The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
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IAEA
International Atomic Energy Agency

1866-4

School on Pulsed Neutrons: Characterization of Materials

15 - 26 October 2007

Cage Structures and Clathrates

Werner Press

Christian-Albrechts-Universitat Kiel
Institut fur Experimentelle un Angewandte Physik
Olsausenstr. 40 - 60
24098 Kiel
Germany

Cage-systems

Werner Press (Kiel)

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AG Prof. Dr. W.Press

H_2O plus Xe or CH_4 (seafloor -gashydrates)

O_2Si plus CH_4 or CO_2 (volcanoes - clathrasils)

Si/Ge plus Na, K, Rb...

Skutterudites XRu_4Se_{12}

Inclusion compounds
Form structures stable in surprising p, T-regions
not: H in metals or systems with interconn. channels

Cage-systems: properties

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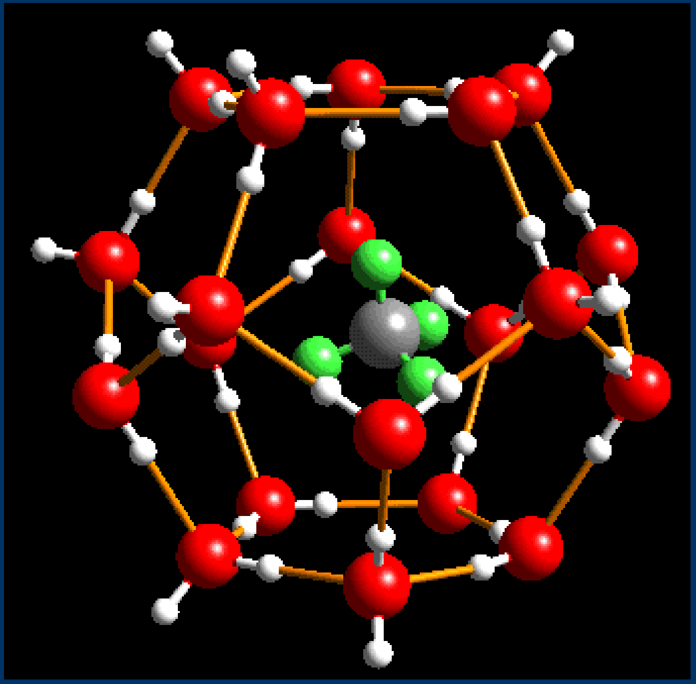
Framework & (inert) host

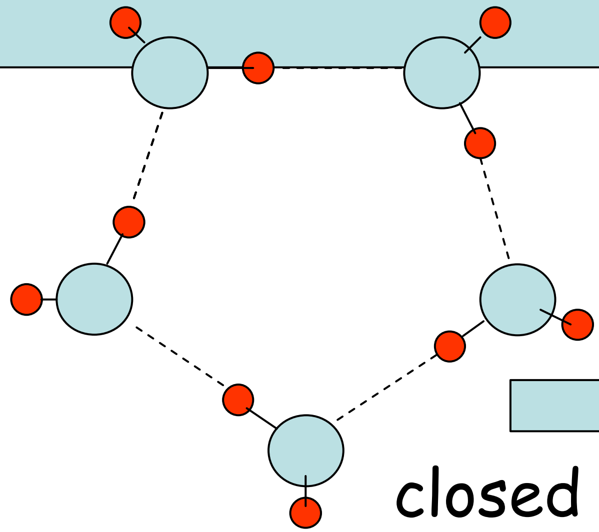
Polyhedra

Marine research
Store energy
Electrochemical systems
Rattling modes
- Einstein oscillationors
- glass-like thermal conductivity

Neutron moderators ?

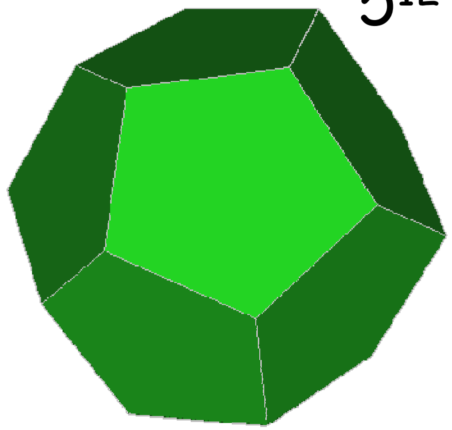


motif **Cage-formation**

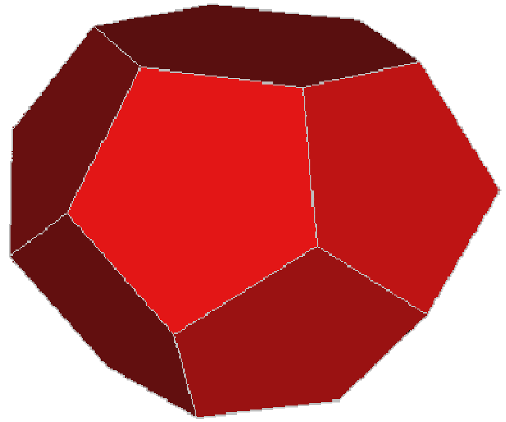


closed surface

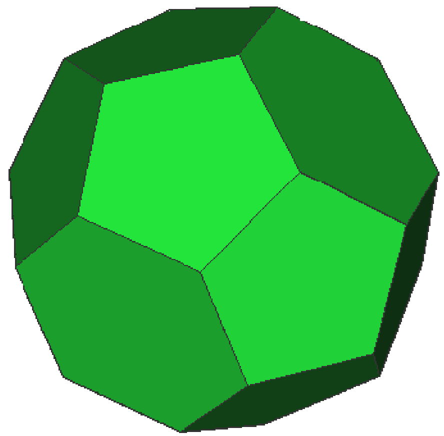
5^{12}



$5^{12}6^{2}$



$5^{12}6^{4}$



Cageology

1) Polyeder is instable without enclosed guest
2) There are not enough bonds in the surface

1 vertex (= oxygen)
3 edges/vertex (= 1.5 hydrogens)
4th → edge/vertex needed
out-of-surface bonds, 3rd dimension

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Outline of talk

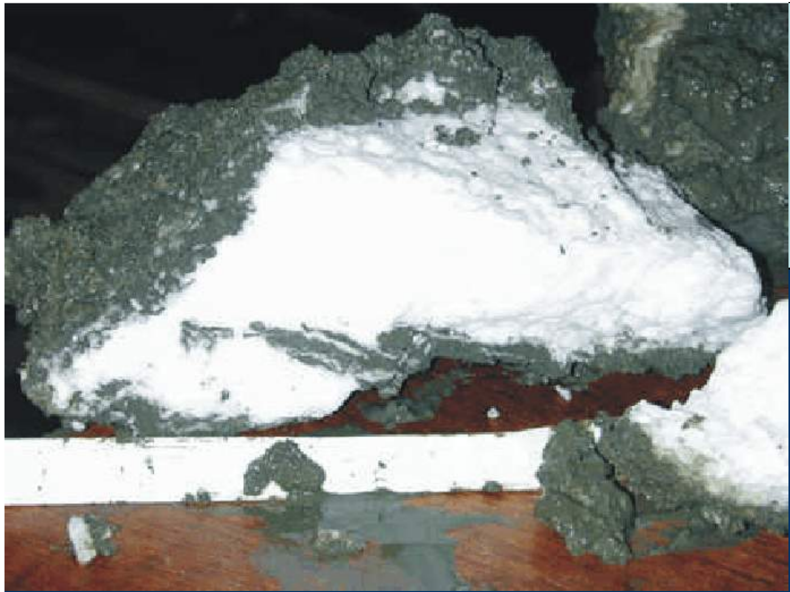
Introduction

Gashydrates

Skutterudites

Alkali-silicon system

Summary/outlook



Methane hydrate (burning ice)

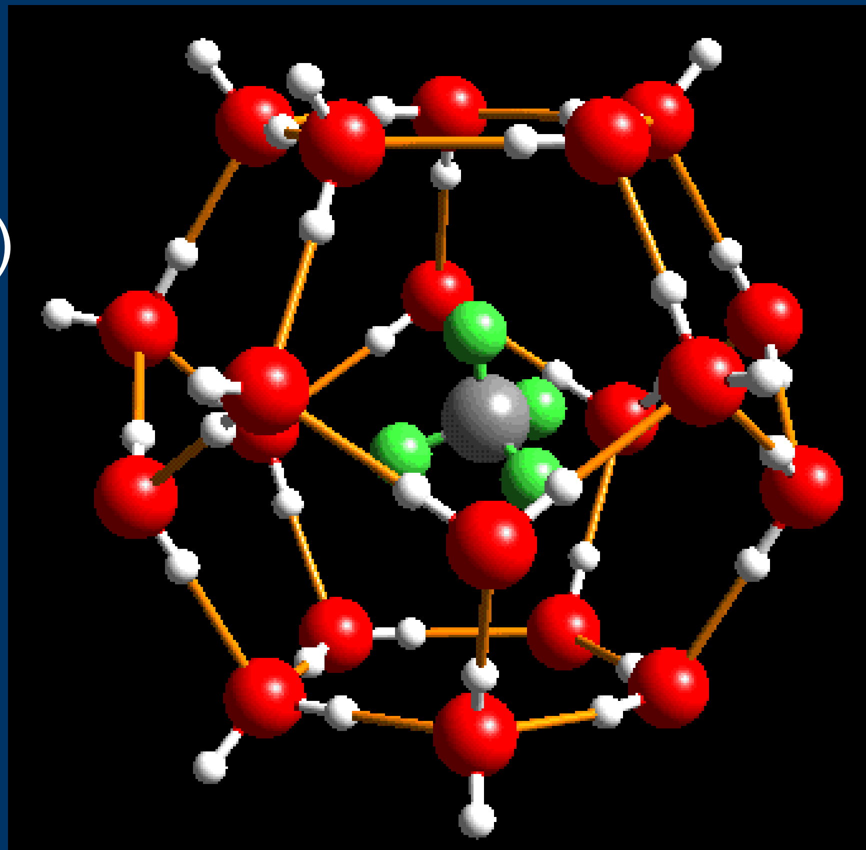
Werner Press (Univ. Kiel)

Macroscopic (from Pacific)

←

→

Microscopic (hydrate cage)



Methane hydrate
(burning ice)

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Study with neutrons & X-rays

1997 – 2003
2006 – 2007

Julian Baumert †
Christian Gutt (DESY Hamburg)

Alfred Hüller (Uni Erlangen)
John Tse (Saskatchewan, Canada)
Mark Johnson (ILL)
Sasha Krivchikov (Charkow, Ukraine)

