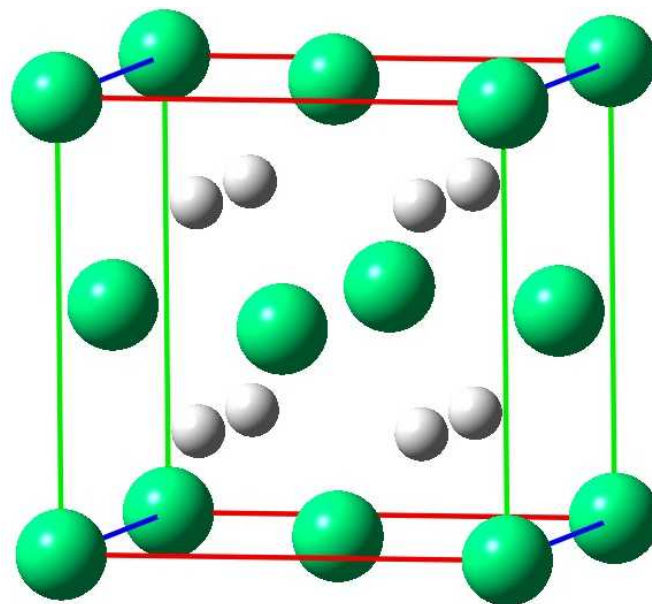
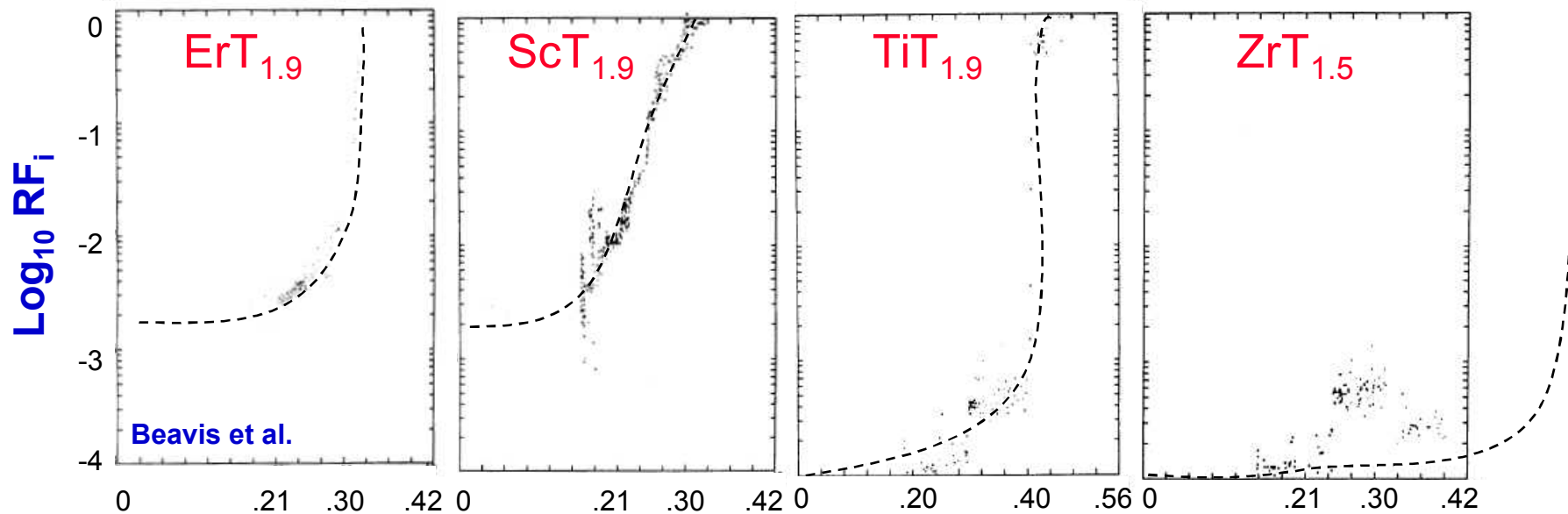


Elastic Constants of Rare Earth and Transition Metal Di-Hydrides

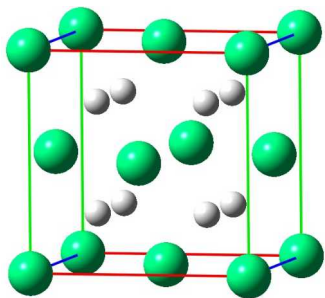


Clark S. Snow and Thomas Mattsson
Sandia National Laboratories
Albuquerque, NM

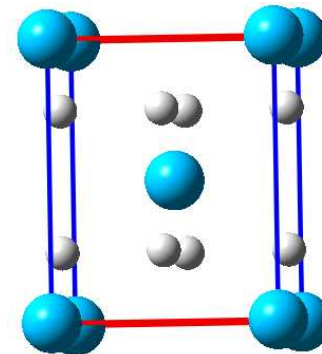
The amount of helium released depends on the crystal structure.



