JEFF-DOC 1053

Thermal Neutron Scattering Cross Sections for H in CaH_2 and Ca in CaH_2

O. Serot

CEA - Cadarache, DEN / DER / SPRC / LEPh, Bat. 230,

F- 13108 St Paul lez Durance CEDEX, France

- Context
- CaHx phonon frequency spectrum measurement
  - Samples
  - Experimental setup
  - Measurement and data reduction
  - Interpretation
- Thermal neutron scattering cross section for H in CaH_2
  - Formalism
  - NJOY calculations
  - Results
- Thermal neutron scattering cross section for Ca in CaH_2
- 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**

- Interests in using CaH_2 moderator material:
  - Relatively stable in liquid sodium,
  - Good mechanical properties,
  - High density of Hydrogen,
  - No activation by neutron irradiation.

In this context, and due to the lack of information on H-CaHx thermal cross section:

- **A measurement of the CaHx 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 CaHx and Ca bound in CaHx were deduced**

- Context

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

- Thermal neutron scattering cross section for H in CaH_2
  - Formalism
  - NJOY calculations
  - Results

- Thermal neutron scattering cross section for Ca in CaH_2

- Conclusion and outlook

CaHx Phonon frequency spectrum measurement (1)

This experiment has been performed by:
P. Morris, D.K. Ross, S. Ivanov, D.R. Weaver and O. Serot
All the details can be found in Ref [1]

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.

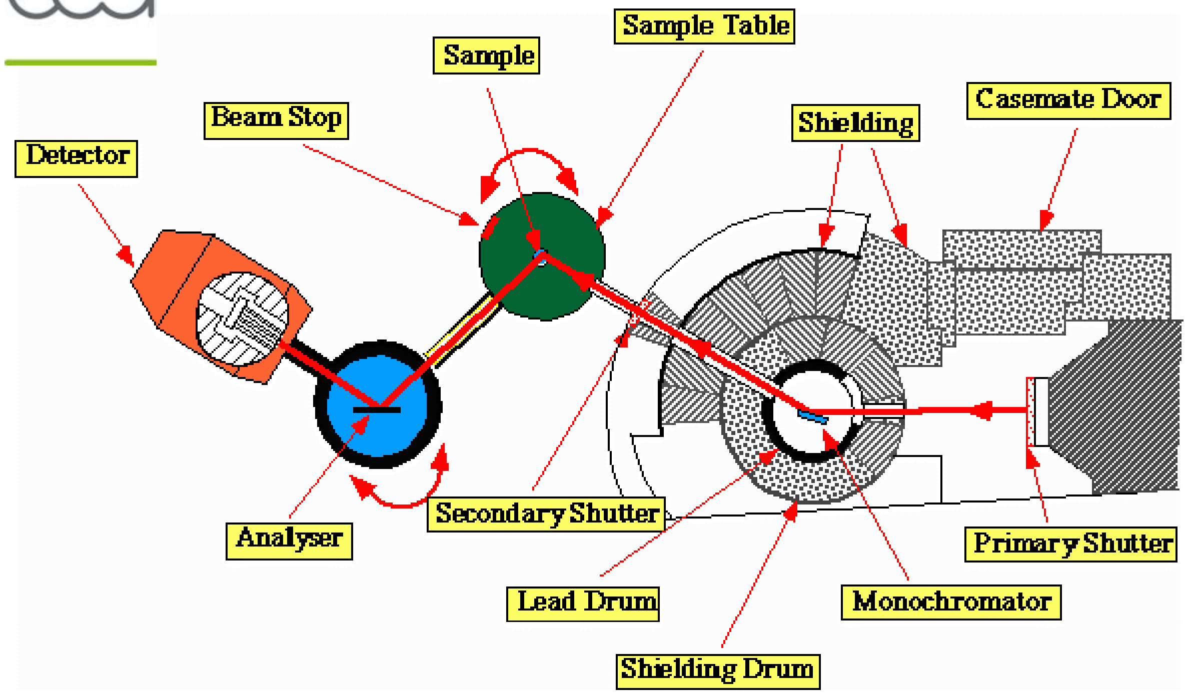
So, three samples (powder samples) were used:

- CaH_x unexposed to air (~95% pure)
- $Ca(OH)_2$ (for reference)
- CaH_x 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).