Molecular Solids:
Position R   Orientation φ,Ω,ω

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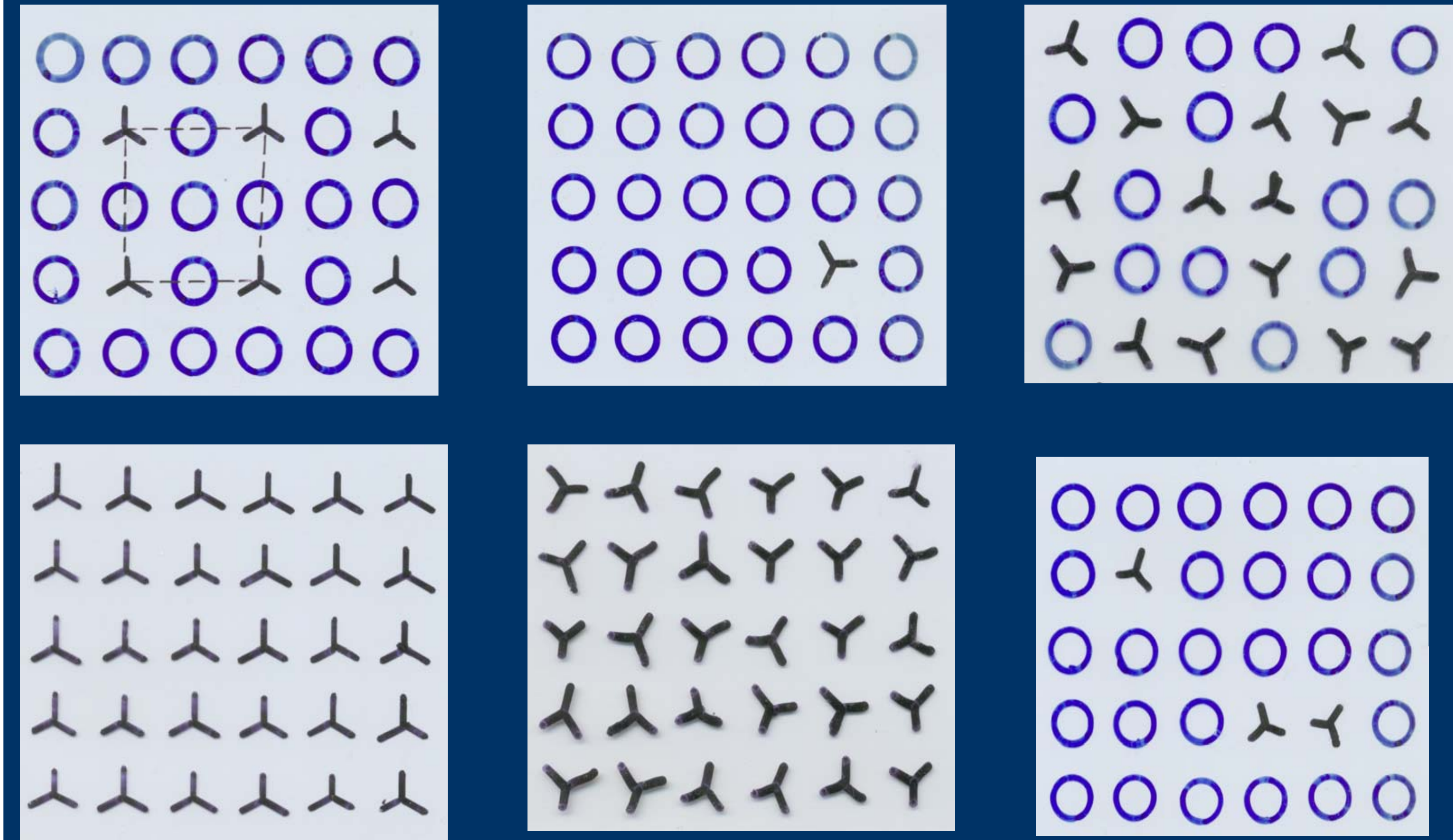

Long personal history of research with XH_y

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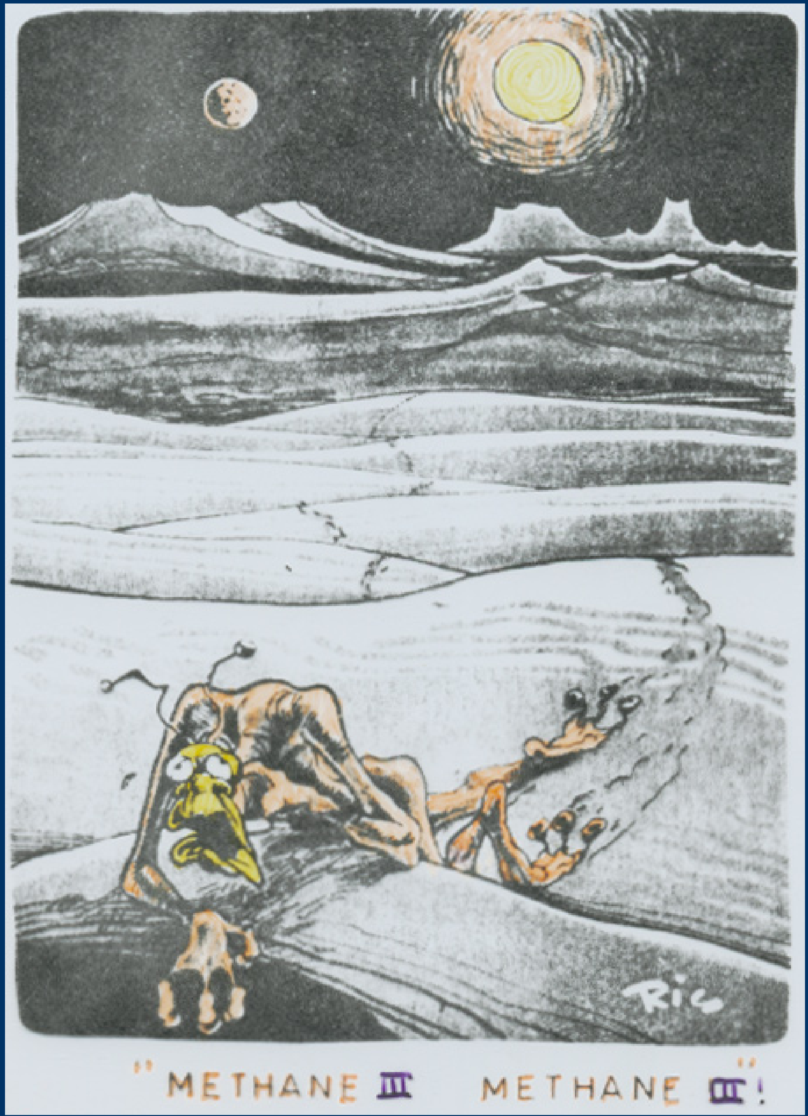


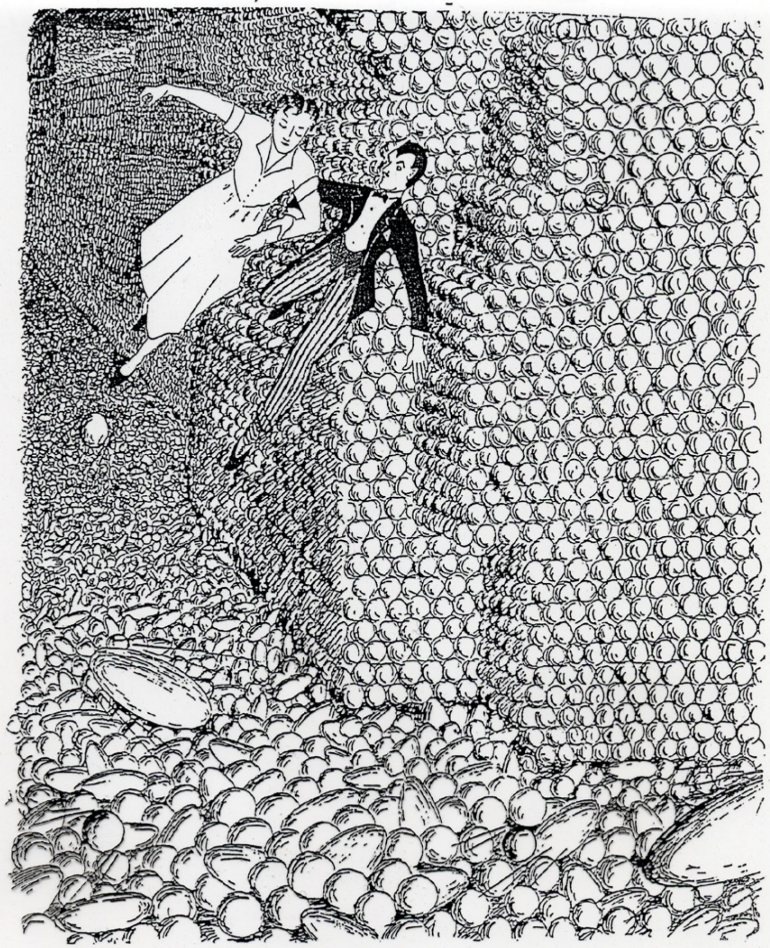
CH_4 NH_3 OH_2

$\sigma_{inc}(H) = 80$ barn $B = \hbar^2/2\Theta$

- fundamental research
- energy storage
- geosciences
- planetary environments

Phase III
Structure
Tunneling (CH_4, CD_4)

???????
meaning



Sieht etwa so die Hölle aus?

Gamov

H_2O

Ice:many phases

close: hexagonal Ice I_h

Dipole moment

Gas Hydrates

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Combine the two:

$CH_4 + H_2O \rightarrow 8\ CH_4 * 46\ H_2O$

More stable than ice
(presence of pressure
> ~50 bar)

Preparation:

need pressure
Biomaterials(CH_4)
H_2O

nature
laboratory

Research Ship “Sonne”

Research Ship "Sonne"

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Storage & transport

History of Gas Hydrate Research

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~ 1810 Davy , Faraday
1928 Review : W .Schroeder , "Gashydrate"
~ 1935 Pipelines blocked
~ 1950 Structural comprehension : Stackelberg
~ 1970 small quantities of natural samples (Soviet Union & USA/Canada)
1984 Type I Structure
1997 E. Sloan " Clathrate Hydrates of Natural Gases "
etc

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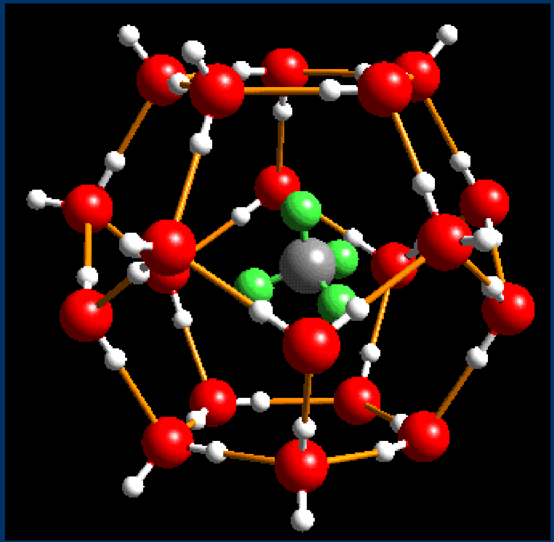
How did it all start ?

phone call ~1997
article in "Die Zeit"
burning ice

IFM-Geomar, Kiel
NRC Ottawa

Small cubic cage 5^{12}



Gas Hydrates

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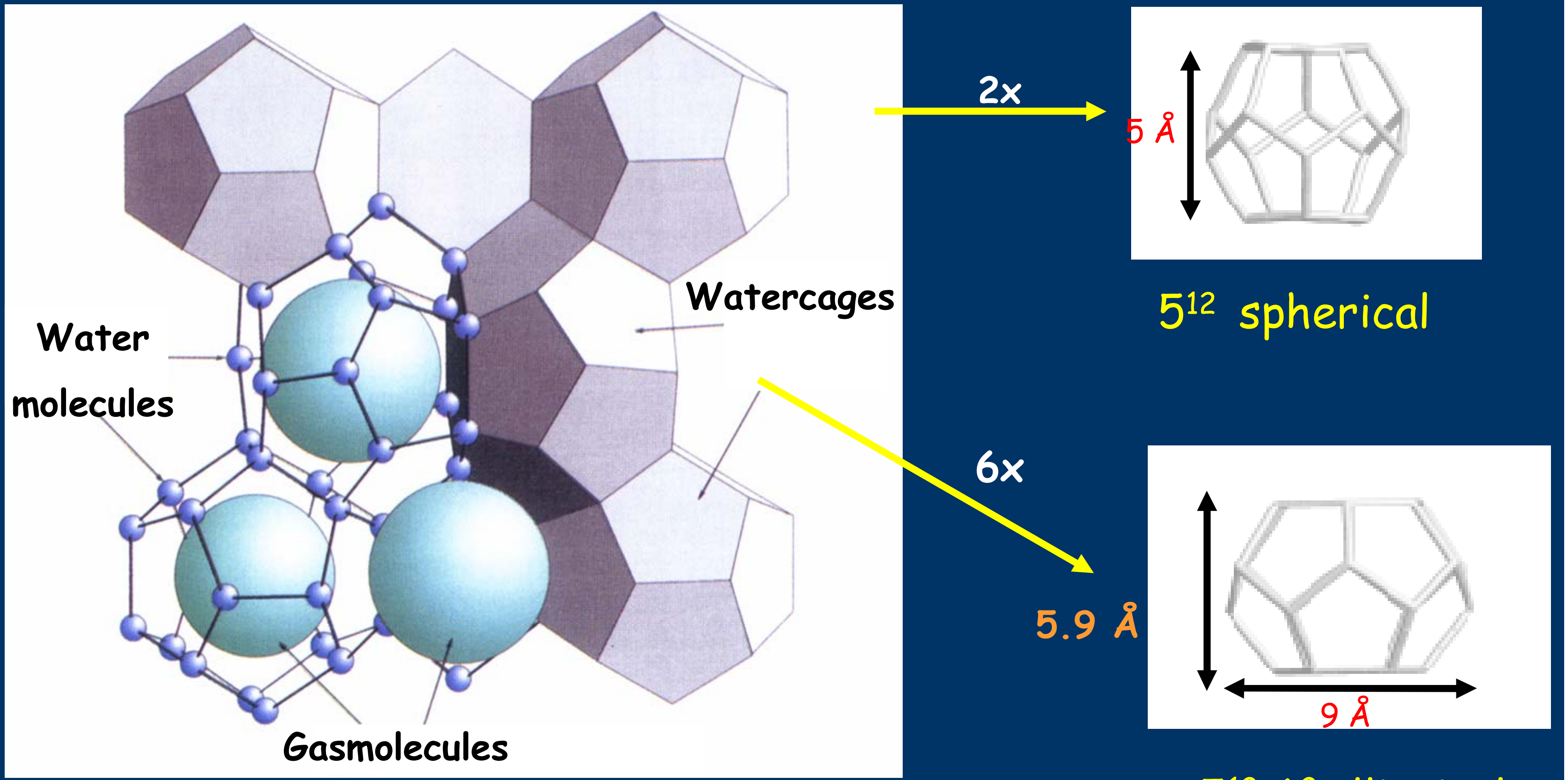


5^{12} 6^{2} elliptical

Structure I : cubic Pm3n (CH_4, Xe, ...)