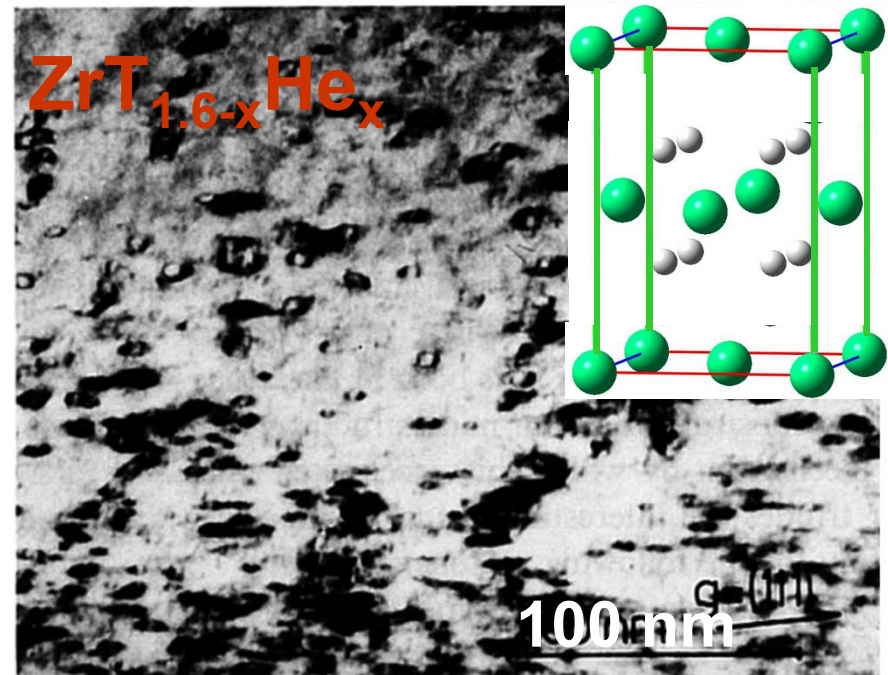
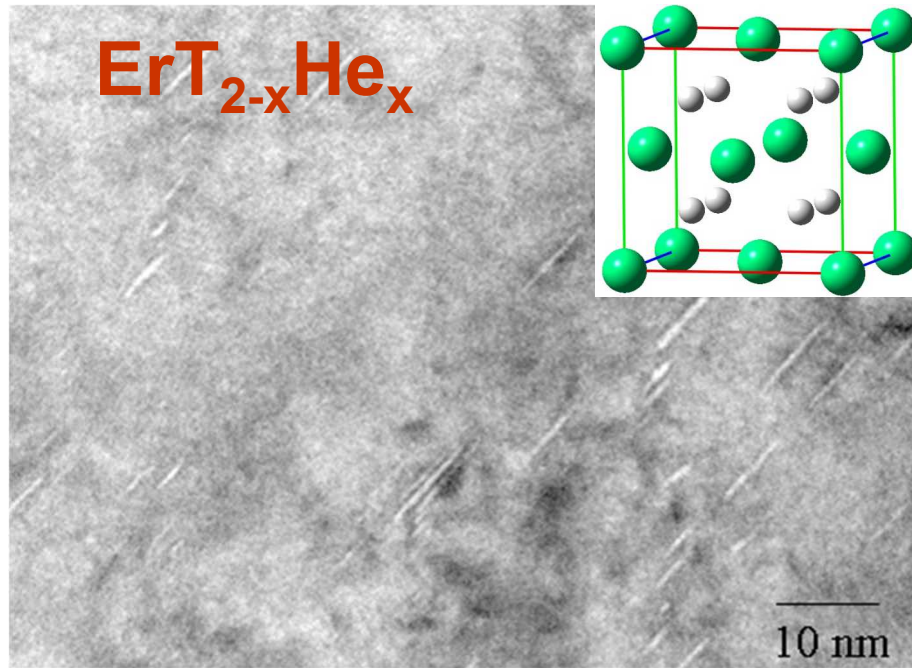
He Generated/Metal



- Similar release numbers from similar crystal structures.