CaHx Phonon frequency spectrum measurement (2)

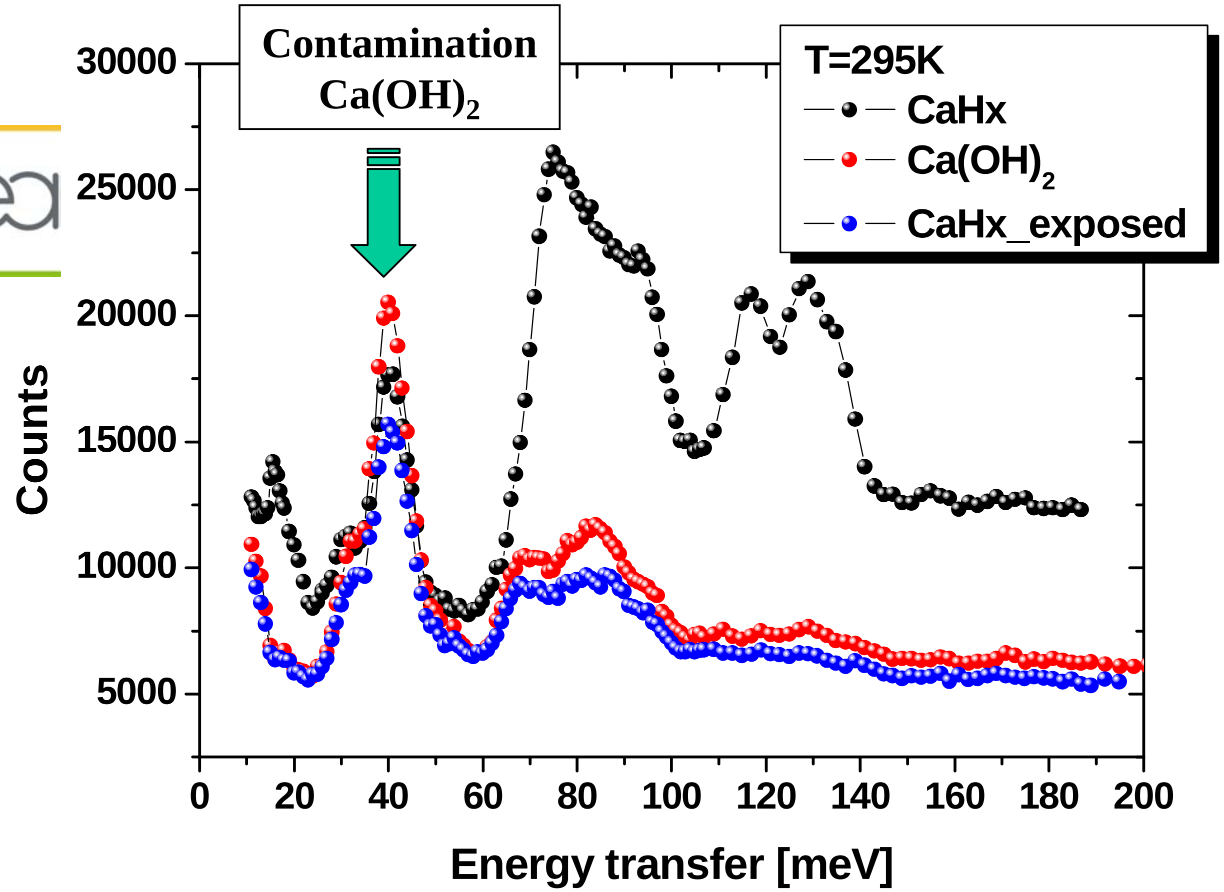
Experimental Setup:
Three Axis Spectrometer (IN1 at Laue Langevin Institute)



The neutrons detected (He3) with a fixed final energy (4meV) were recorded for monochromatic incident neutrons over 15 – 200 meV energy range.

- **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.

CaHx Phonon frequency spectrum measurement (3)

