx = 8.51 g/cm^3

Silicon 640c used as internal standard

D_{oct} ~10%



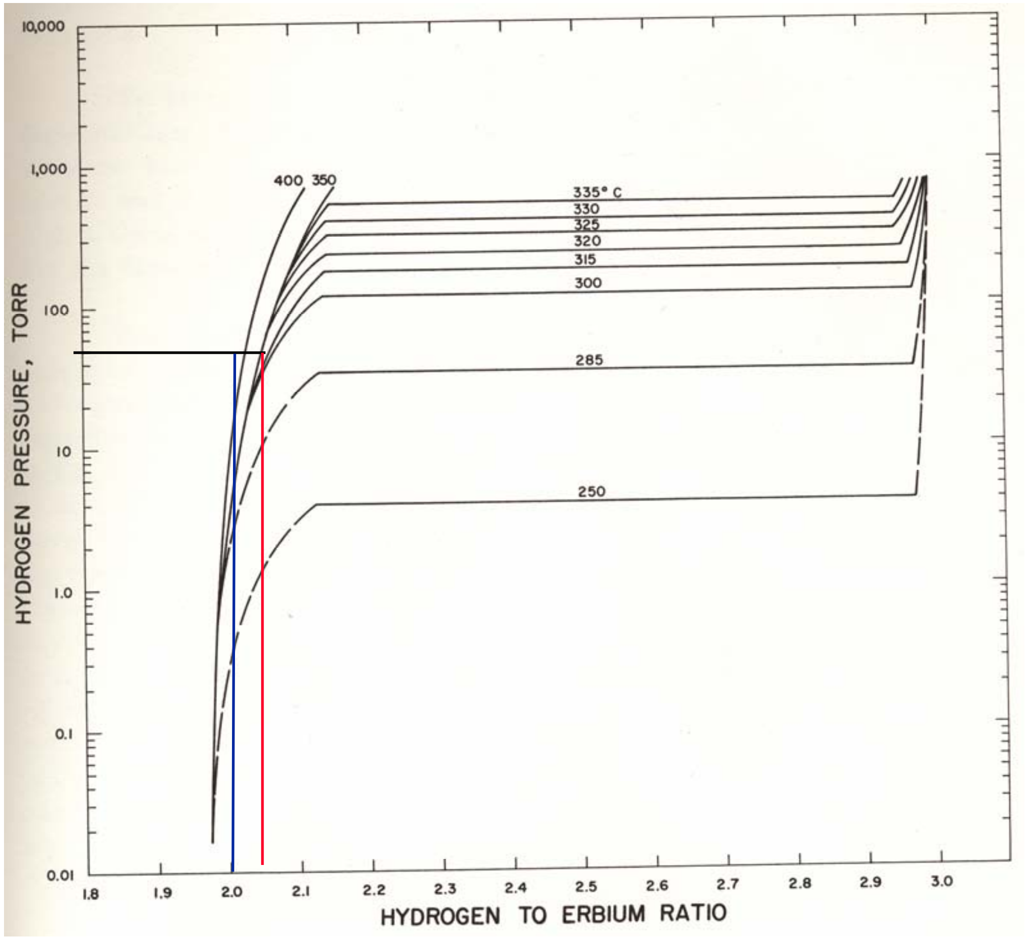
XRD shows a = 5.116(1)

The site-occupancy and lattice parameter correlate with the PCT curve

NPD measures $ErD_{2.10}$ for 350 C powder (red)

NPD measures $ErD_{2.02}$ for 450 C powder (blue)

Measured lattice constant is less for $ErD_{2.10}$ (5.1166 Å) than for $ErD_{2.02}$ (5.1187 Å) as expected from other RE Metal-Hydrides