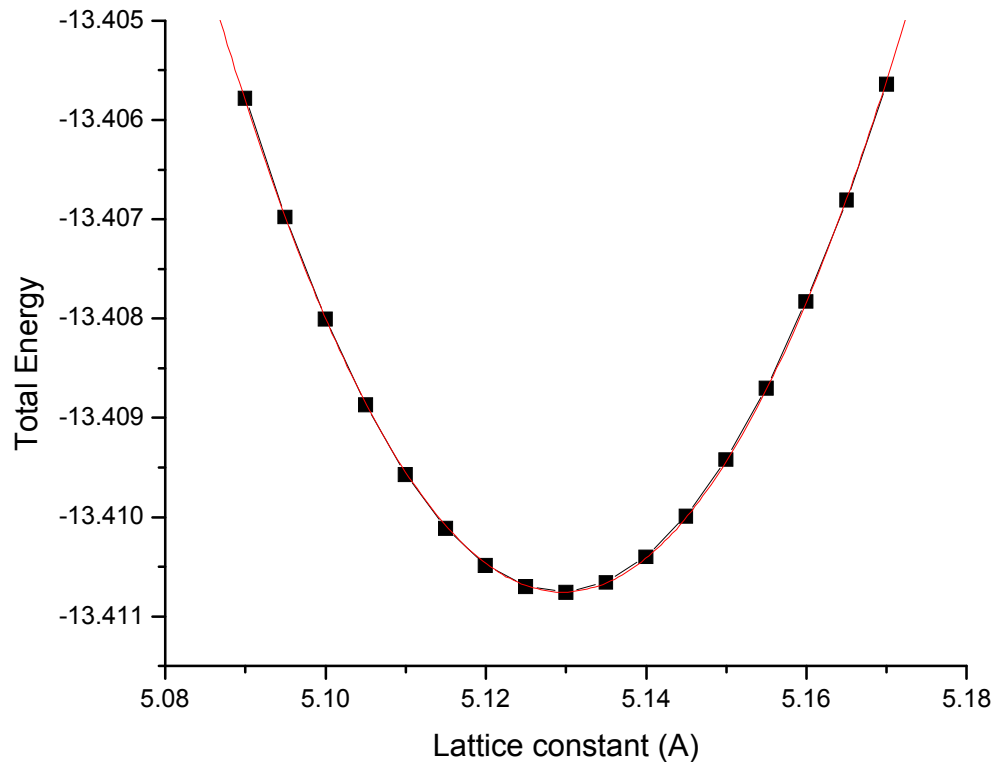
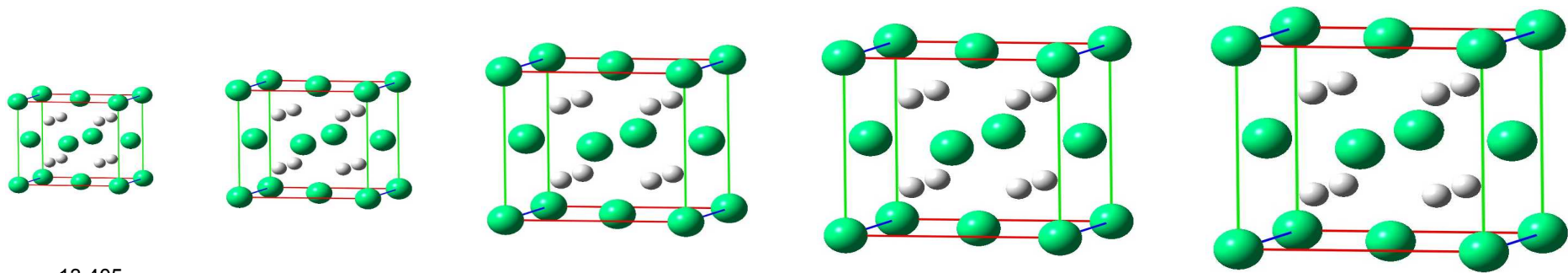


The majority of the generated helium is stored in helium bubbles.