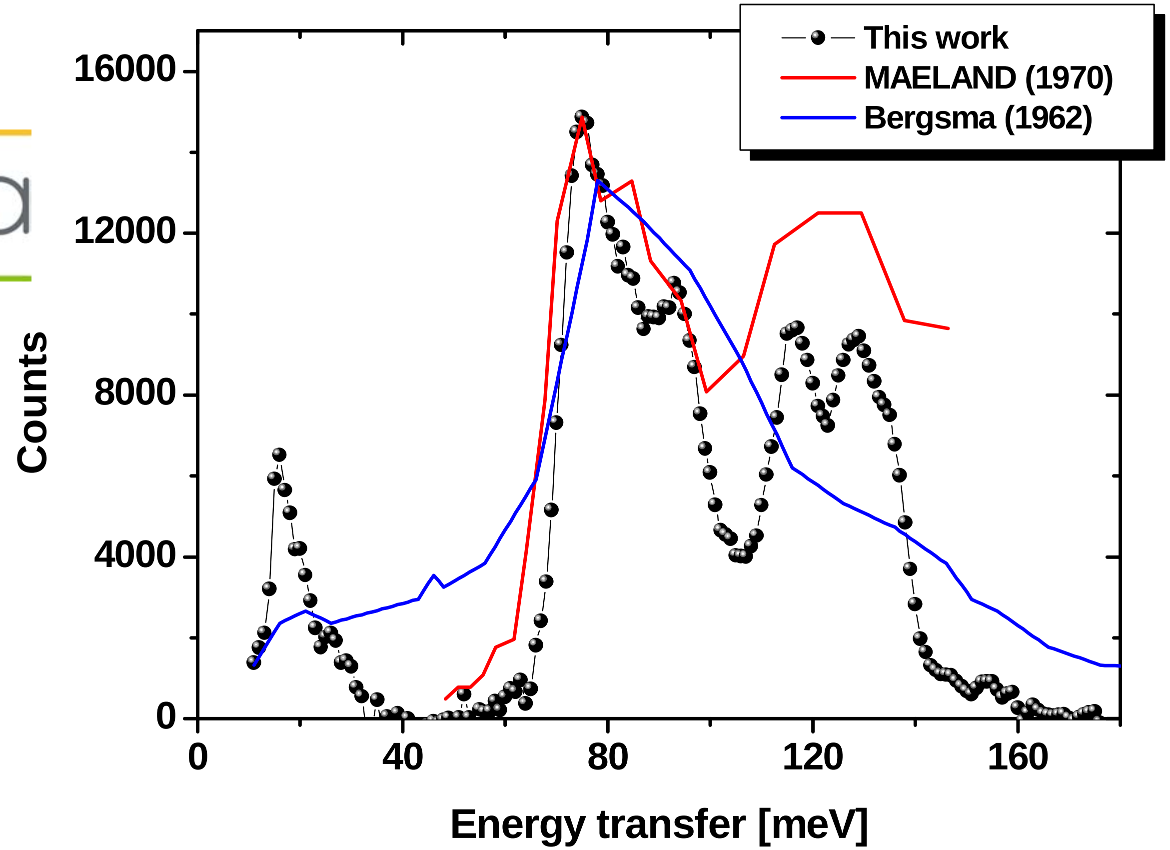


- Identical spectra for $Ca(OH)_2$ and CaHx exposed to air , except differences of the intensity due to different amounts of sample in the beam (which were loaded by hand).

→ **The CaHx exposed to air has been transformed into $Ca(OH)_2$**

- 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.

CaHx Phonon frequency spectrum measurement (4)



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]

CaHx Phonon frequency spectrum measurement (5)

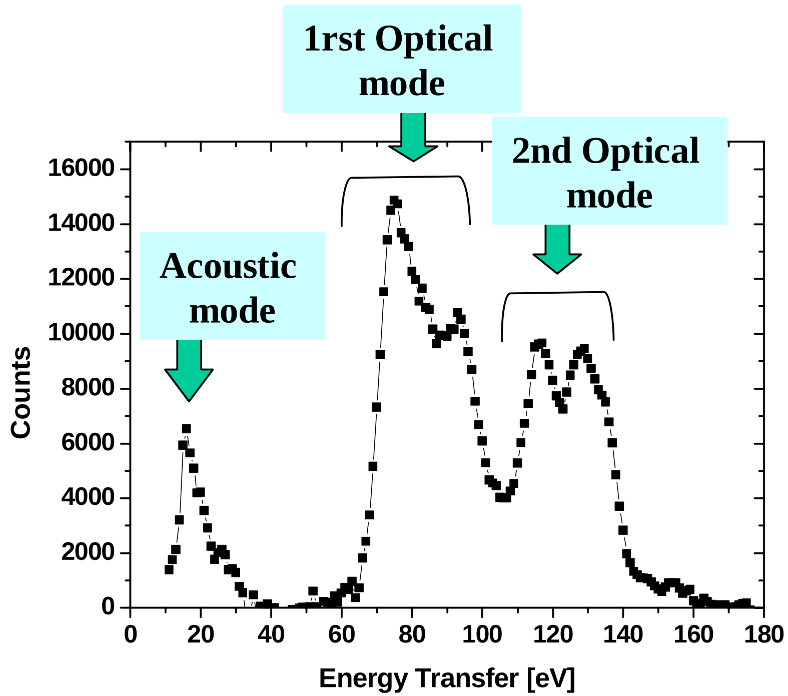
Interpretation of the CaHx phonon frequency spectrum

- 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])

- Context

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

- ***Thermal neutron scattering cross section for H in CaH_2***
  - Formalism
  - NJOY calculations
  - Results

- Thermal neutron scattering cross section for Ca in CaH_2

- Conclusion and outlook

Thermal neutron scattering cross section for H in CaH_2 (1)

Formalism

- 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,
- σ_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 α and β take the forms:

$$\begin{cases} \alpha = \dfrac{E' + E - 2\mu\sqrt{E'E}}{AkT} & \Rightarrow \text{Momentum transfer} \\ \beta = \dfrac{E' - E}{kT} & \Rightarrow \text{Energy transfer} \end{cases}$$

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:

$$S(\alpha,\beta)=\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\beta t}\cdot e^{-\gamma(t)}\,dt$$

with $$\gamma(t)=\alpha\int_{-\infty}^{\infty} P(\beta)\left[1-e^{-i\beta t}\right]e^{-\beta/2}\,d\beta$$

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

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

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

Expanding the exp(-γ(t)) term leads to the so-called 'phonon expansion' expression:

$$S(\alpha,\beta)=e^{-\alpha\lambda}\sum_{n=0}^{\infty}\frac{1}{n!}(\alpha\lambda)^n\,\tau_n(\beta)$$