$8\ CH_4 \cdot 46\ H_2O$ Lattice Parameter $a_0 \approx 11.81$ Å

Structure of gas hydrates: Cages !

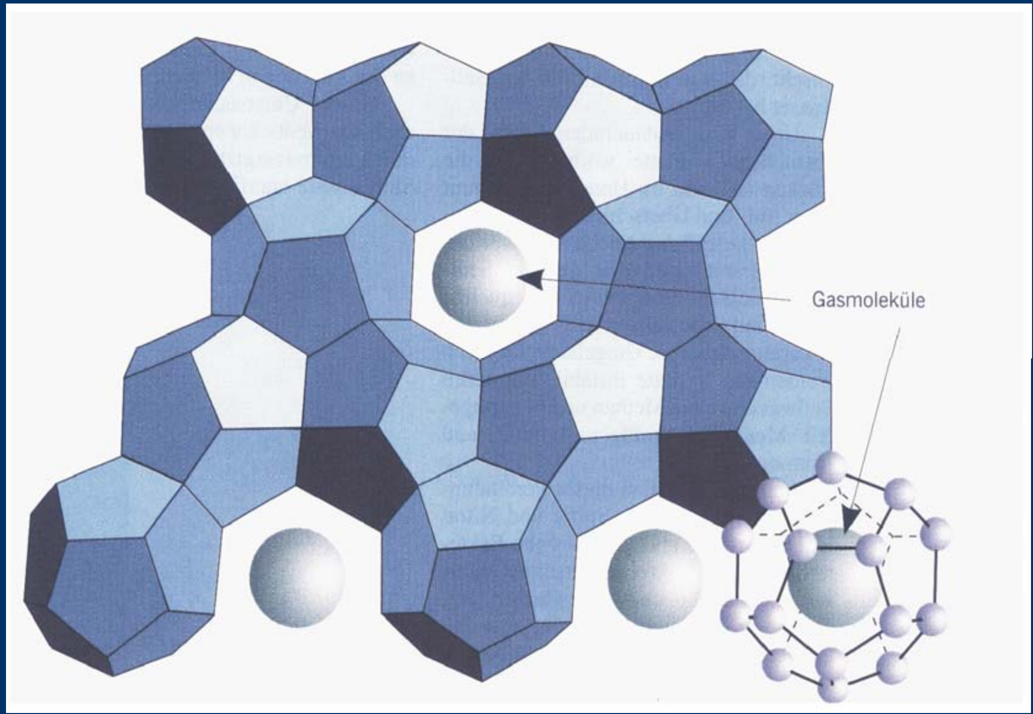
host: ice framework
guest: CH_4, Xe
NB alkanes are hydrophobic

(1) low temperature

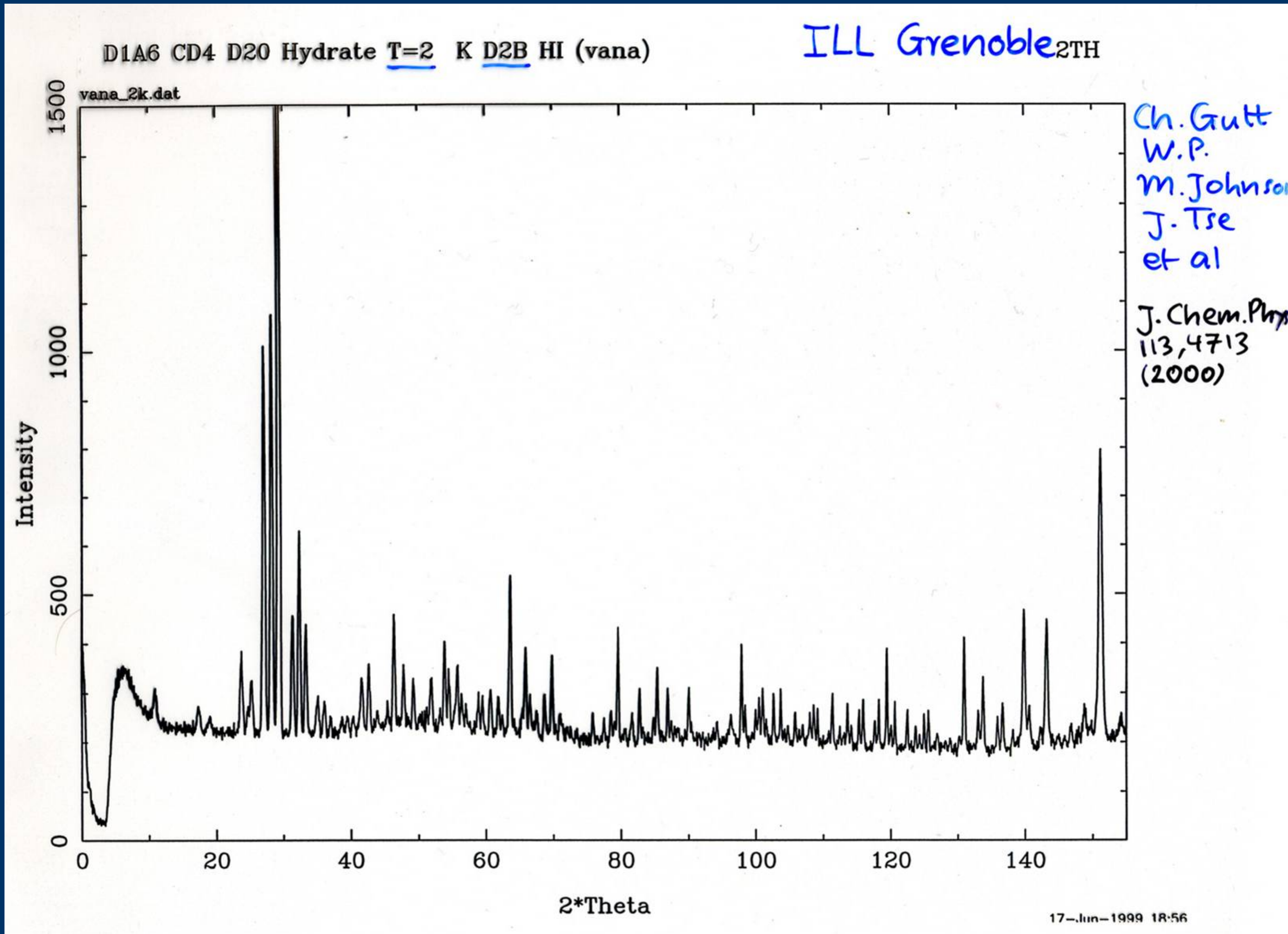
(2) natural conditions

Powder diffraction
ILL D2B
deuterated compound

T = 2K, 20K etc
Normal pressure



Structure :
Diffraction at ILL/D2B (old) λ = 1.59Å



Density on spherical surface: expansion into symmetry-adapted harmonics

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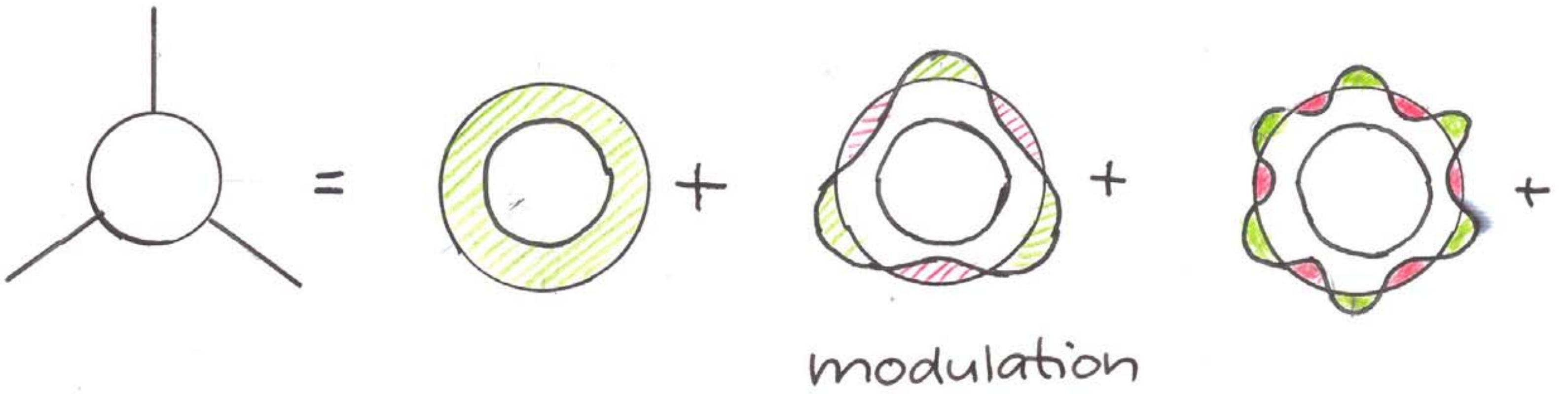
$$\rho(r) = \int \rho_T(R)\,\rho_{Rot}(r - R)\,dR$$

$$F(Q) = \exp(iQR_0)\exp[-W(Q)]F_{Rot}(Q)$$

$$F_{Rot}(Q) = 4\pi \sum_{l=0}^{\infty} \sum_{m=1}^{2l+1} i^l j_l(Q\rho)\,c_{lm} K_{lm}(\Omega_Q)$$

Guests:
Site-occupation
Centered?



