Needs for improving TSL data file for H in CaH$_2$ and Ca in CaH$_2$

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Calcium Hydride (CaH$_2$) was used in several experiments performed in the fast reactors MASURCA (CEA Cadarache, France) and PHENIX (CEA Marcoule, France) for transmutation studies. The goal of these experiments (COMODORE-4, COSMO-3, ECRIX-H) was to study the neutronic properties of CaH$_2$ in cold and hot conditions. Table 1 shows the impacts of H in CaH$_2$ in the frame of the ECRIX-H experiment designed for the transmutation of Am241. The experiment consists in irradiating Am241 samples in a CaH$_2$ can. If no TSL data are used, results indicate that the final Am241 and Am242m is underestimated by 27.2% and 34.5%. If TSL data of H in CaH$_2$ are replaced by H in ZrH, the underestimation is close to 3.9% and 4.6% (ZrH and CaH$_2$ seem to have similar neutronic properties).

In order to interpret the ECRIX-H experiment with the TRIPOLI (Monte-Carlo) and ERANOS (deterministic) codes, an experimental program was carried out at the ILL facility for measuring the phonon spectrum of CaH$_2$ (Cf. JEFDOC 1053) and to produce TSL data for the JEFF library with the LEAPR module of NJOY. A careful validation of the resulting TSL data was never performed.

New experimental program and theoretical calculations are needed to validate/improve the TSL data of CaH$_2$.

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<th>Hydrogène lié dans...</th>
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Table 1: Impacts of the TSL data of H in CaH$_2$ on the calculated isotopic concentrations (ECRIX-H experiment).
Thermal Neutron Scattering Cross Sections for H in CaH$_2$ and Ca in CaH$_2$

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Context

CaHx phonon frequency spectrum measurement
- Samples
- Experimental setup
- Measurement and data reduction
- Interpretation

Thermal neutron scattering cross section for H in CaH₂
- Formalism
- NJOY calculations
- Results

Thermal neutron scattering cross section for Ca in CaH₂

Conclusion and outlook
In the frame of possible methods for the transmutation of actinides and/or long lived fission products: **experimental programs** have been proposed to investigate the neutronic characteristics of fast reactor cores containing small quantities of various moderator materials:

- **COSMO**: carried out in MASURCA reactor (1999-2000).
- **ECRIX**: planned in PHENIX reactor with
  - $B_4C$: **ECRIX-C experiment**
  - ZrHx and CaHx: **ECRIX-H experiments**

Validation of these experimental programs must be done from deterministic and stochastic neutronic codes (ERANOS, MCNP)

Thermal inelastic scattering cross sections are needed:
- thermal data already exist for zirconium hydride,
- **No such data is readily available for calcium hydride**
A measurement of the CaH$_x$ phonon frequency spectrum at the ILL High Flux Reactor facility in Grenoble (France) has been carried out.

From this spectrum, the thermal scattering cross sections for H bound in CaH$_x$ and Ca bound in CaH$_x$ were deduced.
Context

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Thermal neutron scattering cross section for Ca in CaH$_2$

Conclusion and outlook
Samples used:
Impurity in CaHₓ sample is made of Ca(OH)₂ due to the high affinity for hydrogen binding with oxygen from the air.

So, three samples (powder samples) were used:
- CaHₓ unexposed to air (~95% pure)
- Ca(OH)₂ (for reference)
- CaHₓ exposed to air during 12 hours

The exact stochiometry of the samples is not currently known but is thought to be close to two (x~2).
Experimental Setup:
Three Axis Spectrometer (IN1 at Laue Langevin Institute)

- **Axis Monochromator - Sample:**
  Select the energy of the incident neutrons, according to the Bragg's diffraction law.

- **Axis Sample - Analyser:**
  Select the scattering angle (fixed in our experiment).

- **Axis Analyser - Detector:**
  Select only the scattered neutrons with about 4 meV.

- **Neutron Monitor:**
  Control the flux of the incident neutrons. A total count of 250,000 was accumulated for each energy point before moving to the next.

The neutrons detected (He3) with a fixed final energy (4meV) were recorded for monochromatic incident neutrons over 15 – 200 meV energy range.
Consequently, the large peak centred at around 40 meV is almost certainly due to O-H vibration. The same peak is present in the CaHx unexposed confirming a small contamination of this sample with oxygen.