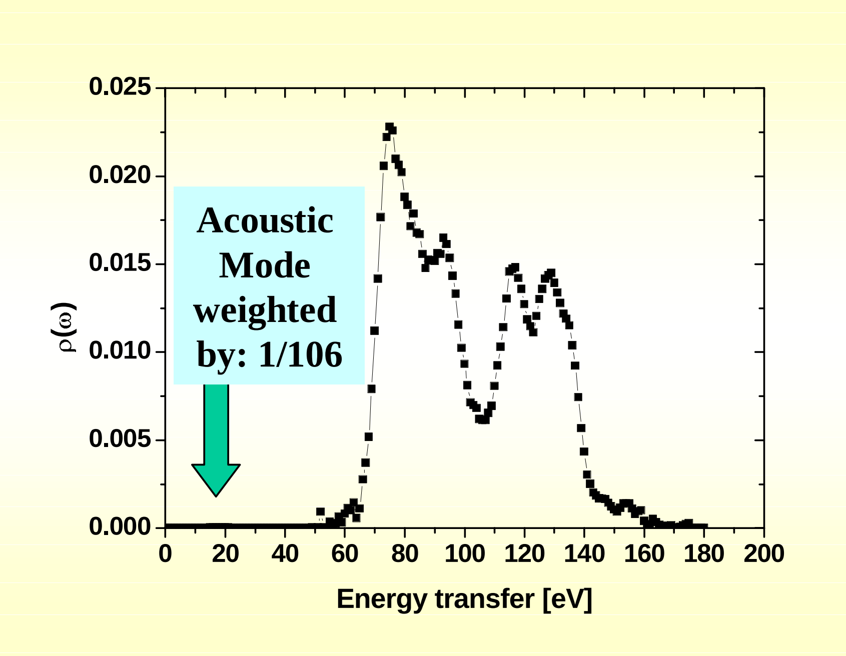
For n=0 ; (zero phonon):
Incoherent elastic term

For n>0 ;
Incoherent inelastic terms

Where λ is the Debye-Waller coefficient: $$\lambda=\int_{-\infty}^{\infty}P(\beta)\,e^{-\beta/2}\,d\beta$$

Thermal neutron scattering cross section for H in CaH_2 (3)

Phonon frequency spectrum used for H in CaHx;



Remark:
This weighting factor could be deduced from rigorous lattice dynamic model (see Ref. [10,11]). Further investigations are needed on the matter.

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

Thermal neutron scattering cross section for H in CaH_2 (4)

NJOY Calculations : MAT=8 (H-CaH_2)

(performed for T= 296; 400; 500; 600; 700; 800; 1000 and 1200 K)

NJOY 99.81 Cad

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:

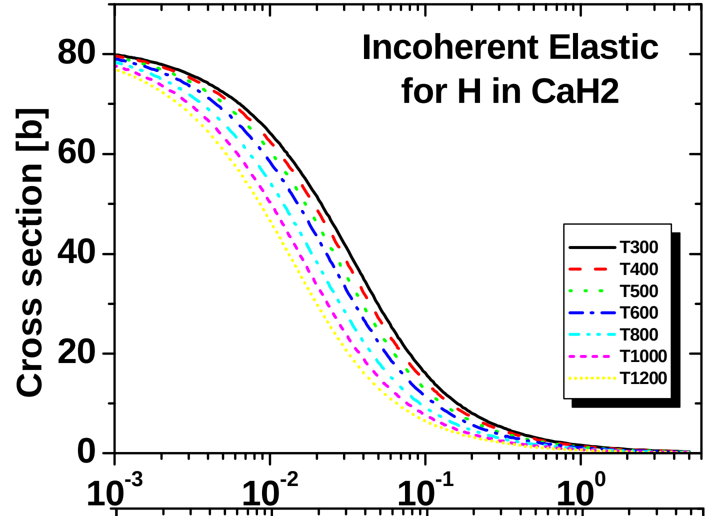
- MT=2 : elastic H-free
- MT=237: incoherent elastic H in CaH2
- MT=238: incoherent inelastic H in CaH2

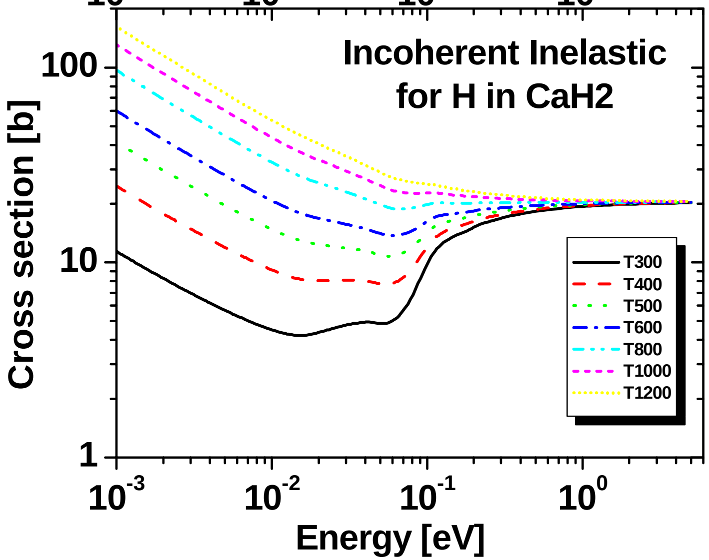
ACER

Generates the thermal scattering data for MCNP code in ACE format

Thermal neutron scattering cross section for H in CaH_2 (5)

