Elastic Constants of Rare Earth and Transition Metal Di-Hydrides

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How much do the helium release properties simply depend on the crystal structure?

- Similar release numbers from similar crystal structures.
Is bubble shape dependent simply on crystal structure?

- Helium bubble shape depends on crystal structure.
What parameters are needed to make “predictions”?

Cowgill’s predictions are predicated on:

\[ p = \frac{2\gamma}{r} + \frac{\mu b}{r(1+\varepsilon)} \]

- \( b \) = Burger’s vector (Lattice)
- \( \mu \) = shear modulus (Elastic Constants)
- \( \gamma \) = surface energy

- We can calculate all of these parameters!!!
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.

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

• For cubic and hexagonal systems the agreement is excellent.
The results for the metal hydride lattice constants are also excellent.

<table>
<thead>
<tr>
<th>Metal/Values</th>
<th>ErH₂</th>
<th>ScH₂</th>
<th>YH₂</th>
<th>ZrH₂</th>
<th>TiH₂</th>
<th>LaH₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated (Å)</td>
<td>a=5.1295</td>
<td>a=4.7815</td>
<td>a=5.2168</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experimental (Å)</td>
<td>a=5.123</td>
<td>a=4.78</td>
<td>a=5.205</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Percent Error</td>
<td>a=0.13%</td>
<td>0.03%</td>
<td>a=0.22%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

• Cubic systems show excellent agreement.

• Still having a few difficulties with the tetragonal systems.
How to calculate elastic constants: stress-strain I

• The stress, $\sigma$, and the strain, $\varepsilon$, must be symmetric. $\sigma_{ij} = \sum c_{ijkl} \varepsilon_{kl}$

• The nature of the $c_{ijkl}$ depends on symmetry of the crystal.

• Short hand
  - $c_{1111} \rightarrow c_{11}$ relations between $\sigma_{11}$ and $\varepsilon_{11}$
  - $c_{1122} \rightarrow c_{12}$ relations between $\sigma_{11}$ and $\varepsilon_{22}$
  - $c_{2323} \rightarrow c_{44}$ relations between $\sigma_{23}$ and $\varepsilon_{23}$
  - 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 II

- 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
  - \( c_{11} = c_{22} = c_{33} \)  
  \( \text{axial compression} \)
  - \( c_{44} = c_{55} = c_{66} \)  
  \( \text{shear modulus} \)
  - \( c_{12} = c_{13} = c_{23} \)  
  \( \text{modulus for dilation on compression} \)
  - All other \( c_{ij} = 0 \)
How to calculate elastic constants: stress-strain III

- Know lattice (primitive) vectors

\[
\begin{pmatrix}
a_1 \\
a_2 \\
a_3 \\
\end{pmatrix} =
\begin{pmatrix}
a_{1x} & a_{1y} & a_{1z} \\
a_{2x} & a_{2y} & a_{2z} \\
a_{3x} & a_{3y} & a_{3z} \\
\end{pmatrix}
\cdot
\begin{pmatrix}
x \\
y \\
z \\
\end{pmatrix}
\]

- Distort lattice vectors

\[
\vec{\alpha}' = (\vec{I} + \vec{\varepsilon}) \cdot \vec{\alpha}
\]

\[
\varepsilon =
\begin{pmatrix}
\frac{1}{2} e_6 & \frac{1}{2} e_6 & \frac{1}{2} e_6 \\
\frac{1}{2} e_6 & \frac{1}{2} e_6 & \frac{1}{2} e_6 \\
\frac{1}{2} e_6 & \frac{1}{2} e_6 & \frac{1}{2} e_6 \\
\end{pmatrix}
\]

- New lattice vectors

\[
\begin{pmatrix}
a_1' \\
a_2' \\
a_3' \\
\end{pmatrix} =
\begin{pmatrix}
1 + e_1 & \frac{1}{2} e_6 & \frac{1}{2} e_5 \\
\frac{1}{2} e_6 & 1 + e_2 & \frac{1}{2} e_4 \\
\frac{1}{2} e_5 & \frac{1}{2} e_4 & 1 + e_3 \\
\end{pmatrix}
\cdot
\begin{pmatrix}
a_{1x} & a_{1y} & a_{1z} \\
a_{2x} & a_{2y} & a_{2z} \\
a_{3x} & a_{3y} & a_{3z} \\
\end{pmatrix}
\cdot
\begin{pmatrix}
x \\
y \\
z \\
\end{pmatrix}
\]
How to calculate elastic constants:
stress-strain IV