Identically spectra for Ca(OH)$_2$ and CaHx exposed to air, except differences of the intensity due to different amounts of sample in the beam (which were loaded by hand).

The CaHx exposed to air has been transformed into Ca(OH)$_2$
Data reduction:
- Contribution from Ca(OH)$_2$ has been removed,
- Background has been determined and removed.

Comparison with previous measurements (all curves were normalised at 80 meV):
- The first optical mode (75-105 meV) observed by both Maeland [2] and Bergsma [3]
- The second optical mode (110-140 meV) observed by Maeland [2]
One acoustic mode around 20 meV which corresponds to vibrations where the motions of the H and Ca atoms are in phase; This mode could be in principle described by a Debye spectrum;

Two optical modes:
- between 75 and 105 meV,
- between 110 and 140 meV
Correspond to the vibrations of the H-atoms from two different sites.

Fine structure or sub-peaks visible in each optical mode

Consistent with the known crystal structure of CaHx, which has two H sites, one a distorted octahedral site (lower band) and the other a distorted tetrahedral site (upper band) (see Ref. [4,5,6])
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Conclusion and outlook
It can be shown that the double differential scattering cross section of solids consisting of randomly ordered micro crystals takes the form (see Ref.[7]):

$$\frac{d\sigma}{d\Omega \, dE} = \frac{\sigma_b}{2KT} \sqrt{\frac{E'}{E}} S(\alpha, \beta)$$

- $S(\alpha, \beta)$ is the so-called scattering laws that need to be calculated for the given material,
- $\sigma_b$ = characteristic bound scattering cross section for the material
- $E, E'$: incident and scattered neutron energies in the lab frame
- $m$: cosine of the scattering angle in the lab frame
- The dimensionless parameters $\alpha$ and $\beta$ take the forms:

$$\begin{align*}
\alpha &= \frac{E' + E - 2\mu \sqrt{E' E}}{AkT} & \text{Momentum transfer} \\
\beta &= \frac{E' - E}{kT} & \text{Energy transfer}
\end{align*}$$
Thermal neutron scattering cross section for H in CaH$_2$ (2)

Working in the incoherent and gaussian approximations, the S($\alpha, \beta$) takes the following form:

$$S(\alpha, \beta) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \rho(\beta) \left[ 1 - e^{-\beta t} \right] e^{-i \beta t} dt$$

with

$$\rho(\beta) = \frac{1}{\beta} e^{-\beta \lambda / 2}$$

and

$$P(\beta) = \frac{1}{\beta \sinh(\beta/2)}$$

where $\rho(\beta)$ is the phonon frequency spectrum, usually found by direct measurement:

$$\int_0^\infty \rho(\beta) d\beta = 1$$

Expanding the $\exp(-\gamma(t))$ term leads to the so-called ‘phonon expansion’ expression:

$$S(\alpha, \beta) = e^{-\alpha^2 / 2} \sum_{n=0}^\infty \frac{1}{n!} P(\beta) e^{-\beta / 2} d\beta$$

For $n=0$: (zero phonon)

- **Incoherent elastic term**

For $n>0$

- **Incoherent inelastic terms**

Thermal neutron scattering cross section for H in CaH$_2$ (2)
Phonon frequency spectrum used for H in CaHx;

The spectrum was obtained using the following approximation:

- In the case of the ZrH2, the phonon frequency spectrum for H in ZrH2, has been calculated by Slaggie [8]. He shows that the weight of the acoustic part was: 1/242;

- For H in CaH2, we have assumed that this weighting factor must be increased by the ratio: $A_{Zr} / A_{ca}$. In this way, we obtained: 1/106 (0.94%). A similar assumption was adopted by Picton [9] for TiH2.