Results





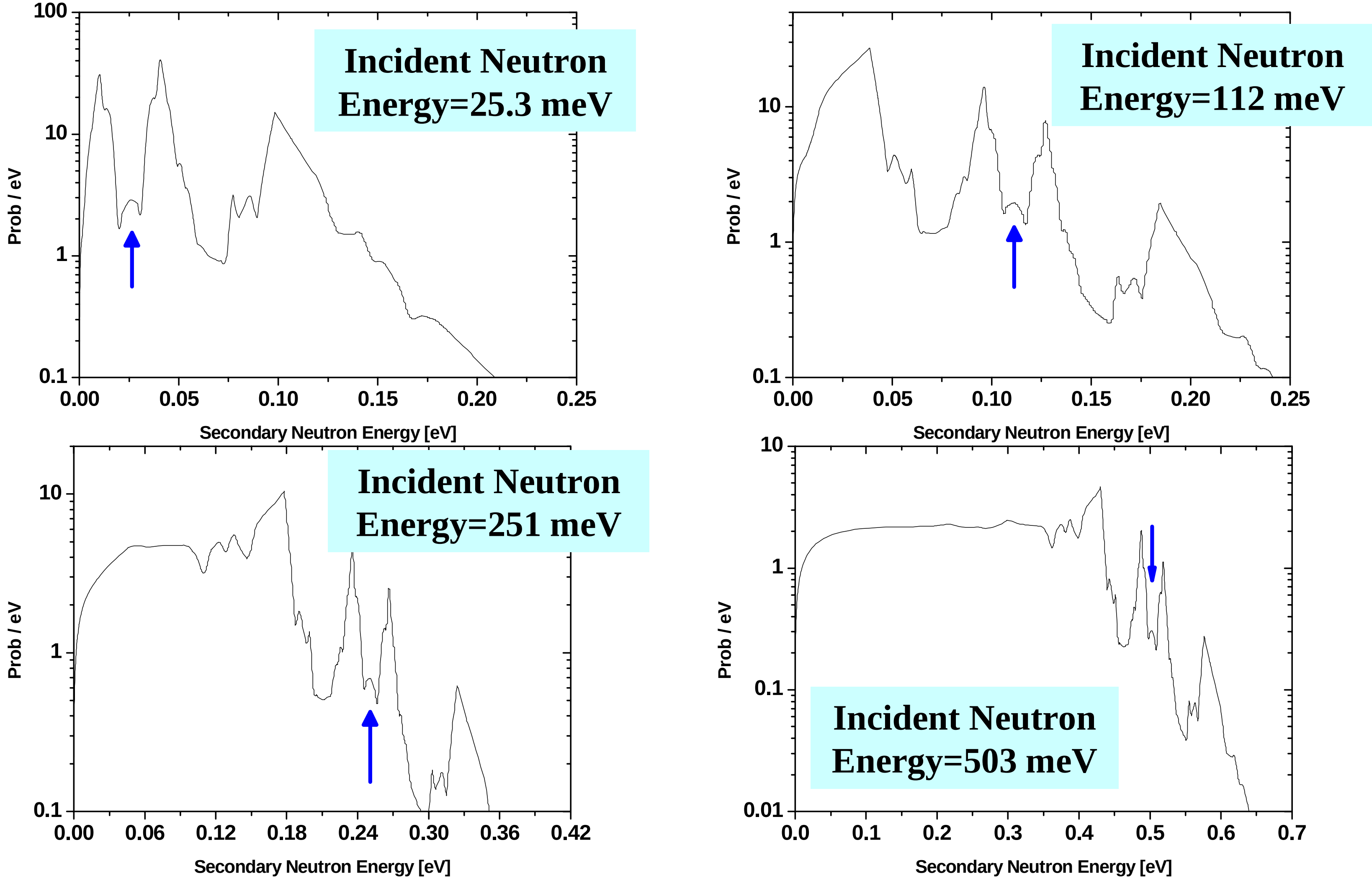
Thermal incoherent elastic cross sections (0 phonon exchange)

$$\begin{cases} \sigma(E) = \dfrac{\sigma_b}{2}\left\{\dfrac{1-e^{-4WE}}{2WE}\right\} \\ W = \dfrac{\lambda}{AkT} \quad \text{(Debye –Waller factor)} \end{cases}$$