- Helium bubble shape depends on crystal structure.

Calculating the lattice constant is easy.



Murnaghan EOS:

$$E(V) = E_0 + \frac{B_0 V}{B'_0} \left(\frac{(V_0/V)^{B'_0}}{B'_0 - 1} + 1 \right) - \frac{B_0 V_0}{B'_0 - 1}$$



The results for the metallic lattice constant calculations are excellent.

Metal/Values	Erbium	Scandium	Titanium	Zirconium	Yttrium	Palladium
Calculated (Å)	a=3.586 c=5.5578	a=3.321 c=5.163	a=2.9390 c=4.646	a=3.2390 c=5.1780	a=3.6605 c=5.6721	a=3.9598
Experimental (Å)	a=3.5588 C=5.5874	a=3.309 c=5.2733	a=2.9508 c=4.6855	a=3.2320 c=5.147	a=3.6474 c=5.7306	a=3.8907
Percent Error	a=0.76% c=0.53%	a=0.36% c=2.1%	a=0.399% c=0.8%	a=0.2% c=0.6%	a=0.36% c=1%	a=1.77%

•For cubic and hexagonal systems the agreement is excellent.



The results for the metal hydride lattice constants are also excellent

Metal/Values	ErH ₂	ScH ₂	YH ₂	ZrH ₂	TiH ₂	LaH ₂
Calculated (Å)	a=5.1295	a=4.7815	a=5.2168			
Experimental (Å)	a=5.123	a=4.78	a=5.205			
Percent Error	a=0.13%	0.03%	a=0.22%			

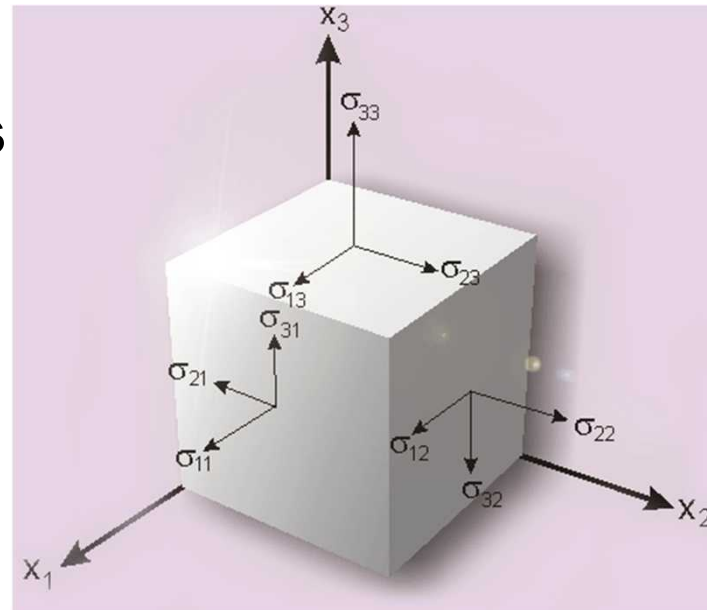
- Cubic systems show excellent agreement.
- Still having a few difficulties with the tetragonal systems.

How to calculate elastic constants: stress-strain I

- σ is the stress
- ϵ is the strain

$$\begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{pmatrix}$$

- σ_{ij} is the stress acting in the x_i direction on the plane perpendicular to the x_j direction.
 - $i=j$ are axial stresses
 - $i \neq j$ are shear stresses
- $\sigma_{ij} = \sum c_{ijkl} \epsilon_{kl}$
 - C_{ijkl} = elastic moduli or elastic constants





How to calculate elastic constants: stress-strain II

- The stress, σ , and the strain, ϵ , must be symmetric. $\sigma_{ij} = \sum c_{ijkl} \epsilon_{kl}$
- The nature of the c_{ijkl} depends on symmetry of the crystal.
- Short hand
 - $c_{1111} \rightarrow c_{11}$ relations between σ_{11} and ϵ_{11}
 - $c_{1122} \rightarrow c_{12}$ relations between σ_{11} and ϵ_{22}
 - $c_{2323} \rightarrow c_{44}$ relations between σ_{23} and ϵ_{23}
 - In general, $11 \rightarrow 1; 22 \rightarrow 2; 23=32 \rightarrow 4; 13=31 \rightarrow 5; 12=21 \rightarrow 6$