C. E. Lundin "The Erbium-Hydrogen System" (1965)

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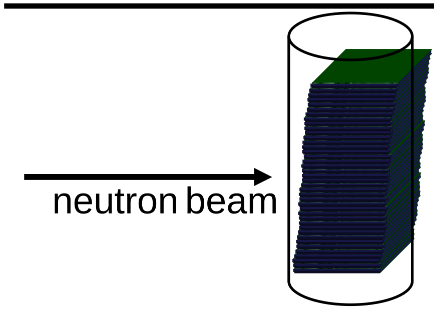
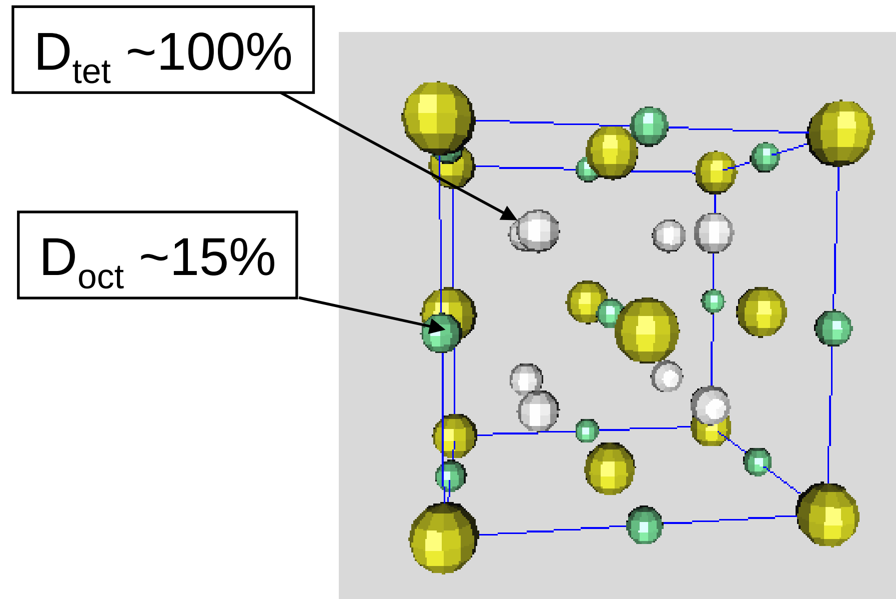
Neutron Diffraction can also be performed on ErD_2 films





R_{wp} = 0.87 %   Wt fraction ErD_2 = 4.5 %
R_p = 0.73 %   Wt fraction exp. = 3 %

Crystal structure data

atom	x,y,z	occ.	B(Å²)
Er	0,0,0	1.0	0.15
D_{tet}	¼,¼,¼	1.04(2)	1.01
D_{oct}	½,½,½	0.15	1.01

a = 5.119(1) Å

Formula: $ErD_{tet(2.0)}D_{oct(0.15)}$

Vol = 134.2 Å³

D_x = 8.5 g/cm³

Film loaded at 450C, 20 Torr

Measured ~$ErD_{2.15}$

PCT diagram less than $ErD_{2.10}$

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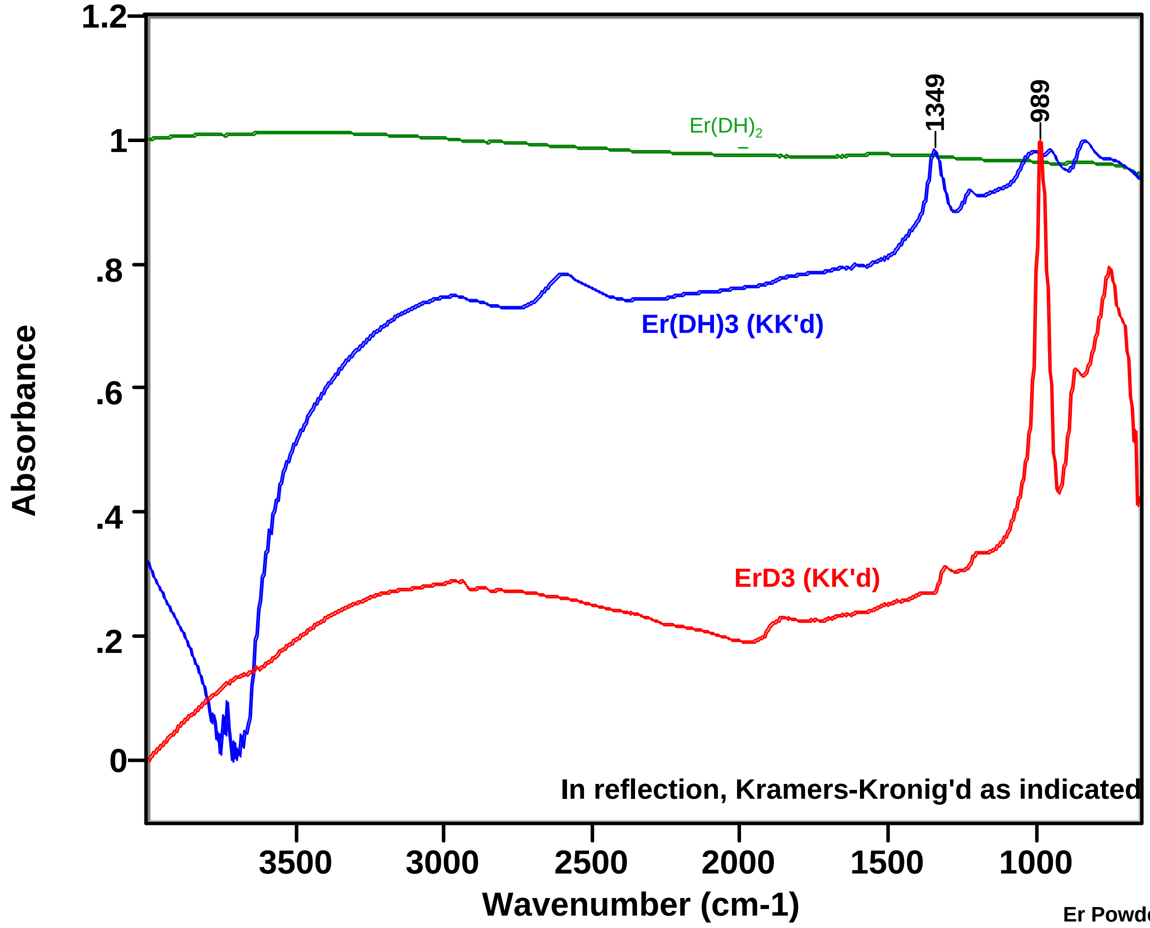
FTIR Spectroscopy results on $Er(DH)_2$ and $Er(DH)_3$ powders