Fourier TF (3D) $\quad j_0(Q\rho) - b_{31}\,i\,j_3(Q\rho)K_{31}(\Omega_Q) + \cdots$

Scattering Length Density in CH_4 Hydrate

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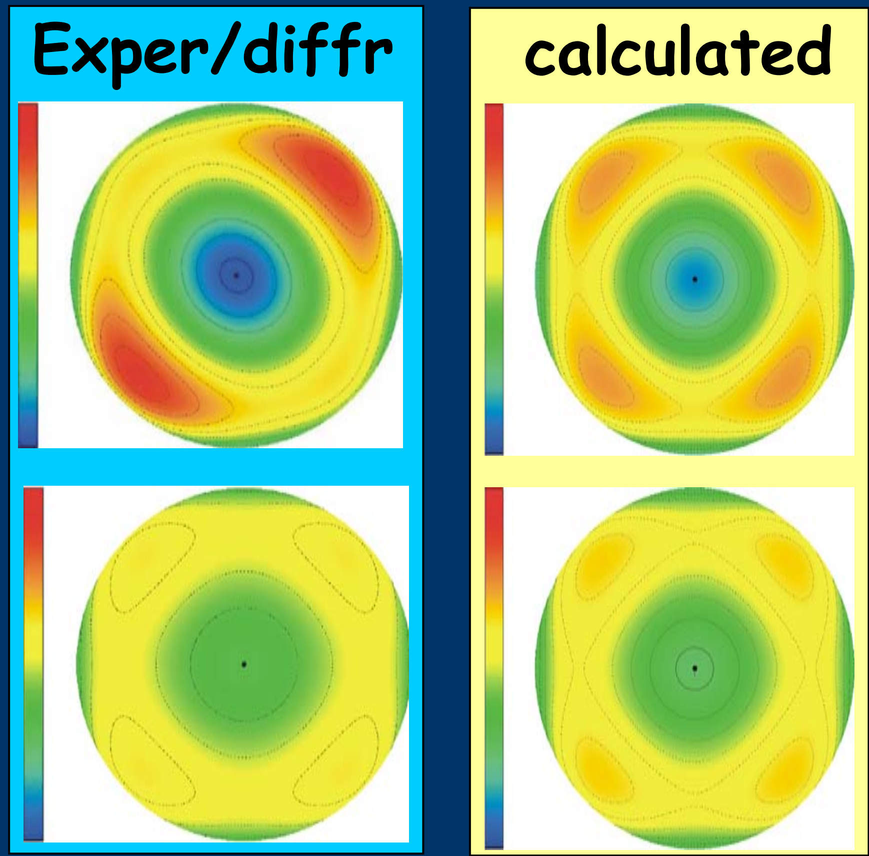
elliptical $\bar{4}m2$
cages

spherical m3
cages



C. Gutt, W. Press, A. Huller, J.S. Tse and H. Casalta, *J. Chem. Phys.*, 114, 4160 (2001)

Structure of Methane Hydrate

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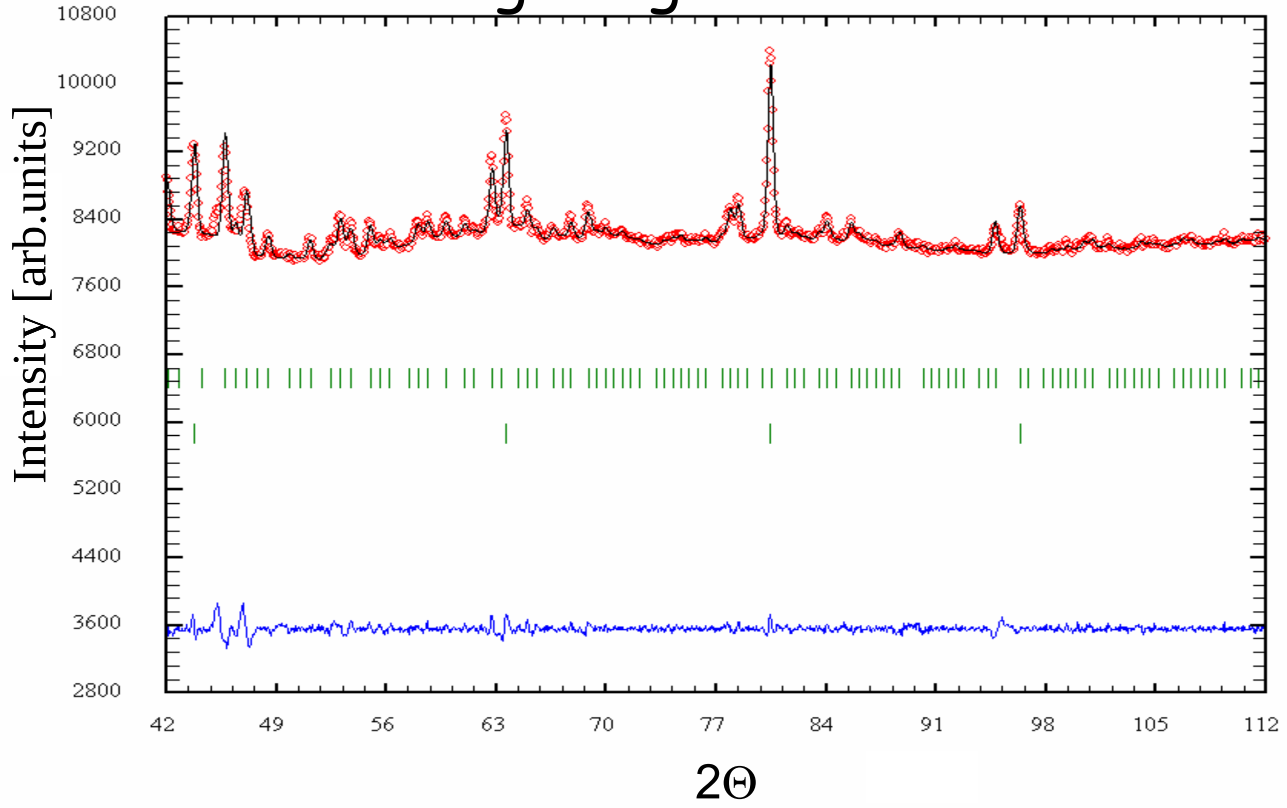
Diffraction pattern of CD_4-D_2O hydrate under geological conditions



T=280K, p=100bar ⟷ T=4°C, 1000m water depth

Julian Baumert

Scattering Length Density

Low temp.
T=2K, ambient pressure

High temp.
T=285K, p=100bar

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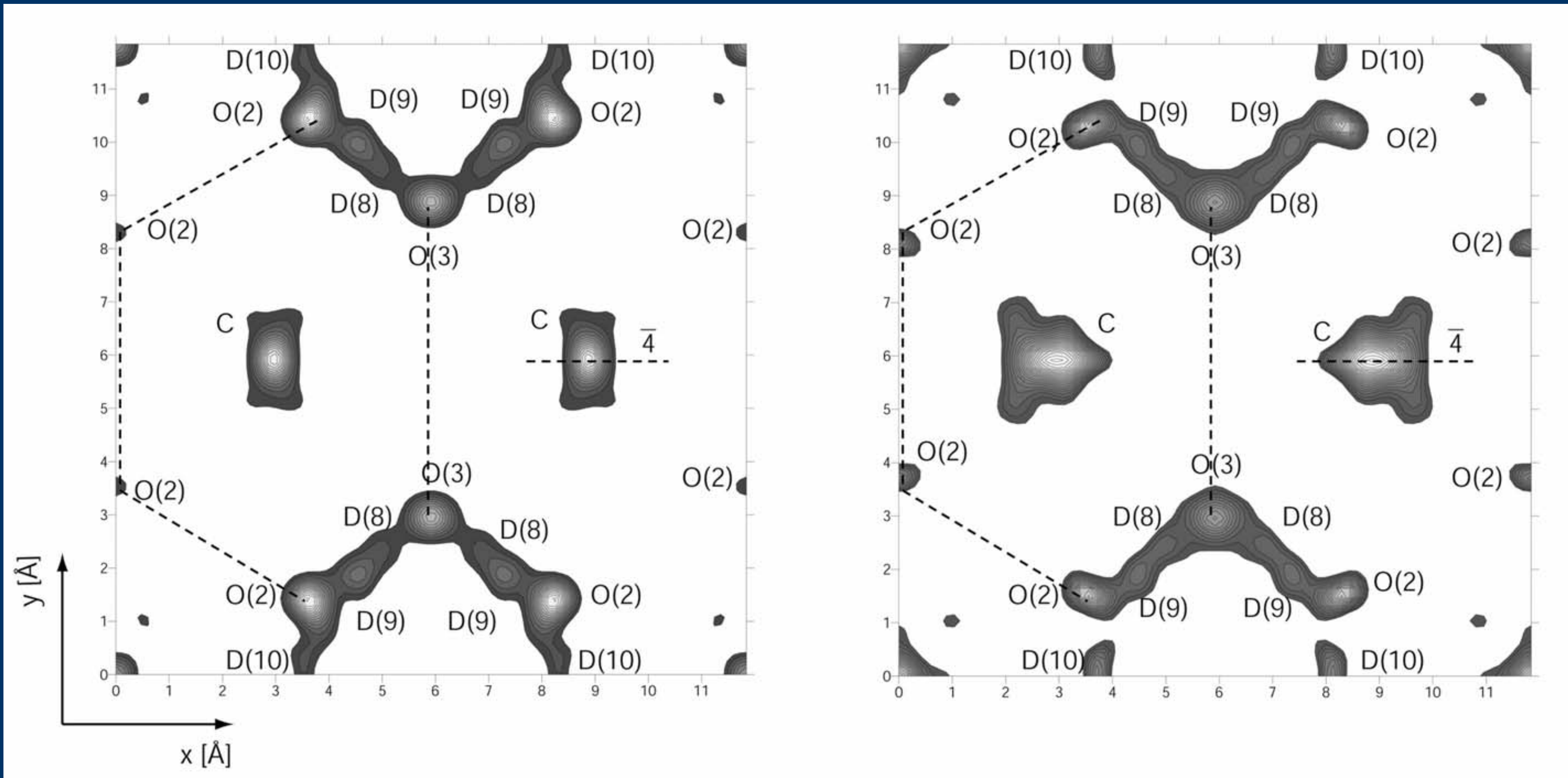

Scattering length density map ([barn/Å^3]) of the (001) plane obtained from MEM analysis

Decomposition kinetics

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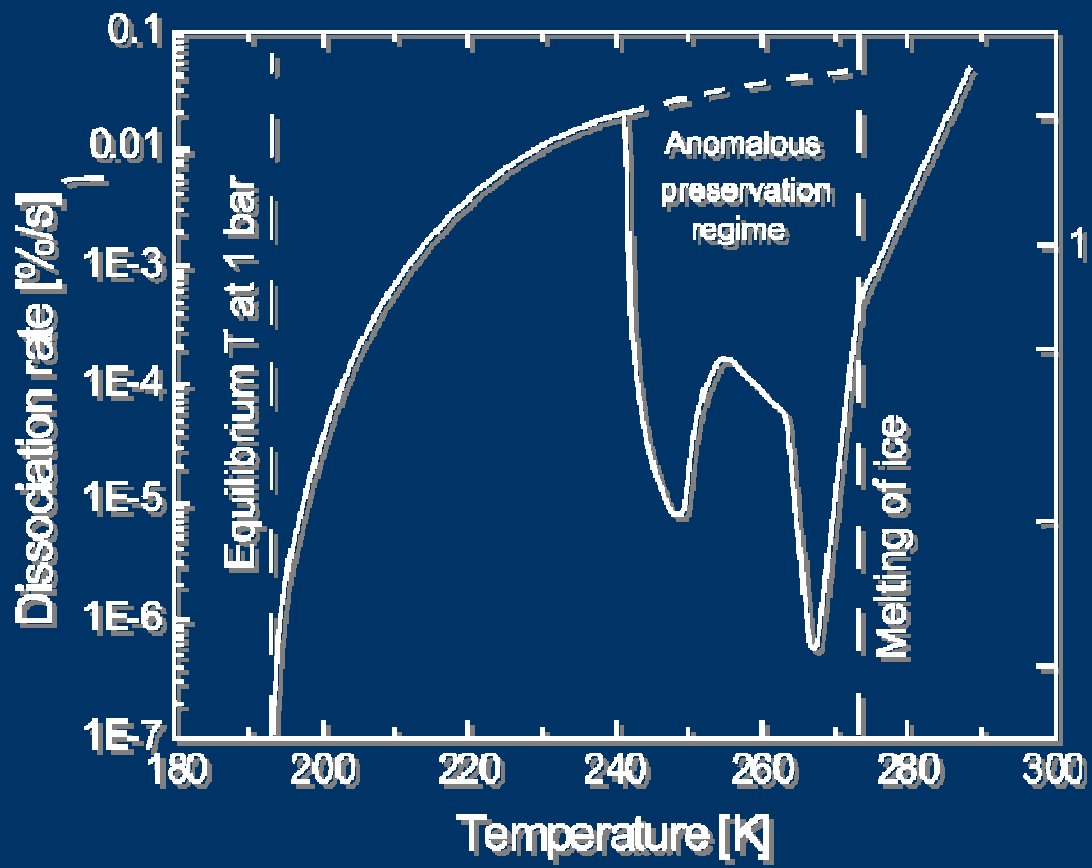
Dissociation rate of methane hydrate
Stern et al
J.Phys.Chem. B105 , 1756 (2001)