Thermal incoherent inelastic cross sections (one and more phonons exchange)

Thermal neutron scattering cross section for H in CaH_2 (6)

Examples of secondary neutron energy spectra from H in CaH_2 for various incident neutron energies



Thermal neutron scattering cross section for H in CaH_2 (7)

The ENDF file for H in CaH_2 is ready for JEFF3.1:

```
JEFF-3.0 file header. Release October 2004                                  1 0  0    0
 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
                       DIST-OCT04                                           8 1451    6
----JEFF-3.0           MATERIAL    8                                        8 1451    7
-----THERMAL NEUTRON SCATTERING DATA                                        8 1451    8
------ENDF-6 FORMAT                                                         8 1451    9
                                                                            8 1451   10
 Temperatures = 296. 400. 500. 600. 700. 800. 1000. 1200. K.                8 1451   11
                                                                            8 1451   12
 The present evaluation is based on measurements of CaH2 phonon             8 1451   13
 frequency spectra performed at the ILL high flux reactor                   8 1451   14
 (Grenoble/France) (ref 1). The contribution of the Ca(OH)2                 8 1451   15
 impurity has been removed.                                                 8 1451   16
                                                                            8 1451   17
 The phonon frequency spectrum obtained has the following                   8 1451   18
 characteristics:                                                           8 1451   19
                                                                            8 1451   20
        - an acoustic mode, centered at around 20 meV.                      8 1451   21
        - two optic mode bands centered respectively in the energy          8 1451   22
        range 70-100 meV and 110-140 meV. In each optic mode, fine          8 1451   23
        structures could be observed and explained from the known           8 1451   24
        crystal structure of CaH2 (ref 2,3).                                8 1451   25
                                                                            8 1451   26
```

Thermal neutron scattering cross section for H in CaH_2 (8)

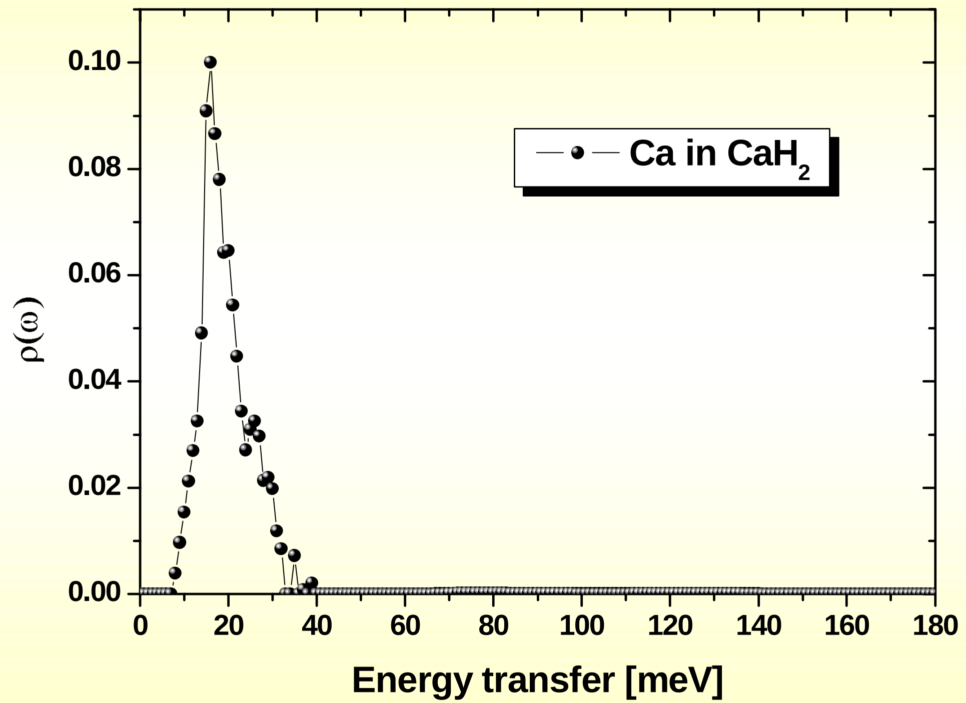
```
In order to treat Hydrogen atom bound in CaH2, the acoustic mode      8 1451   27
has been weighted relative to the optical modes by a factor 1/106     8 1451   28
(see Ref.4).                                                          8 1451   29
This weighting factor was not deduced from rigorous lattice           8 1451   30
dynamic model, but from physical grounds. This aspect could be        8 1451   31
improved and further investigations are needed on the matter.         8 1451   32
                                                                      8 1451   33
The S(alpha,beta) scattering laws have been generated using the       8 1451   34
tools and methodologies given in ref 5. The alpha and beta grids      8 1451   35
are the same as used for H in ZrH2 allowing energy transfers of       8 1451   36
almost 2 eV at T=296. K.                                              8 1451   37
                                                                      8 1451   38
The following ENDF MAT and MT's have been chosen in order to          8 1451   39
remain compatible with other materials: MAT 8, MT 237 and 238 for     8 1451   40
incoherent inelastic and elastic cross sections.                      8 1451   41
                                                                      8 1451   42
The following options have been used in the processing:               8 1451   43
                                                                      8 1451   44
Leapr:  spr 20.478, npr 1, iel 0                                      8 1451   45
Thermr: icoh 0, natom 1, mtref 237                                    8 1451   46
Acer:   mti 237, mte 238, ielas 1 (incoherent elastic), nmix 1        8 1451   47

… … …
```