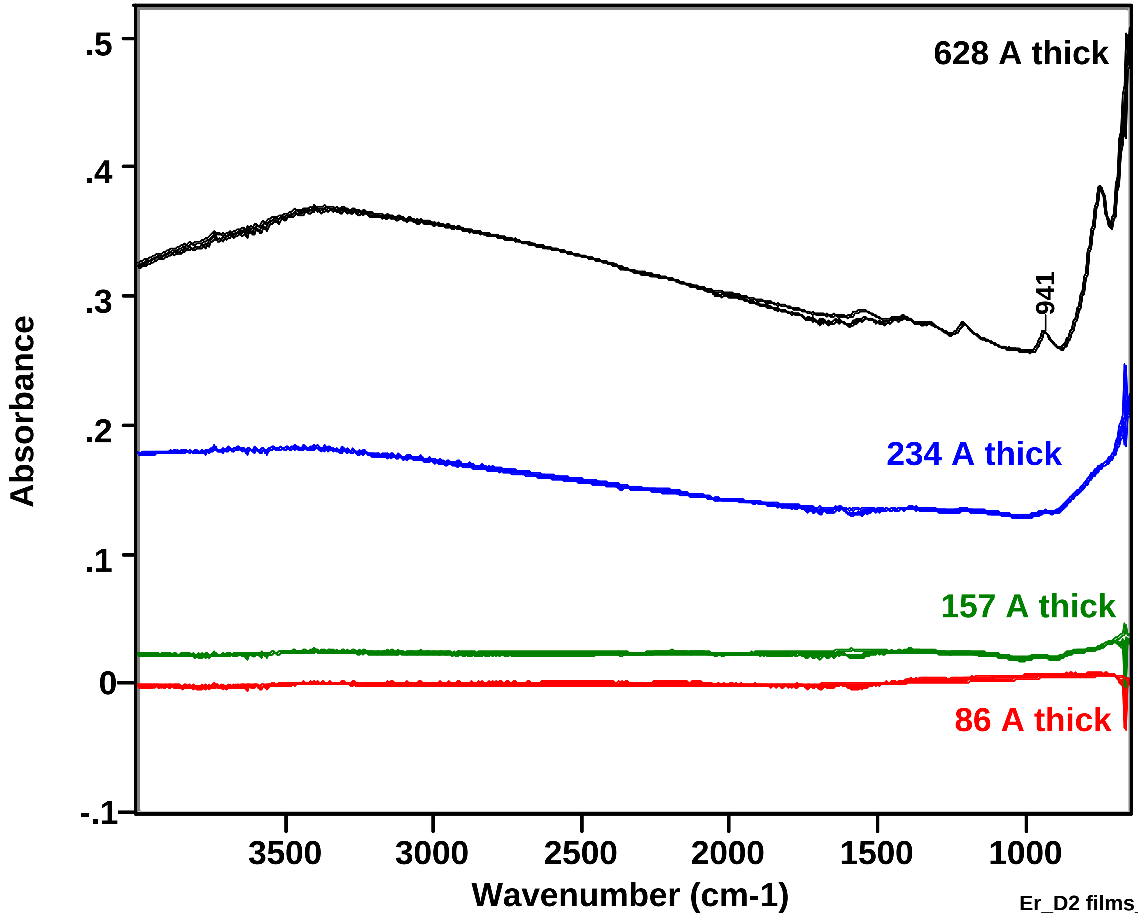
- ErD_2 and ErD_3



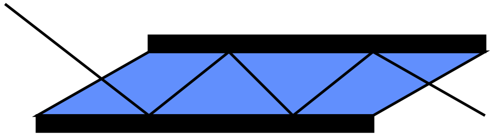
1349/989 = 1.36

FTIR results on ErD_2 films

- ErD_2 films of different thickness



Results suggest
Attenuated Total Reflection (ATR)
technique



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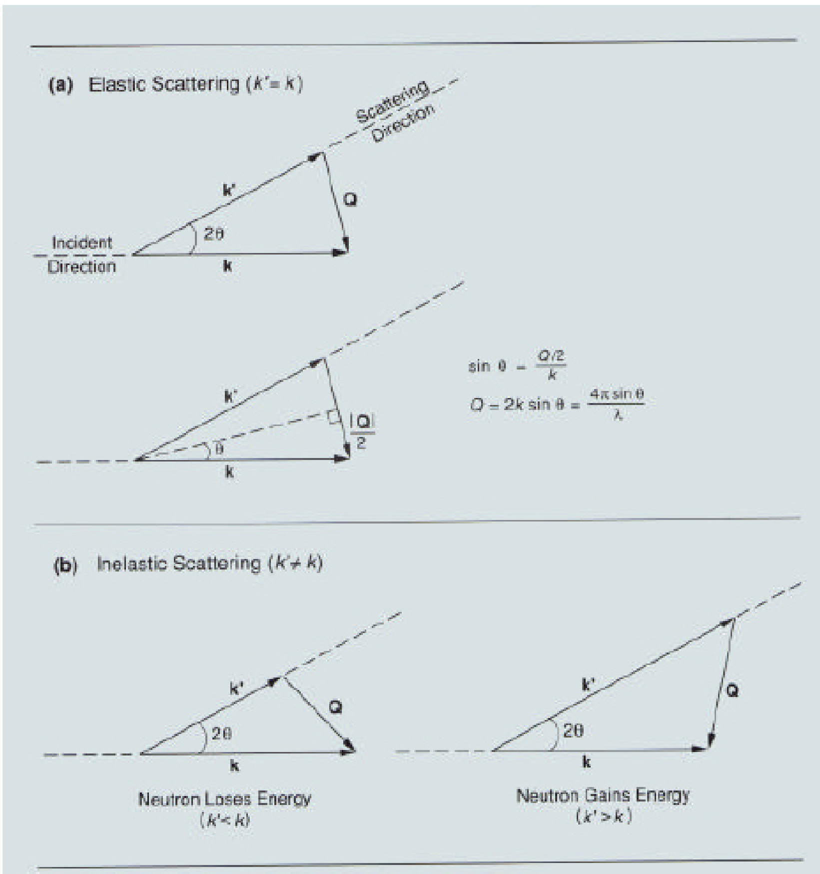
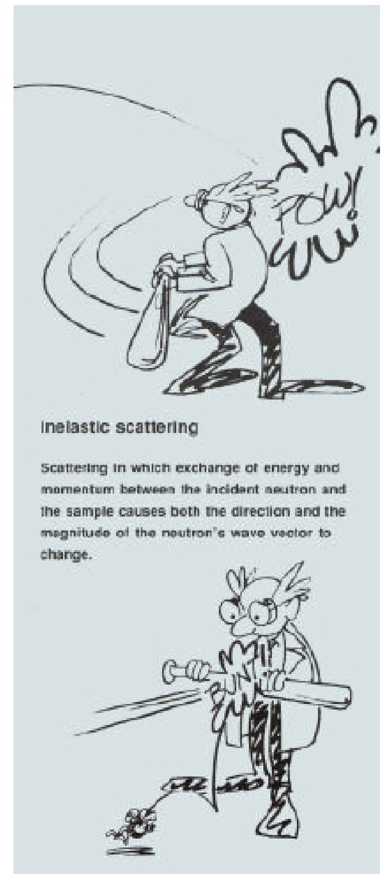
The physics of an inelastic scattering event.