Anomalous preservation of gas hydrates

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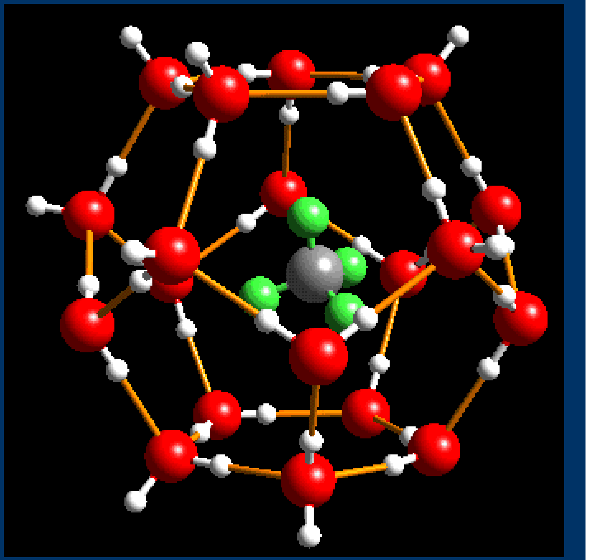
Diffraction study on D20/ILL

ice I_h has many stacking faults

methane diffusion fast

annealed ice I_h stops diffusion

(Kuhs et al: with I_c decomp. & CO_2)
CPPC 6 (2004)



hydrate decomposition : time dependence

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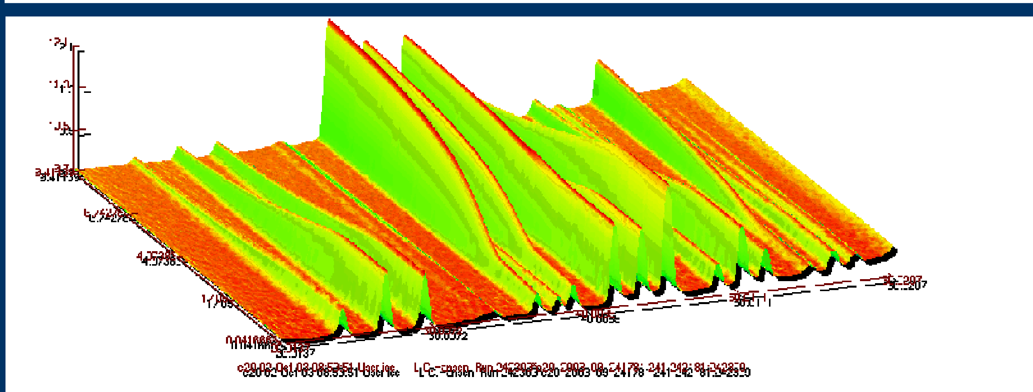
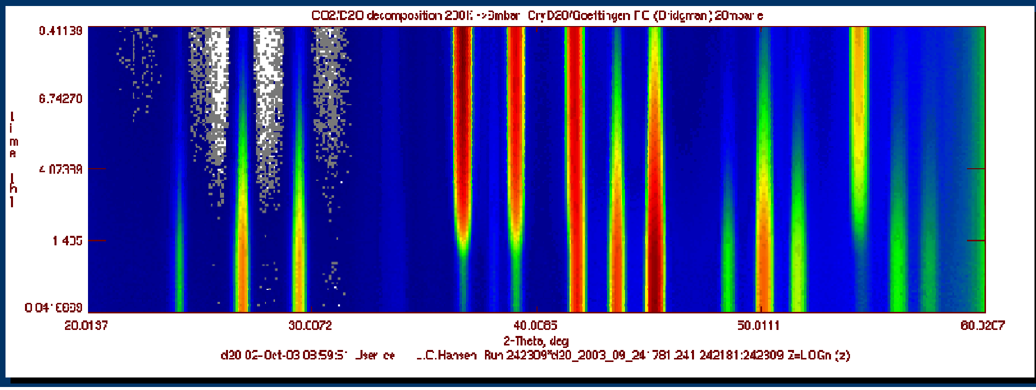
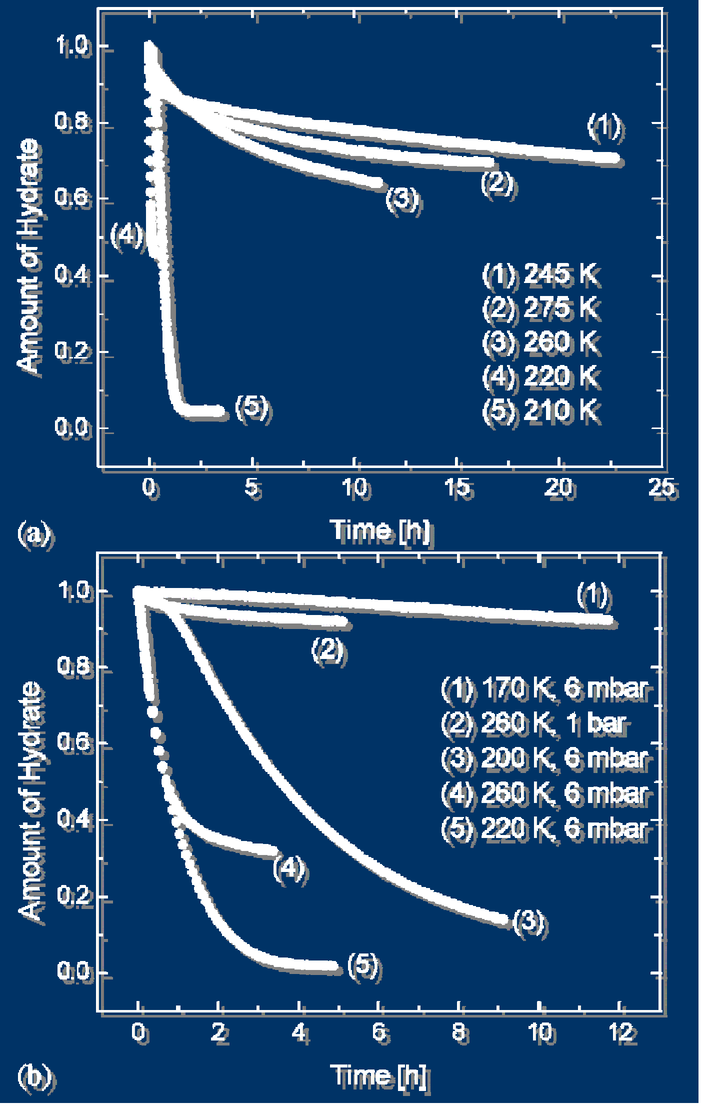
D20 in situ experiment (W.Kuhs,T.Hansen et al)

- Decomposition of CH_4[(a)] & CO_2[(b)] hydrates at different T and p
  - Here: CO_2 at 200 K, 6 mbar
    - Covering 10 hours







interlude: methane hydrate

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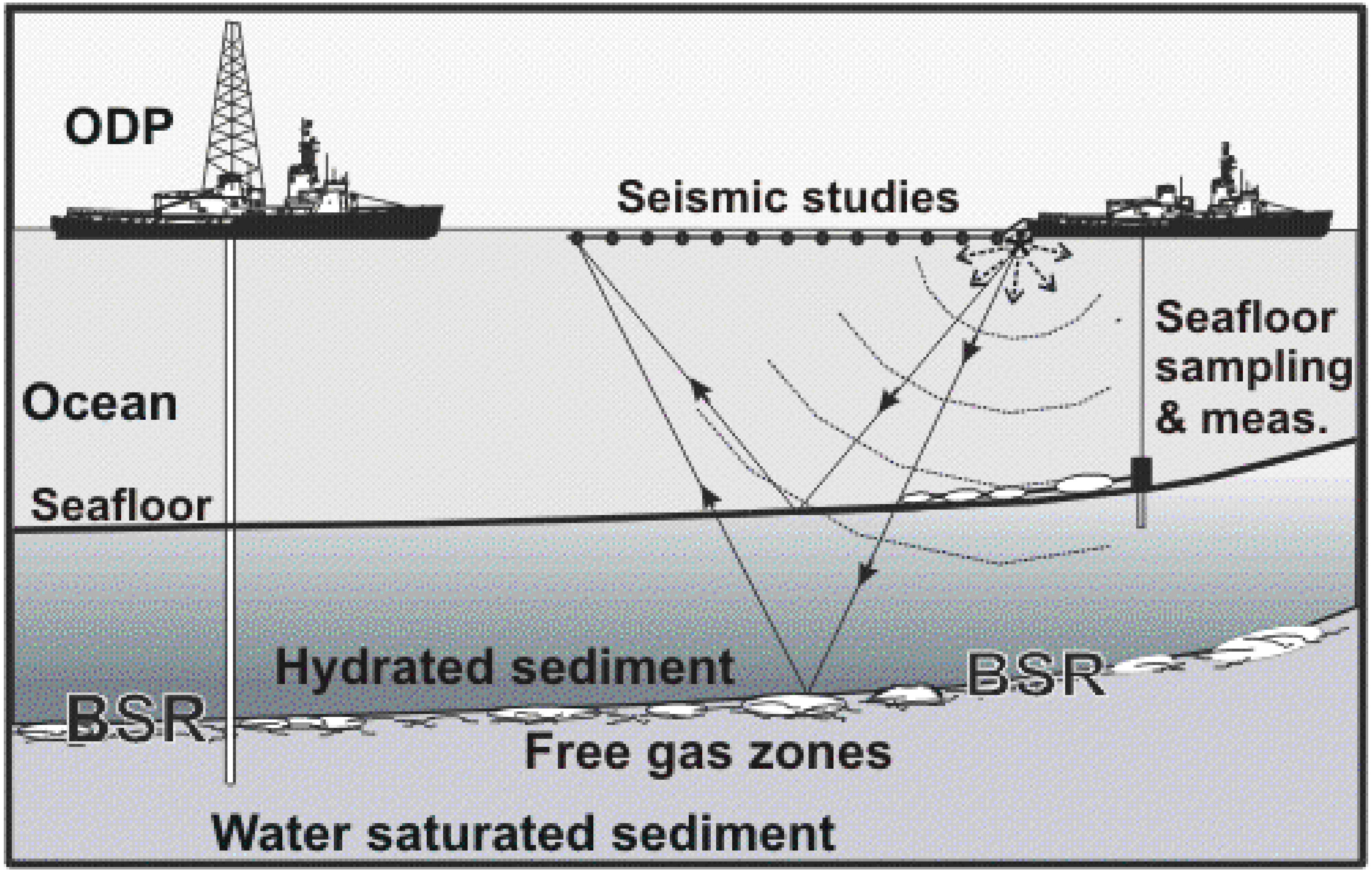
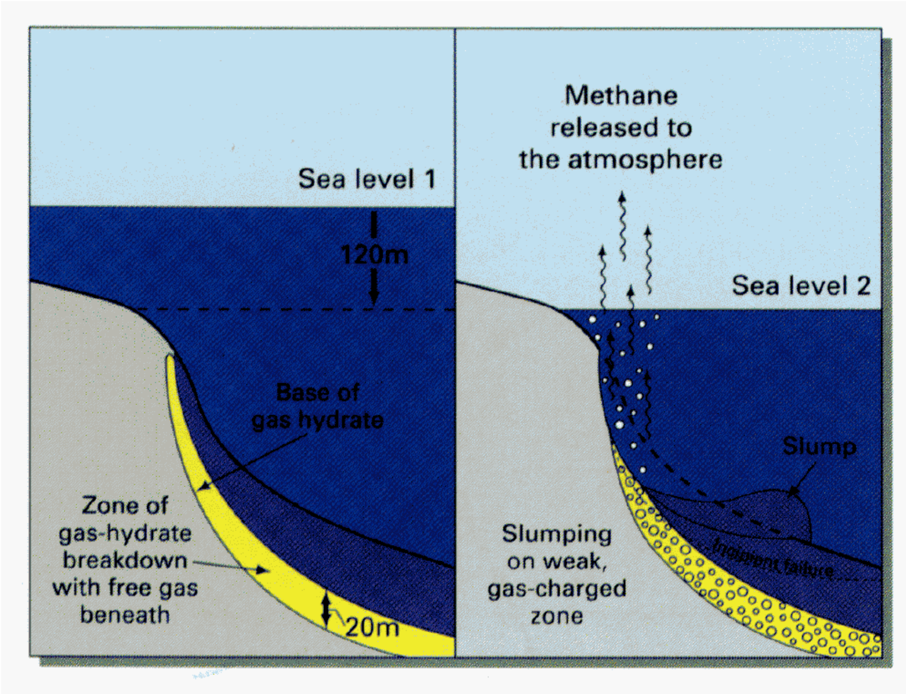
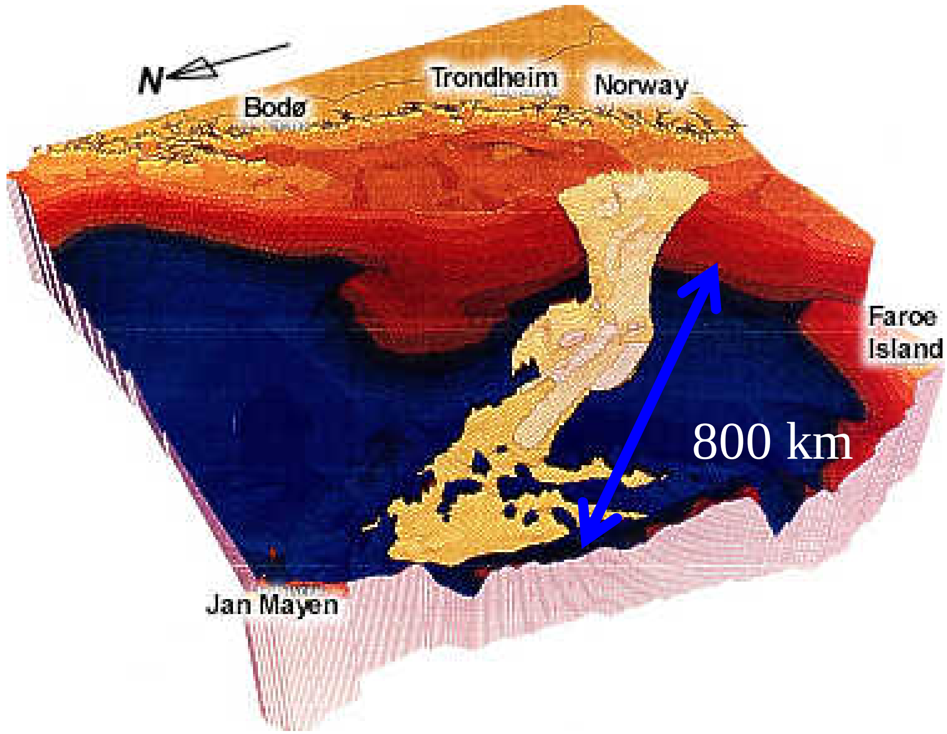
Research
of deep sea : little done
only area ~ a dozen football fields investigated
much remains to be done !!!
yet fragile