How to calculate elastic constants: stress-strain III

- Maximum of 21 elastic constants for a crystalline body.

$$\begin{pmatrix} c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16} \\ & c_{22} & c_{23} & c_{24} & c_{25} & c_{26} \\ & & c_{33} & c_{34} & c_{35} & c_{36} \\ & & & c_{44} & c_{45} & c_{46} \\ & & & & c_{55} & c_{56} \\ & & & & & c_{66} \end{pmatrix}$$

- **Cubic crystals** the elastic constants reduce to just three independent numbers
 - $c_{11}=c_{22}=c_{33}$ axial compression
 - $c_{44}=c_{55}=c_{66}$ shear modulus
 - $c_{12}=c_{13}=c_{23}$ modulus for dilation on compression
 - All other $c_{ij} = 0$

How to calculate elastic constants: stress-strain IV

- Know lattice (primitive) vectors

$$\begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} = \begin{pmatrix} a_{1x} & a_{1y} & a_{1z} \\ a_{2x} & a_{2y} & a_{2z} \\ a_{3x} & a_{3y} & a_{3z} \end{pmatrix} \bullet \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

- Distort lattice vectors

$$\vec{a}' = (\vec{I} + \vec{\varepsilon}) \bullet \vec{a}$$

$$\vec{\varepsilon} = \begin{pmatrix} e_1 & \frac{1}{2}e_6 & \frac{1}{2}e_5 \\ \frac{1}{2}e_6 & e_2 & \frac{1}{2}e_4 \\ \frac{1}{2}e_5 & \frac{1}{2}e_4 & e_3 \end{pmatrix}$$

- New lattice vectors

$$\begin{pmatrix} a_1' \\ a_2' \\ a_3' \end{pmatrix} = \begin{pmatrix} 1+e_1 & \frac{1}{2}e_6 & \frac{1}{2}e_5 \\ \frac{1}{2}e_6 & 1+e_2 & \frac{1}{2}e_4 \\ \frac{1}{2}e_5 & \frac{1}{2}e_4 & 1+e_3 \end{pmatrix} \bullet \begin{pmatrix} a_{1x} & a_{1y} & a_{1z} \\ a_{2x} & a_{2y} & a_{2z} \\ a_{3x} & a_{3y} & a_{3z} \end{pmatrix} \bullet \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$



How to calculate elastic constants: stress-strain V

- Using Hook's law, if ϵ are small, can expand energy in terms of ϵ .

$$E = E_0 + V \sum_{i=1}^6 \sigma_i e_i + \frac{1}{2} V \sum_{i=1}^6 \sum_{j=1}^6 c_{ij} e_i e_j + \mathcal{O}(e^3)$$

- For cubic crystal, energy relation is

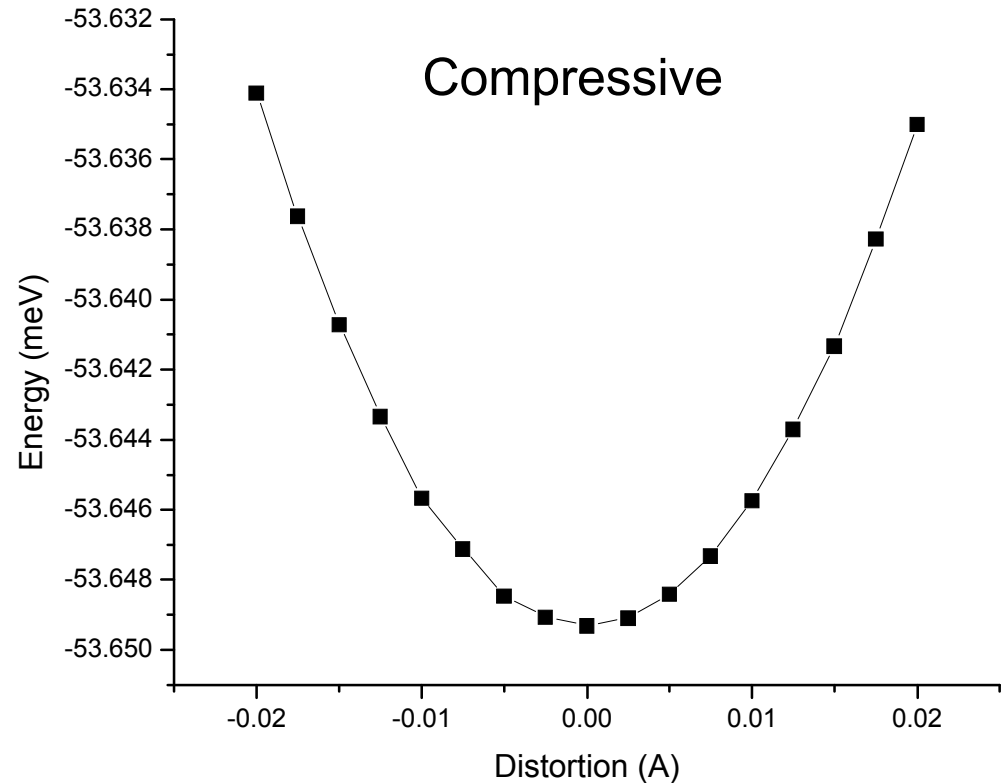
$$E = E_0 + \frac{1}{2} c_{11} [e_1^2 + e_2^2 + e_3^2] + c_{12} [e_1 e_2 + e_2 e_3 + e_3 e_1] + \frac{1}{2} c_{44} [e_4^2 + e_5^2 + e_6^2]$$