- **The neutron changes both energy and momentum when inelastically scattered**

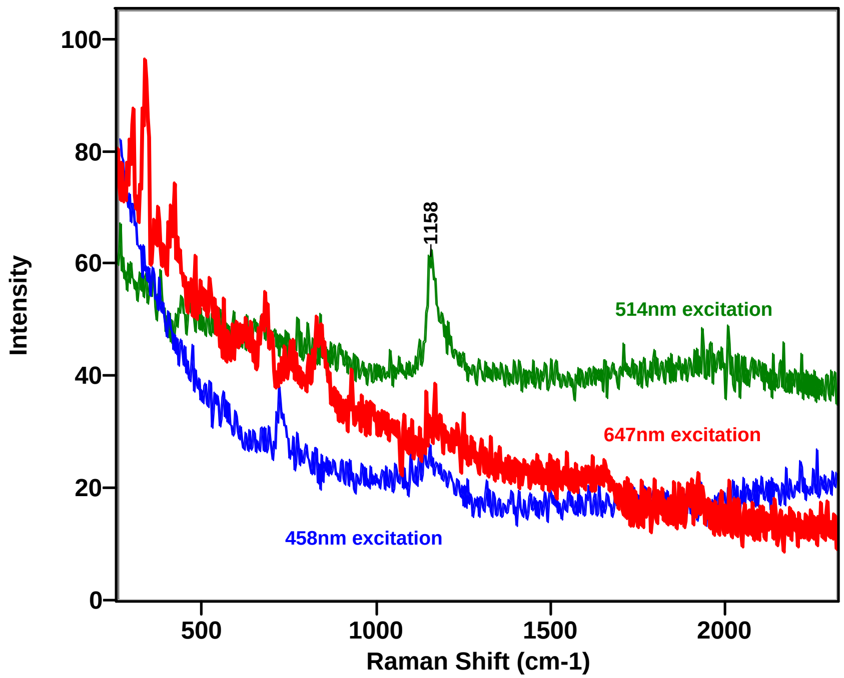




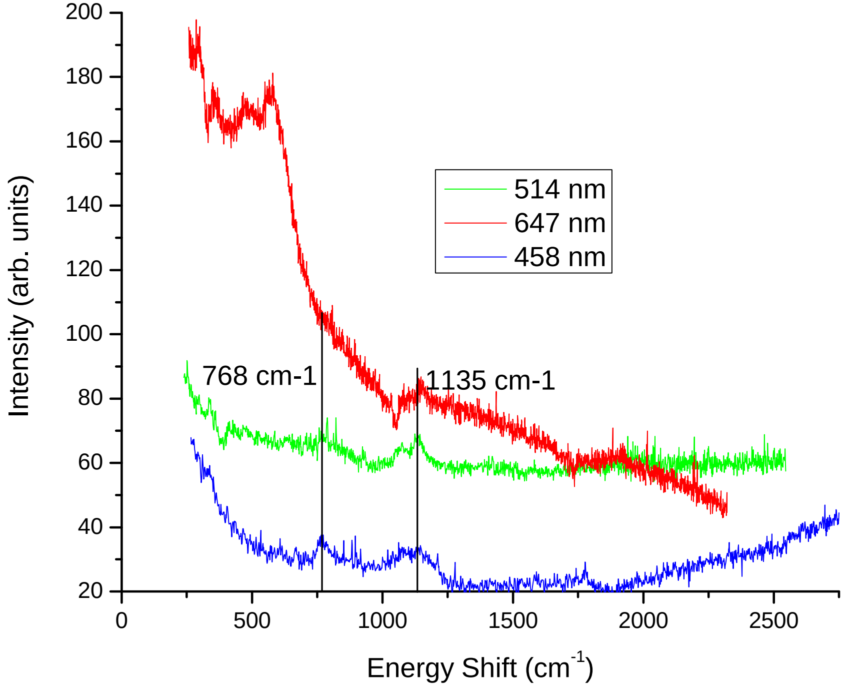
From Roger Pynn, LANL

Raman results on $Er(D_{1-y}H_y)_2$ powders