Hydrate Seismic Detection

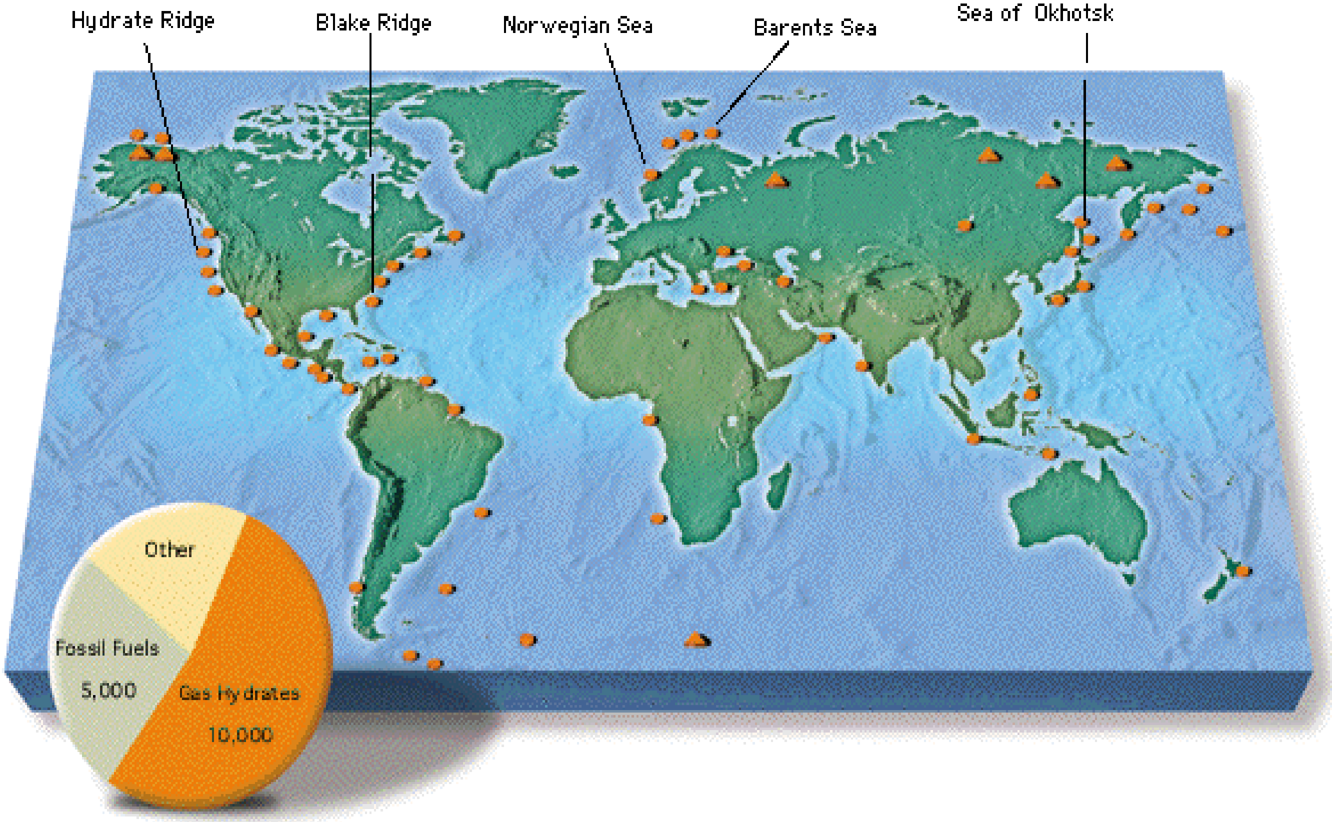


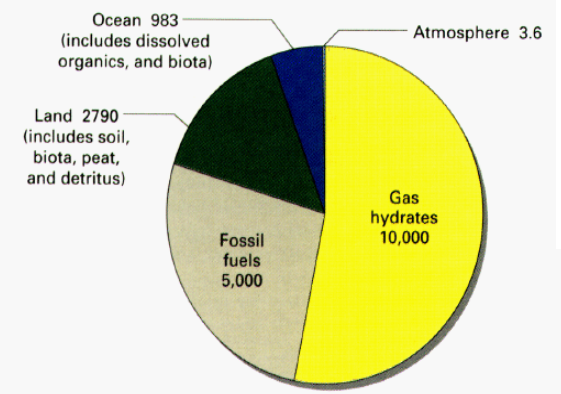
Hang-Slides:
Hydrate Decomposition





Hydrate Deposits





Distribution of organic carbon in Earth reservoirs (excluding dispersed carbon in rocks and sediments, which equals nearly 1,000 times this total amount). Numbers in gigatons (10^{15} tons) of carbon.

Life in CH_4-deposits (discovered 1997) & Schätzing: The Swarm (Der Schwarm)

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Public interest

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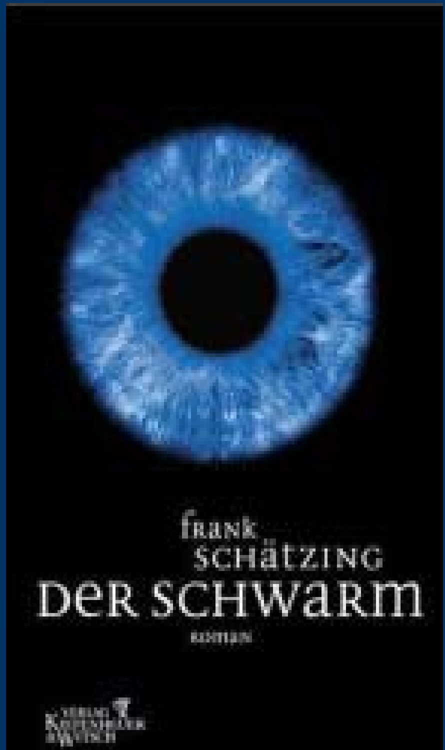
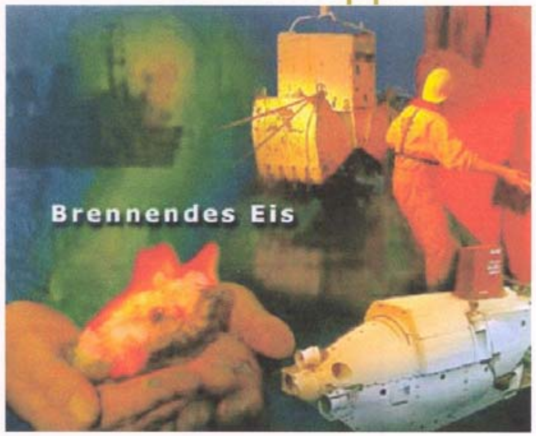


Der Filmtipp



ARTE
+

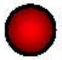
Mit Meeresforschern auf der Suche nach Gashydrat

Global warming

DIE ZEIT

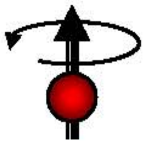
Why neutrons?

„commercial“

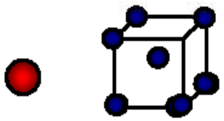


Neutrons are neutral: high penetation power, non-destructive

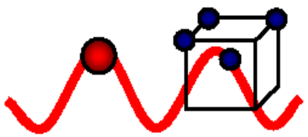
Neutrons have a magnetic moment: magnetic structures and excitations



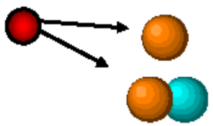
Neutrons have a spin: polarized neutrons, coherent and incoherent scattering, nuclear magnetism rotations



Neutrons have thermal energies: excitation of elemenatry modes, phonons, magnons, librons, rotons, tunneling, etc.



Neutrons have wavelengths similar to atomic spacings: structural information, short and long range order, pore and grain sizes, cavities, etc.



Neutrons see nuclei: sensitive to leight atoms, exploiting isotopic substitution, contrast variation with isotopes

Incoherent & coherent scattering

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Isotopes with different b_j
Nuclei with b_+ and b_- (statistical ! nucl.spin)

σ_{inc} no interference
local structure and dynamics

H

σ_{coh} interference
long range order & collective dynamics

D, C

Quantum rotation of methane hydrate

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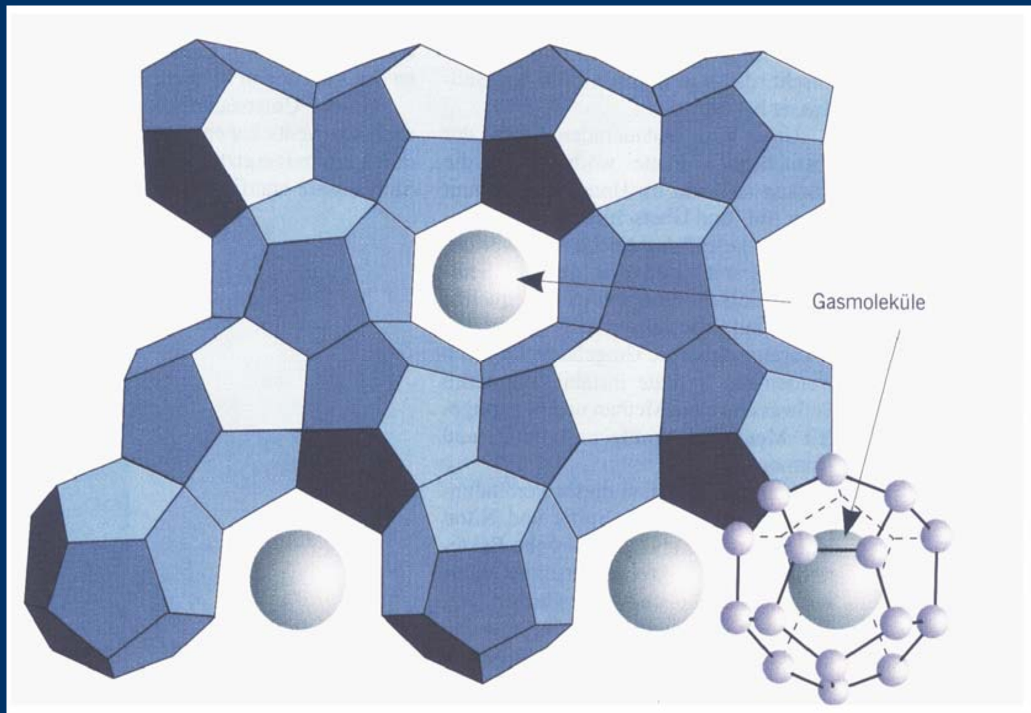
(1) low temperature