- Context
- CaHx phonon frequency spectrum measurement
  - Samples
  - Experimental setup
  - Measurement and data reduction
  - Interpretation
- Thermal neutron scattering cross section for H in CaH_2
  - Formalism
  - NJOY calculations
  - Results
- ***Thermal neutron scattering cross section for Ca in CaH_2***
- Conclusion and outlook

Thermal neutron scattering cross section for Ca in CaH_2 (1)

Phonon frequency spectrum used for Ca in CaH_2;



Thermal neutron scattering cross section for Ca in CaH_2 (2)

NJOY Calculations : MAT=59 (Ca – CaH_2)

(performed for T= 296; 400; 500; 600; 700; 800; 1000 and 1200 K)

NJOY 99.81 Cad

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:

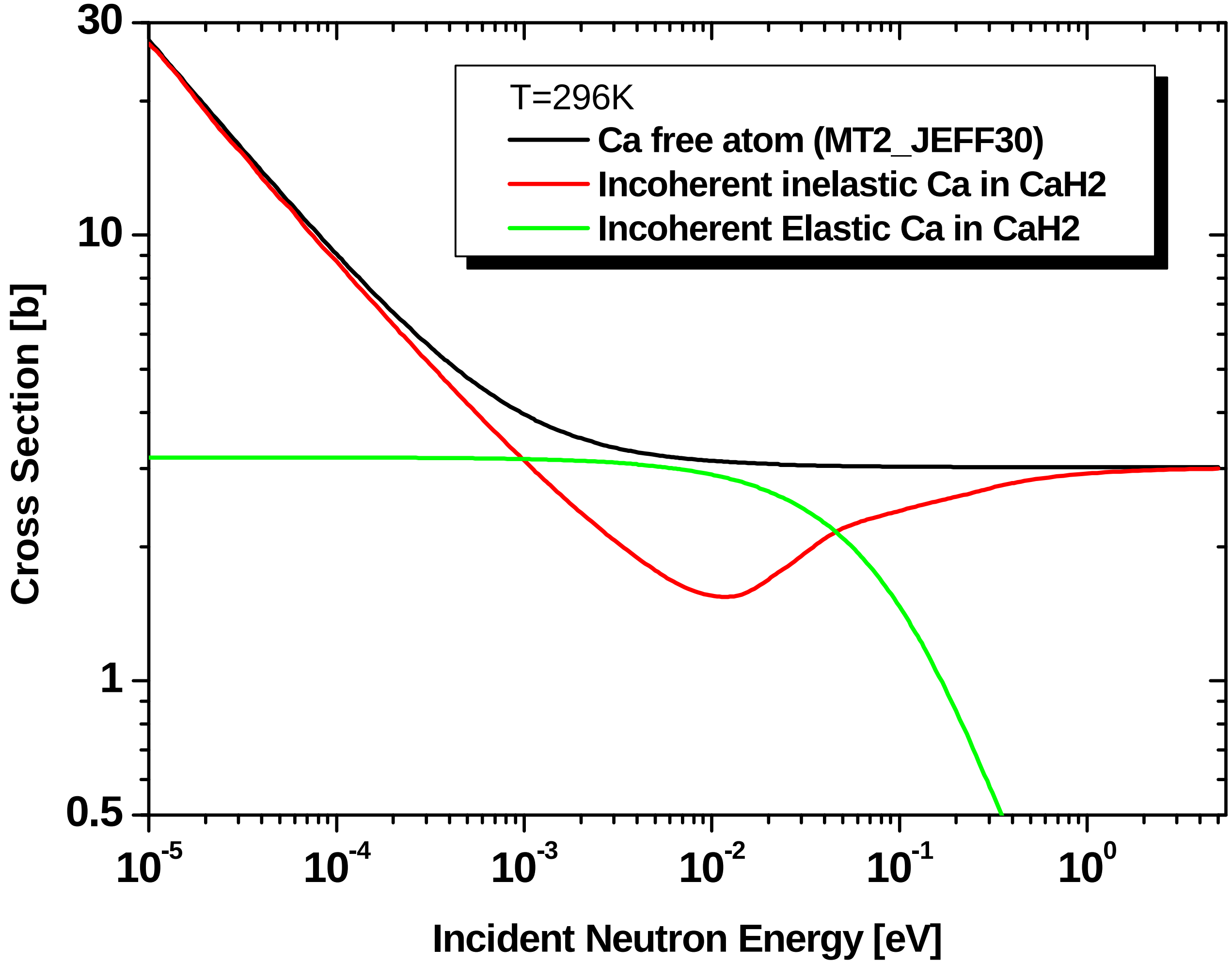
- MT=2 : elastic Ca-40
- MT=239: incoherent elastic Ca in CaH_2
- MT=240: incoherent inelastic Ca in CaH_2