Y=0 $\{ErH_2\}$



Y=0.5 $\{Er(HD)_2\}$



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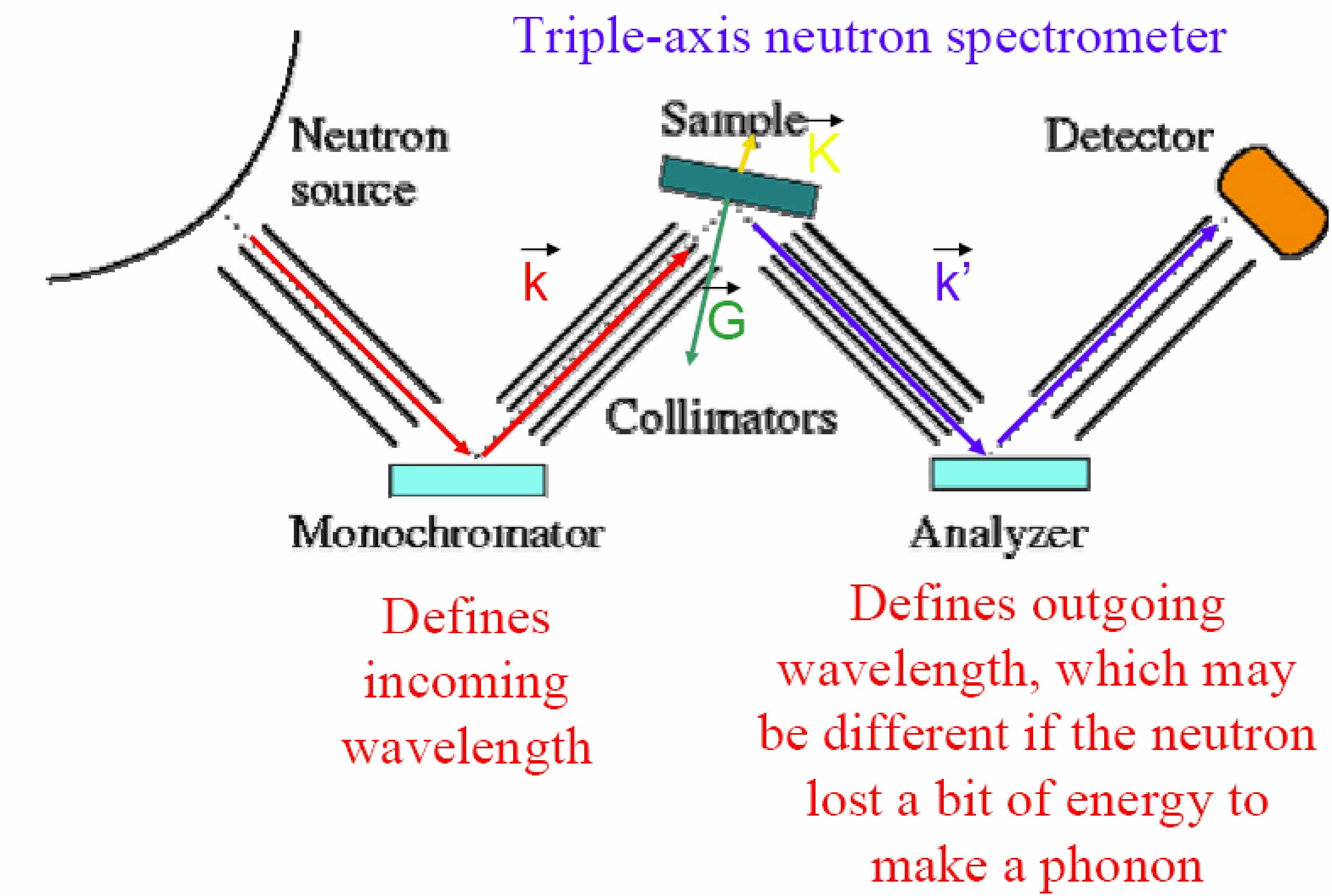
How a basic Inelastic Neutron Scattering (INS) experiment looks.