(2) natural conditions



Methan hydrate : natural sample (quantum rotation)

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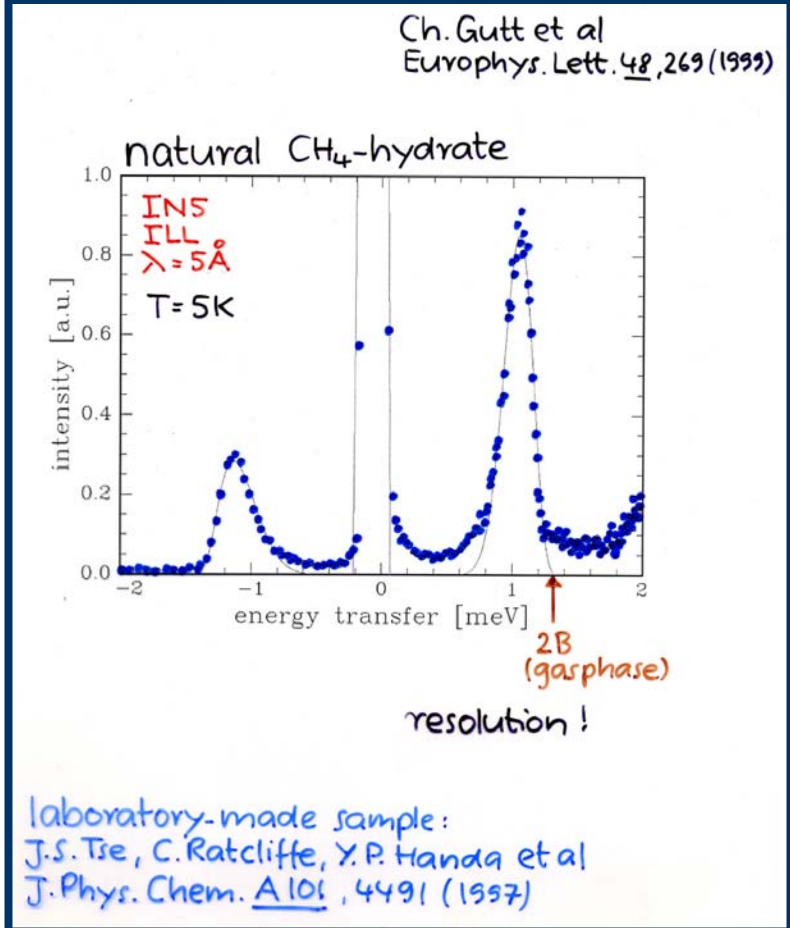
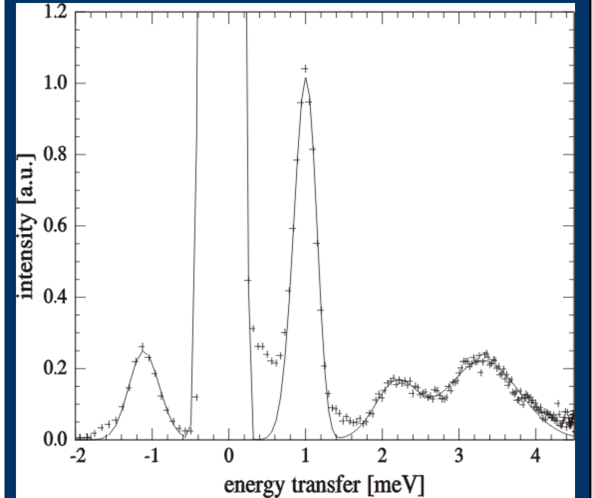
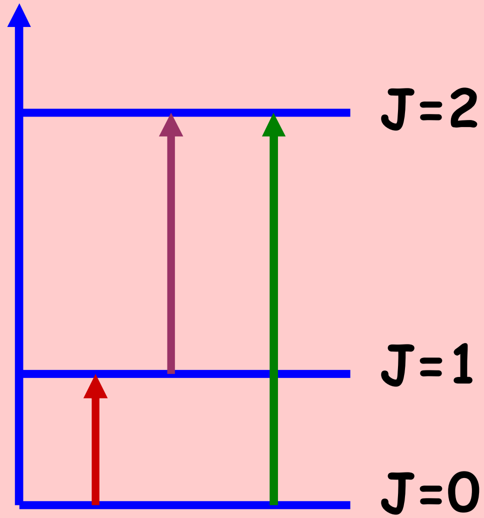


T=5K



$\hbar\omega$ = 1.08 meV

$\Delta E/E_{free}$ = 20 %



C. Gutt, J.Baumert, W. P. et al. *Europhys. Lett.* 48, 269 (1999) FOCUS / PSI

Mathematical description (2D-Rot.)

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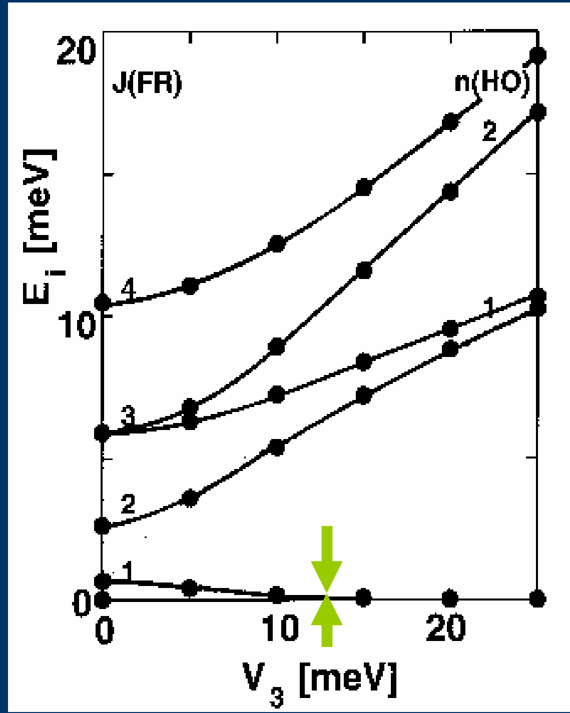
Hamiltonian (Operator $J = \frac{h}{2\pi}\frac{d}{d\varphi}$)

$$\mathbf{H} = \frac{1}{2}\Theta J^2 + V = -\frac{\hbar^2}{2\Theta}\frac{d^2}{d\varphi^2} + V = -B\frac{d^2}{d\varphi^2} + V$$

$$V(\varphi) = \sum_{n=1}^{N} V_{3n}(1 - cos(3n\varphi))$$

Solutions of the Schrödinger equation

$$\frac{\mathbf{H}}{B}\Psi = \frac{E}{B}\Psi$$



F-Rot H-Osc

Eigen functions:

$$\Psi = \Phi\xi$$

$$\Phi = \left(\sum_{m=-M}^{M} a_m exp(im\varphi)\right)$$

ξ: spin-eigenfunction

sensitivity: $\hbar\omega_t \sim e^{-\alpha V(\varphi)^n}$

$\Psi = \Phi_{rot}\chi_{spin}$

Linewidth explained with dipole-octopole interaction & disorder (2 types of cages)

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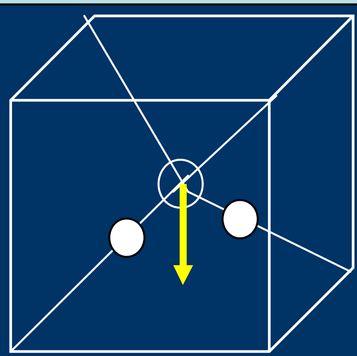
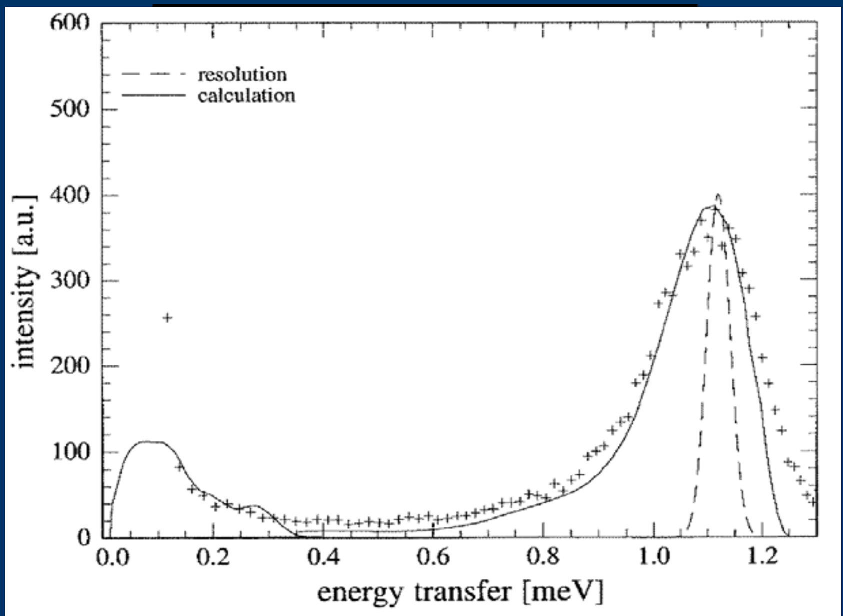
H_2O dipoles
6 orientations
(ice rules)



O is tetrahedrally coordinated

Electrostatic model
q = 0.13e on H of CH_4
q = 0.8 e on H of H_2O

$$W = \iint d\vec{r}_0 d\vec{r} \frac{\rho_{cage}(\vec{r}_0)\rho_{CH4}(\vec{r})}{|\vec{r}-\vec{r}_0|}$$



Cubic harmonics $K_{lm}(\theta,\phi)$
Quaternions τ , $H_{\mu\nu}^{(l)}(\tau)$

Rotational States (J = 0 ⟶ 1)
from 2nd order perturbation theory
~ 3000 configurations

Scattering Length Density in CH_4 Hydrate

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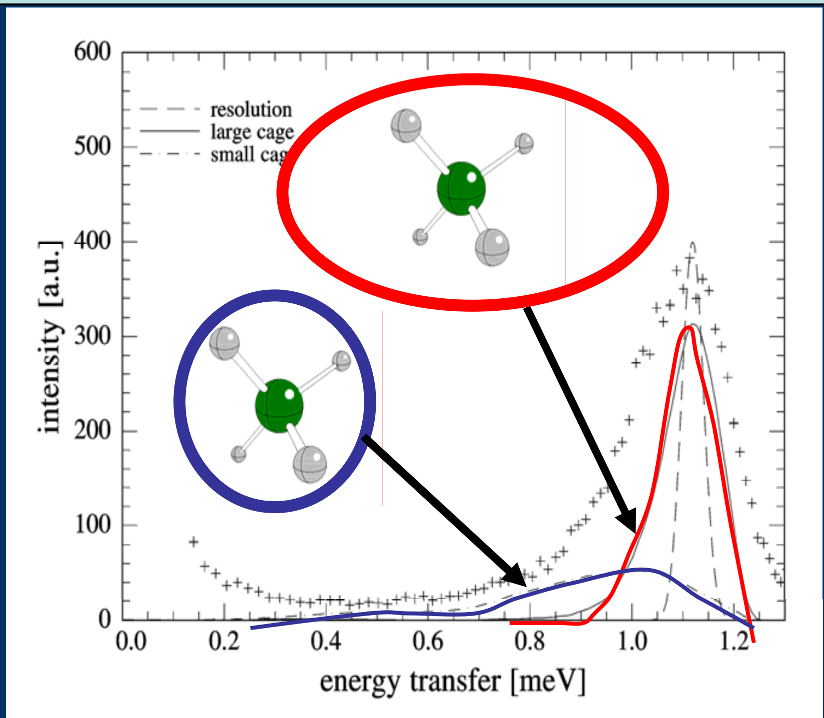