How to calculate elastic constants: stress-strain VI

$$\epsilon_{compressive} = \frac{1}{3} \begin{pmatrix} \delta & 0 & 0 \\ 0 & \delta & 0 \\ 0 & 0 & \delta \end{pmatrix}$$

$$\epsilon_{tetragonal} = \frac{1}{2} \begin{pmatrix} -\delta & 0 & 0 \\ 0 & -\delta & 0 \\ 0 & 0 & 2\delta \end{pmatrix}$$

$$\epsilon_{trigonal} = \begin{pmatrix} \delta^2 & \delta & \delta \\ \delta & \delta^2 & \delta \\ \delta & \delta & \delta^2 \end{pmatrix}$$





Calculated elastic constants for the cubic phases of some di-hydrides.

Quantity	ErD₂	YD₂	ScD₂
C₁₁ (GPa)	146	122	167
C₁₂ (GPa)	58	61	60
C₄₄ (GPa)	74	69	79

$$B = 1/3 (C_{11} + 2C_{12})$$

$$G_R = 5(C_{11} - C_{12})C_{44}/[4C_{44} + 3(C_{11} - C_{12})]$$

$$G_V = (C_{11} - C_{12} + 3C_{44})/5$$

$$G_H = (G_R + G_V)/2$$

$$Y = (9BG_H)/(3B + G_H)$$



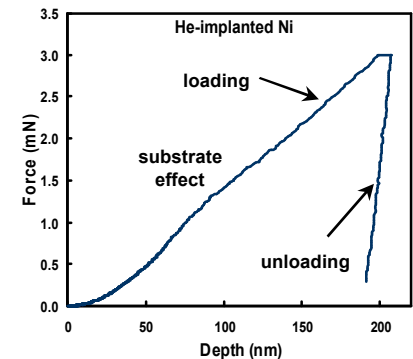
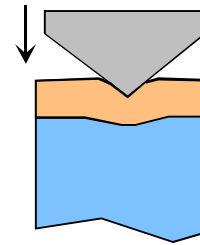
Determined moduli for hydrides compared to the VASP calculated values.

Quantity	ErD_2 (cubic)	YD_2 (cubic)	ScD_2 (cubic)	LaD_2 (cubic)	TiD_2 (tet.)	ZrD_2 (tet.)
Young's Modulus (GPa)	147	124	164			
Shear Modulus (GPa)	60	50	68			
Bulk Modulus (GPa)	87	82	96			

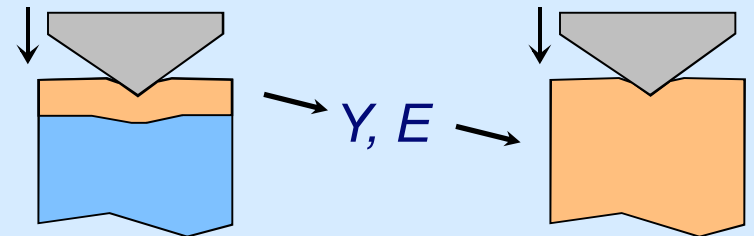
Red = calculated values

Nano-indentation and finite element modeling

- ◆ **Material properties of the thin films are deduced using FEM modeling.**
- ◆ Properties of the indenter and underlying layers and substrate are fixed at known values.
- ◆ Y and E for the layer are varied until a good fit to experiment is obtained.
 - *Tip yielding, stress, friction are all modeled.*
- Two primary simplifications:
 - *2-dimensional axi-symmetric meshes*
 - *isotropic elastic-plastic materials with Mises yield criteria*