From Chris Wiebe, Brock University

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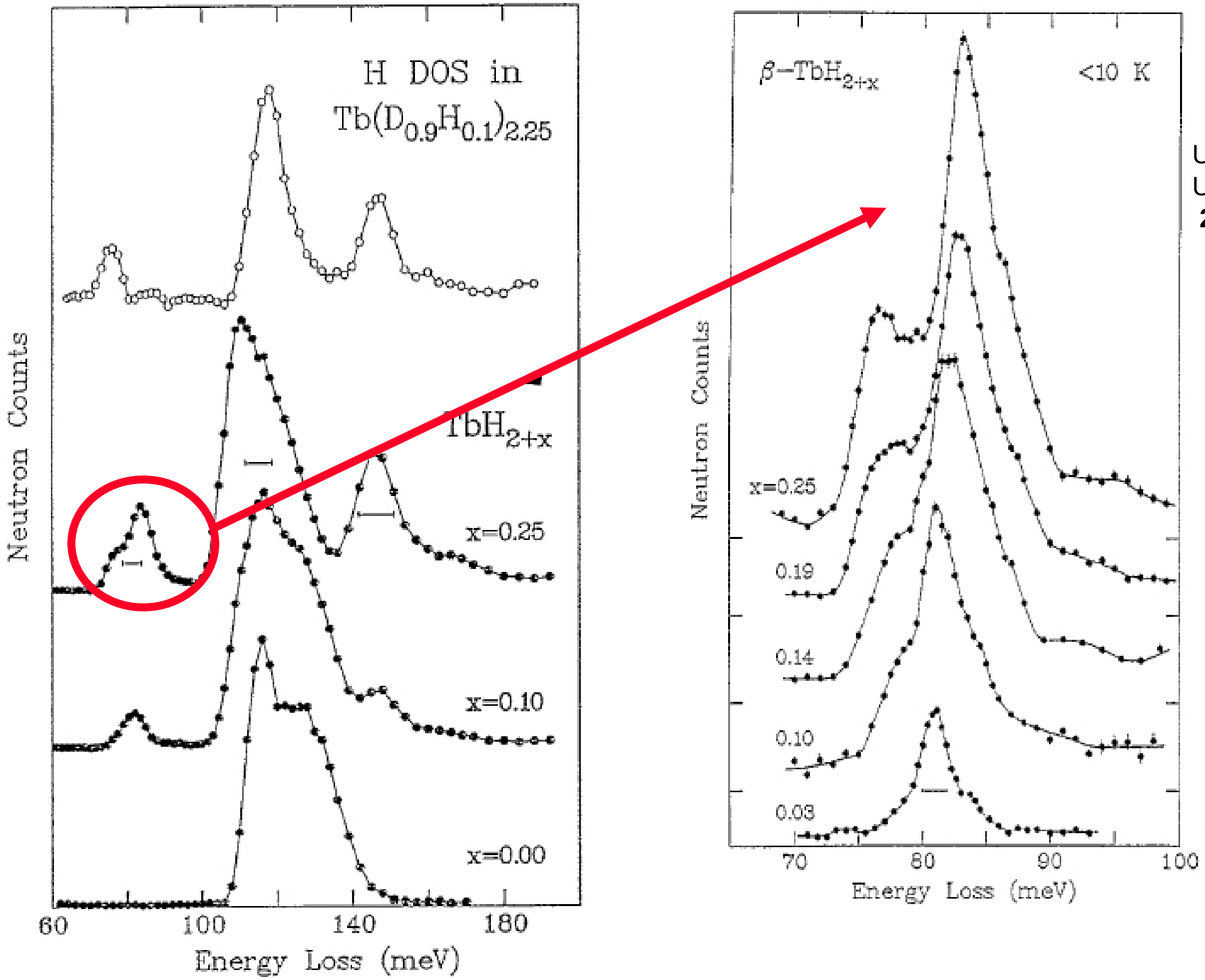
The case study of $Tb(HD)_{2+x}$: Isotope shifts and octahedral site loading

- **Octahedral site loading is clearly observed.**



Udovic *et al*., Phys. Rev. B, **61**, 6611 (2000)
