NNL TSL Evaluations for Yttrium Hydride and Hexagonal Ice

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## NNL TSL Evaluations

<table>
<thead>
<tr>
<th>Material</th>
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</thead>
<tbody>
<tr>
<td>H(YH$_2$)</td>
<td>5</td>
</tr>
<tr>
<td>Y(YH$_2$)</td>
<td>55</td>
</tr>
<tr>
<td>H(ice-Ih)</td>
<td>10</td>
</tr>
<tr>
<td>O(ice-Ih)</td>
<td>50</td>
</tr>
</tbody>
</table>
YH₂ Background

- Yttrium hydride (YH₂) is an advanced high temperature moderator

- Superior hydrogen density (N₉) at elevated temperatures

- Keinert (1971) proposed H(YH₂) TSL based on simple analytic frequency distributions
  - Debye-type for acoustic mode
  - Gaussian-type for optical mode

- Higher-fidelity TSLs for H(YH₂) and Y(YH₂) developed using first-principles calculations
  - Density Functional Theory (DFT) to calculate interatomic Hellman-Feynman forces for crystal structure
  - Lattice Dynamics (LD) to determine dispersion relations and phonon density of states (DOS)

Hydrogen in metallic Zr, Ce, Y and Ca in equilibrium with 1 atm H₂ at various temperatures.

N₉ is number of hydrogen atoms/cc x 10⁻²²
Ab Initio Calculation of Phonon Spectra

**VASP**
- Relax crystal structure
- Calculate Hellmann-Feynman forces from displaced atomic positions

**PHONON**
- Randomly sample \( q \)-points in 1st Brillouin zone
- Solve equations of motion with the dynamical matrix in the harmonic approximation
- Total phonon density of states \( \rho(\varepsilon) \)
- Partial phonon density of states \( \rho(\omega) \)
- Phonon dispersion relations \( \omega(q) \)
YH$_2$ Structure and Lattice Dynamics

- YH$_2$ has a CaF$_2$ type FCC structure
  - 12 atoms
  - 4 Y atoms (blue) at vertices and faces of unit cell
  - 8 H atoms (grey) in tetrahedral holes between Y atoms

- Dispersion relations (at right)
  - Well separated acoustical and optical modes
  - Lower branches are acoustical modes mainly due to heavy Y atom vibrations
  - Higher branches are optical modes mainly due to light H atom vibrations
YH$_2$ Phonon Density of States
High resolution inelastic neutron scattering spectra from Udovic shows similar structure for $\text{YH}_2$ centered on 0.127 eV.
Heat Capacity Based on YH$_2$ Phonon DOS Agrees with Measurement
LEAPR Models YH$_2$ and Ice Ih

- H(YH$_2$), Y(YH$_2$), H(Ice-Ih), and O(Ice-Ih) TSLs generated using NJOY/LEAPR
- Phonon DOS from PHONON calculations
- Incoherent approximation
- Atomic mass ratios and free atom scattering cross sections from ENDF/B-VII.1 evaluations
  - Consistent with ENDF/B-VIII.0(beta3)
- $\alpha$ and $\beta$ grids optimized to treat scattering up to 5 eV
H(YH₂) Inelastic Scattering Cross Section
H(YH₂) Elastic Scattering Cross Section
Y(YH$_2$) Inelastic Scattering Cross Section
$Y(YH_2)$ Elastic Scattering Cross Section
H(YH₂) Differential Inelastic Scattering Cross Section
H(YH₂) Total Scattering Cross Section Agrees with Measurements
YH$_2$ Summary

- H(YH$_2$) and Y(YH$_2$) TSLs developed using first-principles DFT and LD calculations
- $\alpha$ and $\beta$ grids optimized to treat scattering up to 5 eV
  - $\beta$ grid can resolve 1-phonon and multiphonon scattering effects
- Validation
  - Measured lattice parameter
  - High-resolution inelastic neutron scattering spectra
  - Measured heat capacity
  - Measured H scattering cross section for YH$_{1.90}$ and YH$_{1.88}$
Hexagonal Ice Ih (why ice?)

1. Criticality safety analyses routinely examine the reactivity effect of a liquid water environment during the transport and storage of nuclear fuel material.

2. 10 CFR 71 and IAEA SSR-6 transportation regulations require accident analysis at temperatures down to -20 F and -40 F, respectively. Consequently, there is a requirement for a thermal neutron scattering law (TSL) for ice which characterizes the impact of the chemically bound crystalline structure on neutron scattering, moderation, and reflection.

3. The thermal scattering kernel for liquid water has been extensively studied and is available in an ENDF library. However, no published ENDF File 7 TSL for water ice exists.

4. Crystalline ice is a significantly better reflector and less effective moderator than liquid water. Modifying the material density of liquid water to account for ice formation will not capture these effects in benchmark calculations.
Structure of Hexagonal Ice Ih

- $\text{H}_2\text{O}$ molecules are internally bound by strong covalent bonds. Weak intermolecular hydrogen bonds allow for many rotational configurations of the $\text{H}_2\text{O}$ molecules in ice on a fixed oxygen lattice.

- Ice $\text{Ih}$ is the most common form of $\text{H}_2\text{O}$ ice. This structure can be viewed as two superimposed hexagonal lattices, where each lattice site contains an oxygen. The molecular alignments are locally ordered but globally disordered.