- Hardness of the layer material is determined by an additional simulation of a “bulk” sample of just the layer material:





Sample configuration

Metal ~5000 Å thick

Molybdenum 1000 Å thick

Silicon (111)

Moduli determined by nano-indentation for bare metals match “accepted” values.

Quantity	Erbium	Scandium	Titanium	Yttrium	Zirconium
Young's Modulus (GPa)	77+/- 7 (70)	(74)	144 +/- 15 (116)	147+/- 13 (64)	154 +/- 20 (68)
Shear Modulus (GPa)	31 +/- 4 (28)	(29)	58+/- 8 (44)	59 +/- 6 (26)	61 +/- 15 (33)
Bulk Modulus (GPa)	50 +/- 3 (44)	(57)	96 +/- 5 (110)	98 +/- 4 (41)	103 +/- 6 ()

Black = nano-indent values
Red = “accepted values”



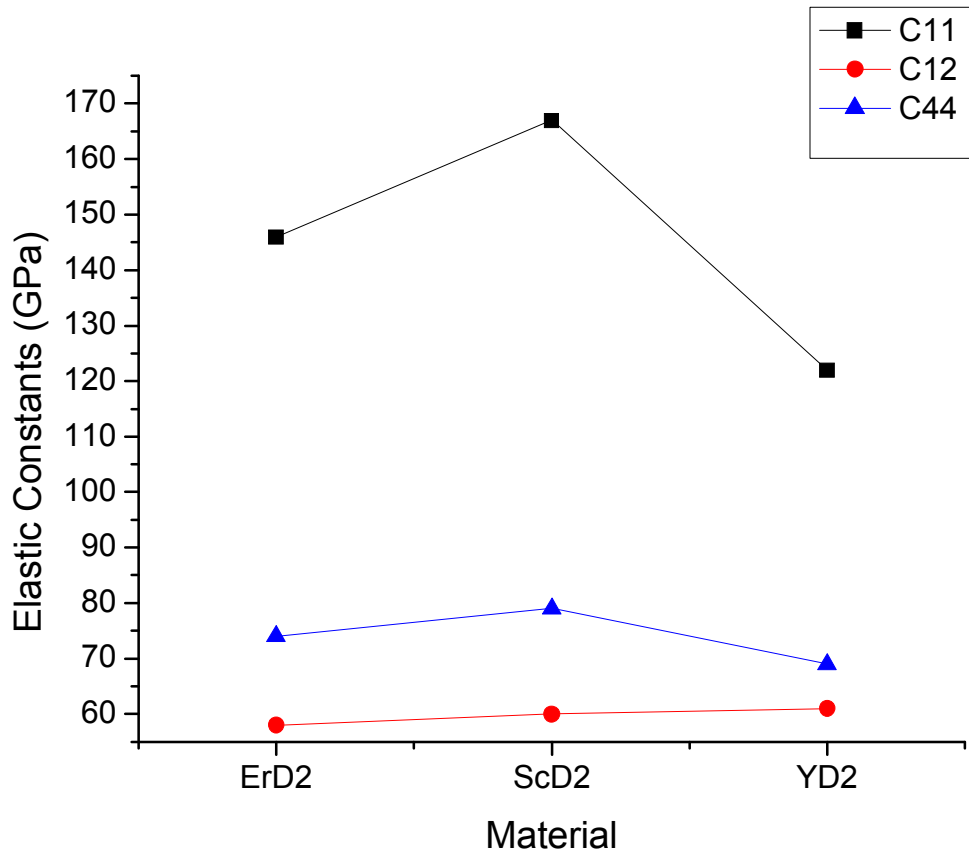
Determined moduli for hydrides compared to the VASP calculated values.