Udovic *et al.,* J. Alloys and Compounds, **231**, 138 (1995)

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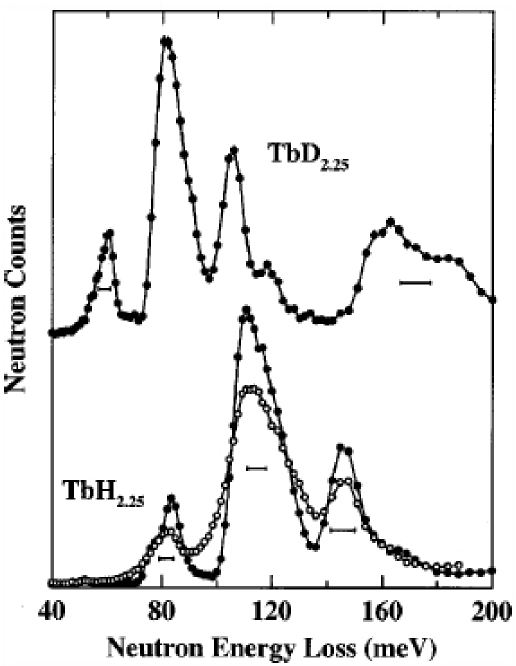
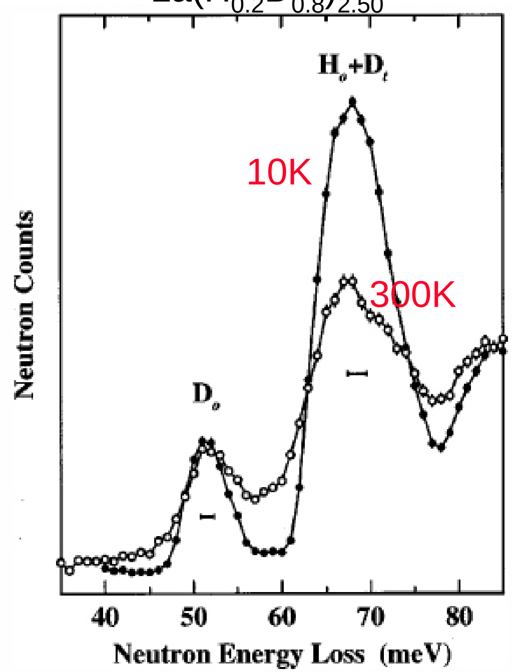
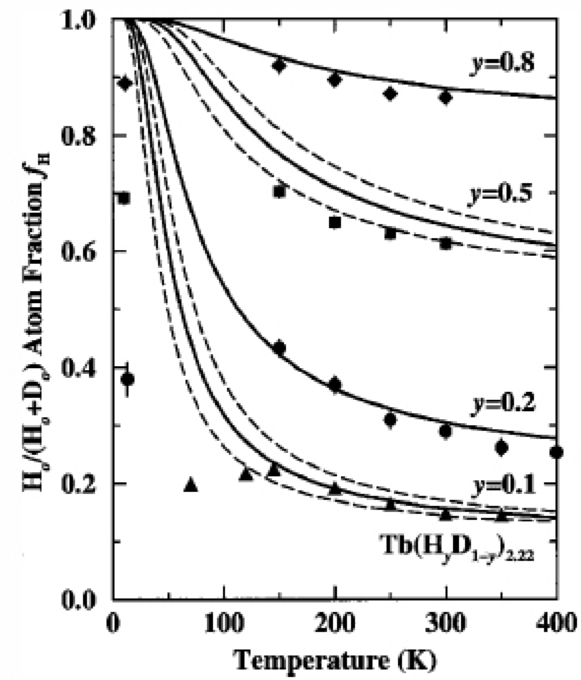
The case study of $Tb(HD)_{2+x}$: Isotopic ordering at low-temperatures