- Ice $\text{Ih}$ has 4 molecules per primitive unit cell (green trapezoid). Larger unit cells can be defined to better capture the varying $\text{H}_2\text{O}$ alignments. The red diamond is a 2-D view of the 12-molecule 3-D unit cell used in this work (top right image).
Phonon Energy Spectra for Ice Ih

Experimental inelastic neutron scattering spectrum for polycrystalline ice Ih (same energy scale as above).

Inelastic Scattering Energy Spectra for H in Liquid Water vs. Ice

T = 273 K

E=0.0253 eV

Differential Cross Section (dσ/dE') vs. Secondary (Scattered) Neutron Energy (eV)
**Total and Inelastic Scattering for Liquid Water vs. Ice**

**Total = Inelastic + Elastic + Absorption**

(There is no elastic scattering in liquid water)

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**Ice Total Cross Section**

**Water Total Cross Section**

$T = 273$ K

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**Ice Inelastic Cross Section**

**Water Inelastic Cross Section**

$T = 273$ K
Theoretical vs. Experimental Total Cross Sections for Ice Ih

Experimental data from:
Inelastic Scattering Cross Sections for H in Ice Ih

Incident Energy (eV)

Inelastic Scattering Cross Section (barns)
A Diffusion Benchmark for TSL Validation

• E. G. Silver measured the diffusion parameters of Ice Ih in the 1960s using a pulsed-neutron die-away experiment to determine the thermal flux decay time eigenvalues for various-sized cylinders of ice over a range of temperatures.

• After sufficient waiting time following the initial pulse, the neutron population is in thermal equilibrium and settles into the fundamental spatial mode with a single decay time eigenvalue. The experiment was modeled in MC21 and eigenvalue results were compared to measured data.

• In the one-speed diffusion model, the flux decay of the fundamental spatial mode can be expressed as

$$\varphi(r,t) = \varphi_0(r) \exp[-(\nu\Sigma_a + \nu DB^2 - CB^4)t],$$

where the time eigenvalue $$\alpha = \nu\Sigma_a + \nu DB^2 - CB^4$$

$$\Sigma_a$$ is the macroscopic absorption cross section
$$D = 1/\Sigma_{\text{transport}}$$ is the diffusion parameter,
$$\nu$$ is the effective average neutron velocity,
$$B^2$$ is geometric buckling, and
$$C$$ is the diffusion cooling parameter

Benchmark Testing Results

Experimental (Black) vs. Theoretical (Red) Eigenvalues vs. Buckling

Top Trajectory: -45 C
Middle Trajectory: -65 C
Bottom Trajectory: -85 C
Benchmark Testing Results

Time Eigenvalues vs. Buckling at -45 C for Selected Theoretical Scattering Kernels

![Graph showing the relationship between time eigenvalues and buckling at -45 C for different libraries.](image)
Benchmark C/E Fit

<table>
<thead>
<tr>
<th>SILVER EXPERIMENTAL</th>
<th>FINAL LIBRARY (-45 C)</th>
<th>FINAL LIBRARY (-85 C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-45 C</td>
<td>-65 C</td>
<td>-85 C</td>
</tr>
<tr>
<td>α</td>
<td>σ</td>
<td>C/E</td>
</tr>
<tr>
<td>B²</td>
<td>α</td>
<td>σ</td>
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<tr>
<td>0.0394 5630 59</td>
<td>0.0395 5579 59</td>
<td>0.0396 6443 35</td>
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<tr>
<td>0.0621 6207 35</td>
<td>0.0621 6031 35</td>
<td>0.0624 5890 61</td>
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<tr>
<td>0.0669 6413 22</td>
<td>0.0690 6266 22</td>
<td>0.0693 6096 53</td>
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<tr>
<td>0.0748 6584 38</td>
<td>0.0749 6455 38</td>
<td>0.0752 6226 66</td>
</tr>
<tr>
<td>0.0880 6888 76</td>
<td>0.0881 6825 76</td>
<td>0.0885 6493 72</td>
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<tr>
<td>0.1352 8214 70</td>
<td>0.1354 8052 73</td>
<td>0.1362 7593 72</td>
</tr>
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For the six highest buckling geometries (B² is in units of cm²), which are the most sensitive to the supplied thermal scattering kernel, the average C/E across all three temperatures is 1.003.

For the six lowest buckling geometries, the average C/E across all three temperatures is 1.019. These cases are relatively insensitive to the supplied thermal scattering kernel, indicating there may be a slight positive bias in the absorption cross sections. These results are consistent with the ~2.5% ENDF quoted uncertainty for H absorption cross sections in the thermal energy range.
Hexagonal Ice Ih Summary

• While the total cross sections for liquid water and solid ice are similar (except at extremely low incident energies), the details of the scattering kernels differ significantly and result in significant differences in the diffusion of neutrons through the material.

• Unlike liquid water, a large fraction of neutron scattering that takes place in ice is elastic. Consequently, Ice Ih has enhanced reflective properties over liquid water that could have important criticality safety implications.

• Combining the first-principles VASP/PHONON methodology with experimentally measured scattering data and a diffusion benchmark has yielded the development and successful testing of a thermal neutron scattering kernel for Ice Ih.

• A full ENDF File 7 thermal neutron scattering library has been submitted to the National Nuclear Data Center for the ice Ih structure for a range of temperatures of interest.