Quantity	ErD₂ (cubic)	YD₂ (cubic)	ScD₂ (cubic)	LaD₂ (cubic)	TiD₂ (tet.)	ZrD₂ (tet.)
Young's Modulus (GPa)	148 +/- 20 (147)	135 +/- 20 (124)	(164)	36 +/- 6 ()	100 +/- 15 ()	175 +/- 20 ()
Shear Modulus (GPa)	60 +/- 10 (60)	55 +/- 10 (50)	(68)	14 +/- 3 ()	40 +/- 7 ()	70 +/- 10 ()
Bulk Modulus (GPa)	97 +/- 4 (87)	90 +/- 7 (82)	(96)	24 +/- 3 ()	66 +/- 5 ()	115 +/- 7 ()

Black = nano-indent values

Red = calculated values

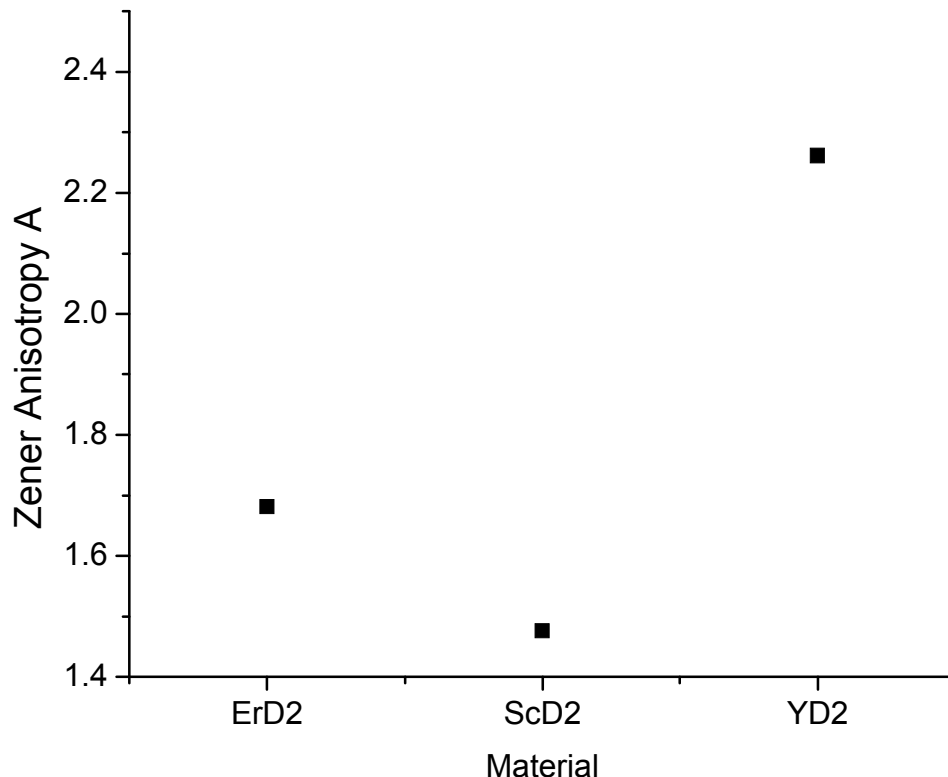
Graphical Summary of Results



• C_{44} resistance to shear on $\{100\}$ in $\langle 0kl \rangle \rightarrow \sigma_{yz} = C_{44}\epsilon_{yz}$

• $(C_{11}-C_{12})/2$ resistance to shear on $\{110\}$ in $\langle -110 \rangle$

What is the degree of anisotropy?



- Zener's Elastic-Anisotropy Index for cubic materials

$$A = 2C_{44} / (C_{11} - C_{12})$$

The ratio of the two extreme elastic-shear constants

- “..higher crystal symmetry may relate to higher elastic anisotropy” , Ledbetter and Migliori, J. Appl. Phys., **100**, 063516 (2006).



Conclusions about elastic constants

- **Nano-indentation gives good results for “most” materials.**
 - Issues are probably due to sample/substrate problems and not the technique.
 - Computational results are generally within error.
- **Definitely need to expand material list beyond cubic crystals.**



Implications for helium retention.

- **What does it say about helium retention and bubble shape?**
 - **Important piece of the puzzle but need more information:**
 - **Tackle more materials**
 - **Re-do some experimental results**
 - **Calculate and measure the Surface Energy**
 - **Bubble shape and size must be a balance between four energy components**
 - **Atomic helium site occupation energy**
 - **Surface Energy**
 - **Elastic Energy**
 - **Dislocation loop punching energy**