- Low-temperature, <10K, little thermal motion.
- Isotopic ordering observed.



La(H0.2D0.8)2.50





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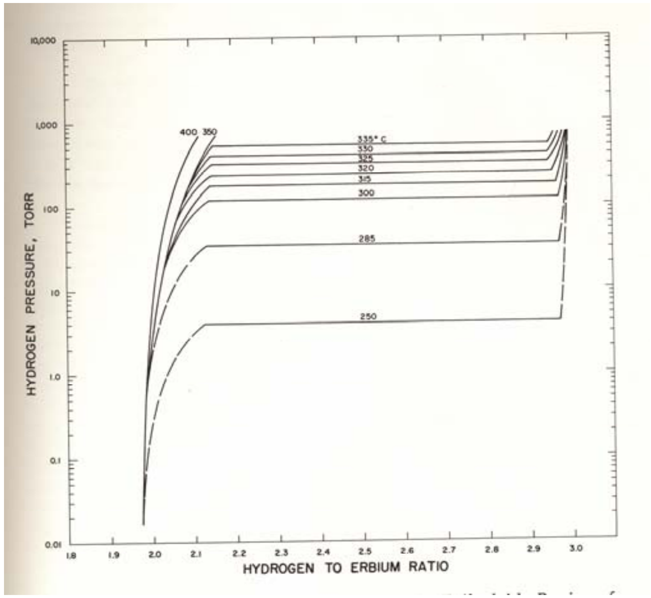
What do we want to do to $Er(HDT)_2$?

- Measure Er-H, Er-D, Er-T vibrations.
- Measurements as a function of sample temperature.
- Determine site-occupancy, isotopic ordering, etc. as a function of hydrogen loading parameters.



What we've learned and what measurements we're going to do next.

- We've learned how to control the hydriding process. (S. King)
- We've measured differences in Octahedral to Tetrahedral site occupancy.
- We've measured different H and D vibrational frequencies.

- Will continue the NPD measurements on a full suite of samples and at different temperatures.
- Will continue pursuing optical vibrational measurements.
- Will perform Inelastic Neutron Scattering measurements.

- This suite of measurements will give a full picture of hydrogen site occupancy and isotopic site preferences in the $Er(H,D,T)_{2+x}$ system.

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$$Rp = \frac{\Sigma|Io-Ic|}{\Sigma Io}$$

$$Rwp = \sqrt{\frac{\Sigma[w(Io-Ic)^2]}{\Sigma[w(Io)^2]}}$$

$$Rexp = \frac{Rwp}{\sqrt{\chi^2}}$$

$$\chi^2 = \frac{\Sigma[w(Io-Ic)^2]}{(Nobs - Nvar)}$$

Where: Io = observed intensity at a given data point

Ic = calculated intensity for a given data point

w = a weighting scheme computed from variances of Io and Ic

Nobs = the number of observations (data points)

Nvar = the number of refinement variables