Remark:
This weighting factor could be deduced from rigorous lattice dynamic model (see Ref. [10,11]). Further investigations are needed on the matter.
NJOY Calculations: MAT=8 (H-CaH₂)
( performed for T = 296; 400; 500; 600; 700; 800; 1000 and 1200 K)

**LEAPR**
- Generates the thermal scattering data in ENDF format: File7
  - MT=2 (elastic): Debye Waller factor given
  - MT4 (inelastic): tabulated $S(\alpha,\beta)$

**THERMR**
- Calculates the pointwise thermal scattering cross sections in pendf format, File3:
  - MT=2 : elastic H-free
  - MT=237: incoherent elastic H in CaH2
  - MT=238: incoherent inelastic H in CaH2

**ACER**
- Generates the thermal scattering data for MCNP code in ACE format

Thermal neutron scattering cross section for H in CaH₂ (4)
Thermal neutron scattering cross section for H in CaH$_2$ (5)

**Results**

**Thermal incoherent elastic cross sections** (0 phonon exchange)

\[ \sigma(E) = \frac{\sigma_b}{2} \left\{ 1 - e^{-\frac{4WE}{2WE}} \right\} \]

\[ W = \frac{\lambda}{AkT} \] (Debye – Waller factor)

**Thermal incoherent inelastic cross sections** (one and more phonons exchange)
Examples of secondary neutron energy spectra from H in CaH₂ for various incident neutron energies.

- Incident Neutron Energy = 25.3 meV
- Incident Neutron Energy = 112 meV
- Incident Neutron Energy = 251 meV
- Incident Neutron Energy = 503 meV
The ENDF file for H in CaH$_2$ is ready for JEFF3.1:

```
JEFF-3.0 file header. Release October 2004

1.001000+3 9.991700-1 -1 0 2 0 8 1451 1
0.000000+0 0.000000+0 0 0 0 6 8 1451 2
1.000000+0 0.000000+0 0 0 12 6 8 1451 3
0.000000+0 0.000000+0 0 0 61 3 8 1451 4
H(CaH2) EVAL-OCT04 O.SEROT CEA Cadarache 8 1451 5

----JEFF-3.0 MATERIAL 8

-----THERMAL NEUTRON SCATTERING DATA

-----ENDF-6 FORMAT

Temperatures = 296. 400. 500. 600. 700. 800. 1000. 1200. K.

The present evaluation is based on measurements of CaH$_2$ phonon
counterparts performed at the ILL high flux reactor
(Grenoble/France) (ref 1). The contribution of the Ca(OH)$_2$
impurity has been removed.

The phonon frequency spectrum obtained has the following
characteristics:

- an acoustic mode, centered at around 20 meV.
- two optic mode bands centered respectively in the energy
  range 70-100 meV and 110-140 meV. In each optic mode, fine
  structures could be observed and explained from the known
  crystal structure of CaH$_2$ (ref 2,3).
```
In order to treat Hydrogen atom bound in CaH2, the acoustic mode has been weighted relative to the optical modes by a factor 1/106 (see Ref.4). This weighting factor was not deduced from rigorous lattice dynamic model, but from physical grounds. This aspect could be improved and further investigations are needed on the matter.

The S(alpha,beta) scattering laws have been generated using the tools and methodologies given in ref 5. The alpha and beta grids are the same as used for H in ZrH2 allowing energy transfers of almost 2 eV at T=296. K.

The following ENDF MAT and MT’s have been chosen in order to remain compatible with other materials: MAT 8, MT 237 and 238 for incoherent inelastic and elastic cross sections.

The following options have been used in the processing:

Leapr: spr 20.478, npr 1, iel 0
Thermr: icoh 0, natom 1, mtref 237
Acer: mti 237, mte 238, ielas 1 (incoherent elastic), nmix 1

... ... ...

Thermal neutron scattering cross section for H in CaH₂ (8)
Context

CaHx phonon frequency spectrum measurement
- Samples
- Experimental setup
- Measurement and data reduction
- Interpretation

Thermal neutron scattering cross section for H in CaH₂
- Formalism
- NJOY calculations
- Results

Thermal neutron scattering cross section for Ca in CaH₂

Conclusion and outlook
Phonon frequency spectrum used for Ca in CaH$_2$;
NJOY Calculations: MAT=59 (Ca – CaH₂)
(performed for T= 296; 400; 500; 600; 700; 800; 1000 and 1200 K)

LEAPR
Generates the thermal scattering data in ENDF format: File7
- MT=2 (elastic): Debye Waller factor given
- MT4 (inelastic): tabulated $S(\alpha,\beta)$

THERMR
Calculates the pointwise thermal scattering cross sections in pendf format, File3:
- MT=2: elastic Ca-40
- MT=239: incoherent elastic Ca in CaH₂
- MT=240: incoherent inelastic Ca in CaH₂