• 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 V

\[ \varepsilon_{\text{compressive}} = \frac{1}{3} \begin{pmatrix} \delta & 0 & 0 \\ 0 & \delta & 0 \\ 0 & 0 & \delta \end{pmatrix} \]

\[ \varepsilon_{\text{tetragonal}} = \frac{1}{2} \begin{pmatrix} -\delta & 0 & 0 \\ 0 & -\delta & 0 \\ 0 & 0 & 2\delta \end{pmatrix} \]

\[ \varepsilon_{\text{trigonal}} = \begin{pmatrix} \delta^2 & \delta & \delta \\ \delta & \delta^2 & \delta \\ \delta & \delta & \delta^2 \end{pmatrix} \]
Calculated elastic constants for the cubic phases of some di-hydrides.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>ErD₂</th>
<th>YD₂</th>
<th>ScD₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₁ (GPa)</td>
<td>146</td>
<td>122</td>
<td>167</td>
</tr>
<tr>
<td>C₁₂ (GPa)</td>
<td>58</td>
<td>61</td>
<td>60</td>
</tr>
<tr>
<td>C₄₄ (GPa)</td>
<td>74</td>
<td>69</td>
<td>79</td>
</tr>
</tbody>
</table>

\[
B = \frac{1}{3} \left( C_{11} + 2C_{12} \right) \\
G_R = \frac{5\left( C_{11} - C_{12} \right)C_{44}}{\left[ 4C_{44} + 3\left( C_{11} - C_{12} \right) \right]} \\
G_V = \frac{\left( C_{11} - C_{12} \right) + 3C_{44}}{5} \\
G_H = \frac{G_R + G_V}{2} \\
Y = \frac{9BG_H}{3B + G_H}
\]
Determined moduli for hydrides compared to the VASP calculated values.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>ErD$_2$ (cubic)</th>
<th>YD$_2$ (cubic)</th>
<th>ScD$_2$ (cubic)</th>
<th>LaD$_2$ (cubic)</th>
<th>TiD$_2$ (tet.)</th>
<th>ZrD$_2$ (tet.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young's Modulus</td>
<td>147</td>
<td>124</td>
<td>164</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(GPa)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shear Modulus</td>
<td>60</td>
<td>50</td>
<td>68</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(GPa)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bulk Modulus</td>
<td>87</td>
<td>82</td>
<td>96</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(GPa)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

Sample configuration

- Silicon (111)
- Molybdenum 1000 Å thick
- Metal ~5000 Å thick
Moduli determined by nano-indentation for bare metals match “accepted” values.

<table>
<thead>
<tr>
<th>Quantity</th>
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<th>Titanium</th>
<th>Yttrium</th>
<th>Zirconium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s Modulus (GPa)</td>
<td>77 +/- 7 (70)</td>
<td>(74)</td>
<td>144 +/- 15 (116)</td>
<td>147 +/- 13 (64)</td>
<td>154 +/- 20 (68)</td>
</tr>
<tr>
<td>Shear Modulus (GPa)</td>
<td>31 +/- 4 (28)</td>
<td>(29)</td>
<td>58 +/- 8 (44)</td>
<td>59 +/- 6 (26)</td>
<td>61 +/- 15 (33)</td>
</tr>
<tr>
<td>Bulk Modulus (GPa)</td>
<td>50 +/- 3 (44)</td>
<td>(57)</td>
<td>96 +/- 5 (110)</td>
<td>98 +/- 4 (41)</td>
<td>103 +/- 6 (1)</td>
</tr>
</tbody>
</table>

Black = nano-indent values
Red = “accepted values”
Determined moduli for hydrides compared to the VASP calculated values.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>ErD$_2$ (cubic)</th>
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<th>LaD$_2$ (cubic)</th>
<th>TiD$_2$ (tet.)</th>
<th>ZrD$_2$ (tet.)</th>
</tr>
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<tbody>
<tr>
<td>Young’s Modulus (GPa)</td>
<td>148 +/- 20</td>
<td>135 +/- 20</td>
<td>36 +/- 6</td>
<td>100 +/- 15</td>
<td>175 +/- 20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(147)</td>
<td>(124)</td>
<td>(164)</td>
<td>()</td>
<td>()</td>
<td>()</td>
</tr>
<tr>
<td>Shear Modulus (GPa)</td>
<td>60 +/- 10</td>
<td>55 +/- 10</td>
<td>14 +/- 3</td>
<td>40 +/- 7</td>
<td>70 +/- 10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(60)</td>
<td>(50)</td>
<td>(68)</td>
<td>()</td>
<td>()</td>
<td>()</td>
</tr>
<tr>
<td>Bulk Modulus (GPa)</td>
<td>97 +/- 4</td>
<td>90 +/- 7</td>
<td>24 +/- 3</td>
<td>66 +/- 5</td>
<td>115 +/- 7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(87)</td>
<td>(82)</td>
<td>(96)</td>
<td>()</td>
<td>()</td>
<td>()</td>
</tr>
</tbody>
</table>

Black = nano-indent values

Red = calculated values
Graphical Summary of Results

- $C_{44}$ resistance to shear on \{100\} in $<0kl>$ $\rightarrow \sigma_{yz} = C_{44}\varepsilon_{yz}$

- $(C_{11}-C_{12})/2$ resistance to shear on \{110\} in $<-110>$
What is the degree of anisotropy?

• Zener’s Elastic-Anisotropy Index for cubic materials
  \[ A = \frac{2C_{44}}{C_{11} - C_{12}} \]

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