ACER

Generates the thermal scattering data for MCNP code in ACE format

Thermal neutron scattering cross section for Ca in CaH_2 (3)

Results (example T=296K)



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
 2.000000+3 3.973190+1         -1          0          0          0  59 1451    1
 0.000000+0 0.000000+0          0          0          0          6  59 1451    2
 1.000000+0 0.000000+0          0          0         12          6  59 1451    3
 0.000000+0 0.000000+0          0          0         61          3  59 1451    4
 Ca (CaH2)            EVAL-OCT04   O.SEROT CEA Cadarache            59 1451    5
                      DIST-OCT04                                    59 1451    6
----ENDF/B-VI         MATERIAL   59                                 59 1451    7
-----THERMAL NEUTRON SCATTERING DATA                                59 1451    8
------ENDF-6 FORMAT                                                 59 1451    9
                                                                    59 1451   10
 Temperatures = 296. 400. 500. 600. 700. 800. 1000. 1200. K.        59 1451   11
                                                                    59 1451   12
 The present evaluation is based on measurements of CaH2 phonon     59 1451   13
 frequency spectra performed at the ILL high flux reactor           59 1451   14
 (Grenoble/France) (ref 1). The contribution of the Ca(OH)2         59 1451   15
 impurity has been removed.                                         59 1451   16
                                                                    59 1451   17
 The phonon frequency spectrum obtained has the following           59 1451   18
 characteristics:                                                   59 1451   19
                                                                    59 1451   20
        - an acoustic mode, centered at around 20 meV.              59 1451   21
        - two optic mode bands centered respectively in the energy  59 1451   22
        range 70-100 meV and 110-140 meV. In each optic mode, fine  59 1451   23
        structures could be observed and explained from the known   59 1451   24
        crystal structure of CaH2 (ref 2,3).                        59 1451   25
                                                                    59 1451   26
```

Thermal neutron scattering cross section for Ca in CaH_2 (5)

```
In order to treat Calcium atom bound in CaH2, the acoustic mode      59 1451   27
has been weighted relative to the optical modes by a factor          59 1451   28
105/106 (see Ref.4).                                                 59 1451   29
This weighting factor was not deduced from rigorous lattice          59 1451   30
dynamic model, but from physical grounds. This aspect could be       59 1451   31
improved and further investigations are needed on the matter.        59 1451   32
                                                                     59 1451   33
The S(alpha,beta) scattering laws have been generated using the      59 1451   34
tools and methodologies given in ref 5. The alpha and beta grids     59 1451   35
are the same as used for H in CaH2 allowing energy transfers of      59 1451   36
almost 2 eV at T=296. K.                                             59 1451   37
                                                                     59 1451   38
The following ENDF MAT and MT’s have been chosen in order to         59 1451   39
remain compatible with other materials: MAT 59, MT 239 and 240       59 1451   40
for incoherent inelastic and elastic cross sections.                 59 1451   41
                                                                     59 1451   42
The following options have been used in the processing:              59 1451   43
                                                                     59 1451   44
Leapr:  spr 3.0193, npr 1, iel 0                                     59 1451   45
Thermr: icoh 0, natom 1, mtref 239                                   59 1451   46
Acer:   mti 239, mte 240, ielas 1 (incoherent elastic), nmix 1       59 1451   47

… … …
```

Conclusion and perspectives

- Thermal scattering cross section for Hin 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

[1] P. Morris et al., Journal of Alloys and Compounds 363 (2004) 85-89
[2] A.J. Maeland, J. Chem. Phys. 52 (1970) 3952-3956
[3] J. Bergsma, J.A. Goedkoop, IAEA Symposium on inelastic Scattering of neutrons in solids and liquids, Vienna, October 1960
[4] J. Bergsma and B. O. Loopstra, Acta Cryst. **15** (1962) 92-93
[5] A. F. Andresen et al., Journal of Solid State Chemistry, **20** (1977) 93-101
[6] D. K. Ross et al., Z.Phys Chem, **114** (1979) 221-230
[7] R E MacFarlane, NJOY suite of manuals, 'New Thermal Neutron Scattering Files for ENDF/B-VI release 2', August 1994.
[8] E.L. Slaggie, J. Phys. Chem. Solids, **vol. 29** (1968) 923-934
[9] D. Picton, PhD thesis, University of Birmingham, 1981
[10] A.I. Hawari et al., 'Physor 2004', Chicago (USA), April 2004
[11] I.I. Al-Qasir et al., 'Physor 2004', Chicago (USA), April 2004