ACER
Generates the thermal scattering data for MCNP code in ACE format

Thermal neutron scattering cross section for Ca in CaH₂ (2)
Thermal neutron scattering cross section for Ca in CaH$_2$ (3)

Results (example T=296K)

![Graph showing cross section vs. incident neutron energy for Ca free atom, incoherent inelastic Ca in CaH$_2$, and incoherent elastic Ca in CaH$_2$.]
Thermal neutron scattering cross section for Ca in CaH$_2$ (4)

The ENDF file for Ca in CaH$_2$ is ready for JEFF3.1:

| JEFF-3.0 file header. Release October 2004 | 1 0 0 0 |
| 2.000000E+3 3.973190E+1 | -1 0 0 0 |
| 0.000000E+0 0.000000E+0 | 0 0 0 0 |
| 1.000000E+0 0.000000E+0 | 0 0 12 6 |
| 0.000000E+0 0.000000E+0 | 0 0 61 3 |
| Ca (CaH2) | EVAL-OCT04 O.SEROT CEA Cadarache |
| DIST-OCT04 | 59 1451 5 |
| ----ENDF/B-VI MATERIAL 59 | 59 1451 6 |
| ------THERMAL NEUTRON SCATTERING DATA | 59 1451 7 |
| ------ENDF-6 FORMAT | 59 1451 8 |
| Temperatures = 296. 400. 500. 600. 700. 800. 1000. 1200. K. | 59 1451 9 |
| | 59 1451 10 |
| The present evaluation is based on measurements of CaH2 phonon | 59 1451 11 |
| frequency spectra performed at the ILL high flux reactor | 59 1451 12 |
| (Grenoble/France) (ref 1). The contribution of the Ca(OH)2 | 59 1451 13 |
| impurity has been removed. | 59 1451 14 |
| | 59 1451 15 |
| The phonon frequency spectrum obtained has the following | 59 1451 16 |
| characteristics: | 59 1451 17 |
| | 59 1451 18 |
| - an acoustic mode, centered at around 20 meV. | 59 1451 19 |
| - two optic mode bands centered respectively in the energy | 59 1451 20 |
| range 70-100 meV and 110-140 meV. In each optic mode, fine | 59 1451 21 |
| structures could be observed and explained from the known | 59 1451 22 |
| crystal structure of CaH2 (ref 2,3). | 59 1451 23 |
| | 59 1451 24 |
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| | 59 1451 26 |
In order to treat Calcium atom bound in CaH2, the acoustic mode has been weighted relative to the optical modes by a factor 105/106 (see Ref.4). This weighting factor was not deduced from rigorous lattice dynamic model, but from physical grounds. This aspect could be improved and further investigations are needed on the matter.

The S(\alpha,\beta) scattering laws have been generated using the tools and methodologies given in ref 5. The alpha and beta grids are the same as used for H in CaH2 allowing energy transfers of almost 2 eV at T=296. K.

The following ENDF MAT and MT’s have been chosen in order to remain compatible with other materials: MAT 59, MT 239 and 240 for incoherent inelastic and elastic cross sections.

The following options have been used in the processing:

Leapr: spr 3.0193, npr 1, iel 0
Thermr: icoh 0, natom 1, mtref 239
Acer: mti 239, mte 240, ielas 1 (incoherent elastic), nmix 1
Conclusion and perspectives

- Thermal scattering cross section for H in CaH$_2$ and Ca in CaH$_2$ are needed for the interpretation of the ECRIX-H experiment (in PHENIX reactor).

- The CaH$_2$ phonon spectrum has been measured at the three axis spectrometer of ILL institute.

- The measured phonon spectrum was transformed and then used in the LEAPR and THERMR modules from NJOY in order to get the $S(\alpha,\beta)$ scattering laws and cross section (in ENDF format) for H in CaH$_2$ and for Ca in CaH$_2$.

- However, bearing in mind the susceptibility of CaH$_2$ to contamination by oxygen it may be also effective to use the phonon spectrum incorporating the component due to OH binding.

- Validation of these data could be done from COSMO-3 experiment (where CaH$_2$ moderator material has been used) as well as from ECRIX-H experiment (near future).
References