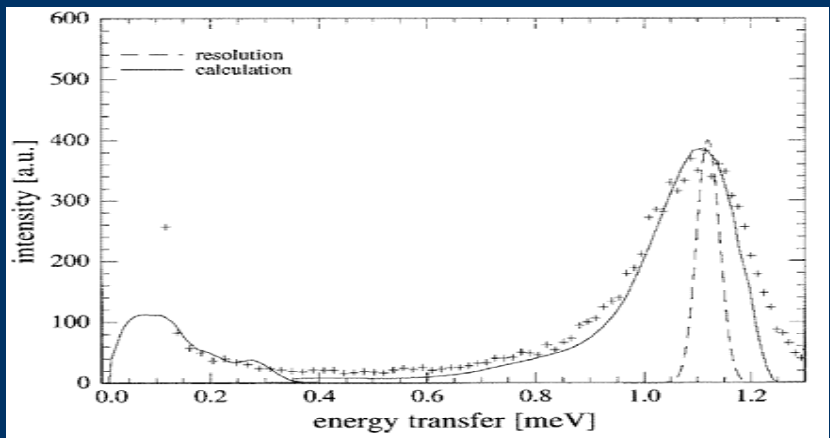

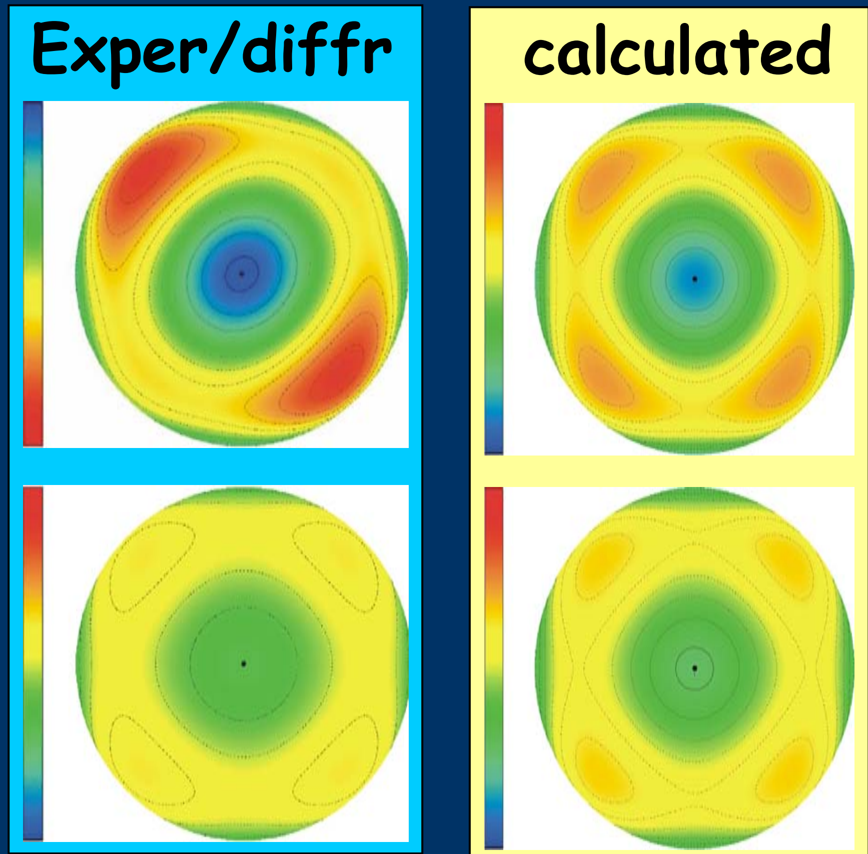

C. Gutt, W. Press, A. Huller, J.S. Tse and H. Casalta, *J. Chem. Phys.*, 114, 4160 (2001)


NA- AUCH DIE SKIER VERGESSEN ?
PERSCHEID

Quantum rotations + translational "rattling" motion

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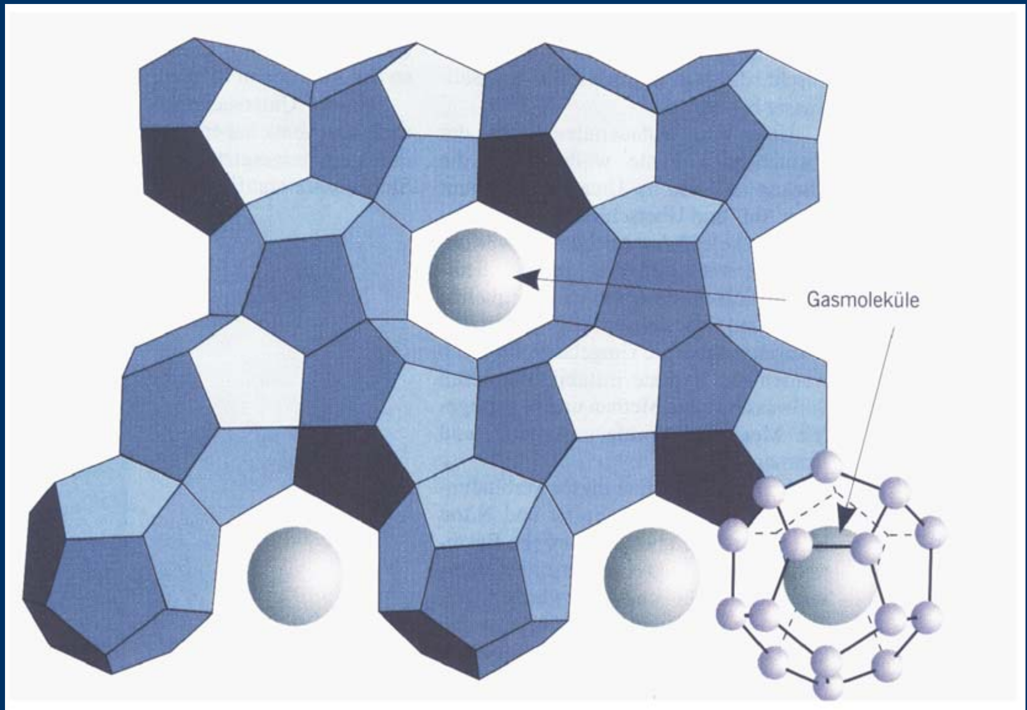
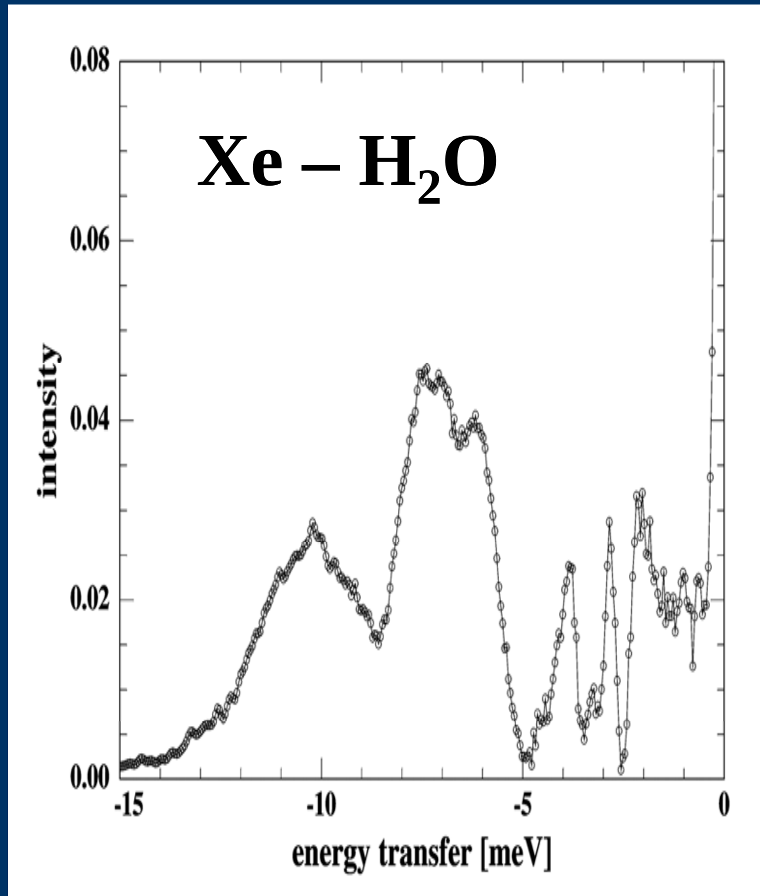


Neutrons
X-ray & nucl. resonance
Simulation
Context: glassy thermal cond.



Inelastic X-ray Spectrometer
ID28

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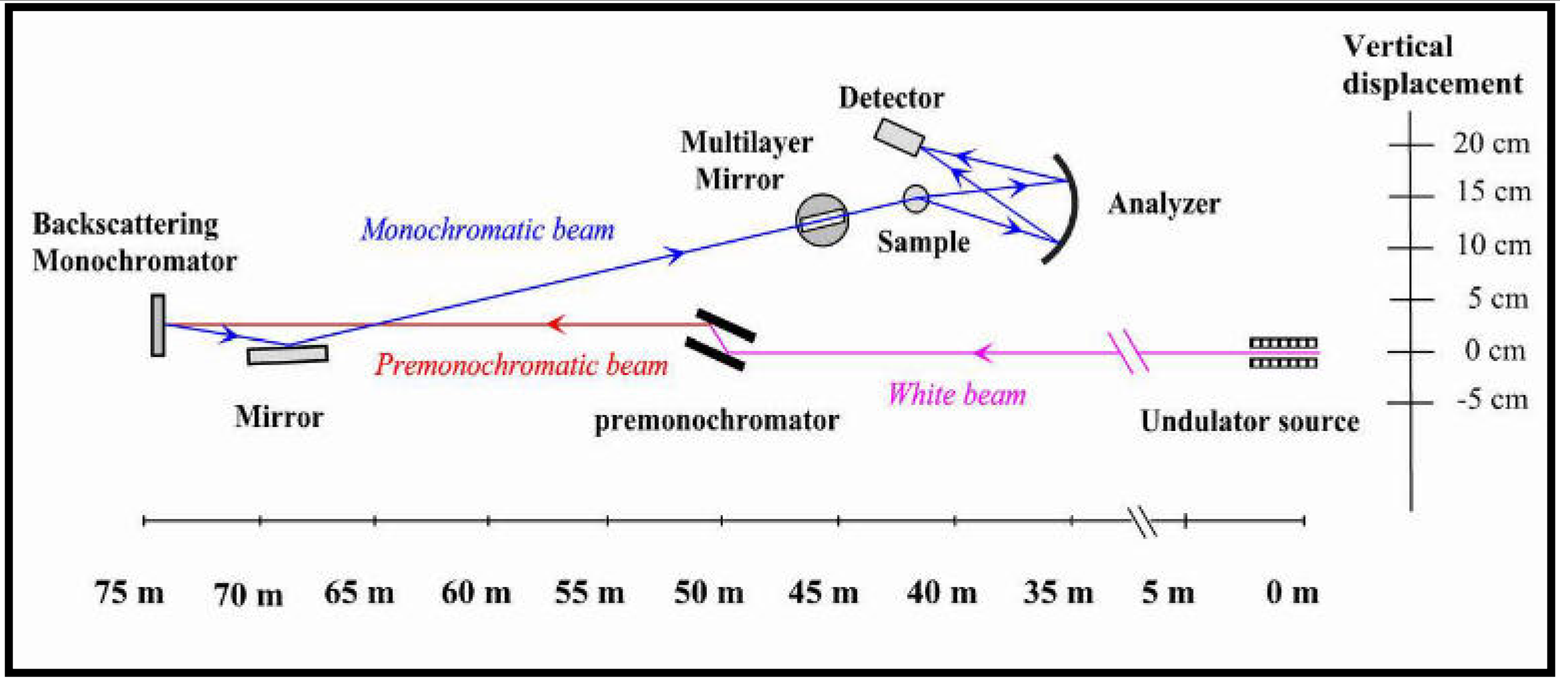

mono-chromator	photon-energy	wavelength	instr. energy-resolution	max. Q-range	dQ betw. analyzers	Q-reso-lution	flux at 200mA (*)
Si(hkl)	[eV]	[Å]	[meV]	[nm^{-1}]	[nm^{-1}]	[nm^{-1}]	[10^9 phot./s]
8 8 8	15817	0.7839	5.5	67.75	2.10	0.245	22.67
9 9 9	17794	0.6968	2.7	76.22	2.38	0.276	5.42
11 11 11	21747	0.5701	1.5	93.16	2.91	0.337	1.81
13 13 13	25703	0.4824	0.9	110.1	3.43	0.399	??

Brillouin Scattering ! $I \sim \vec{Q}.\vec{u}$

Lattice Dynamics of Methane Hydrate

Inelastic x-ray spectra CH_4 – H_2O @ 100K

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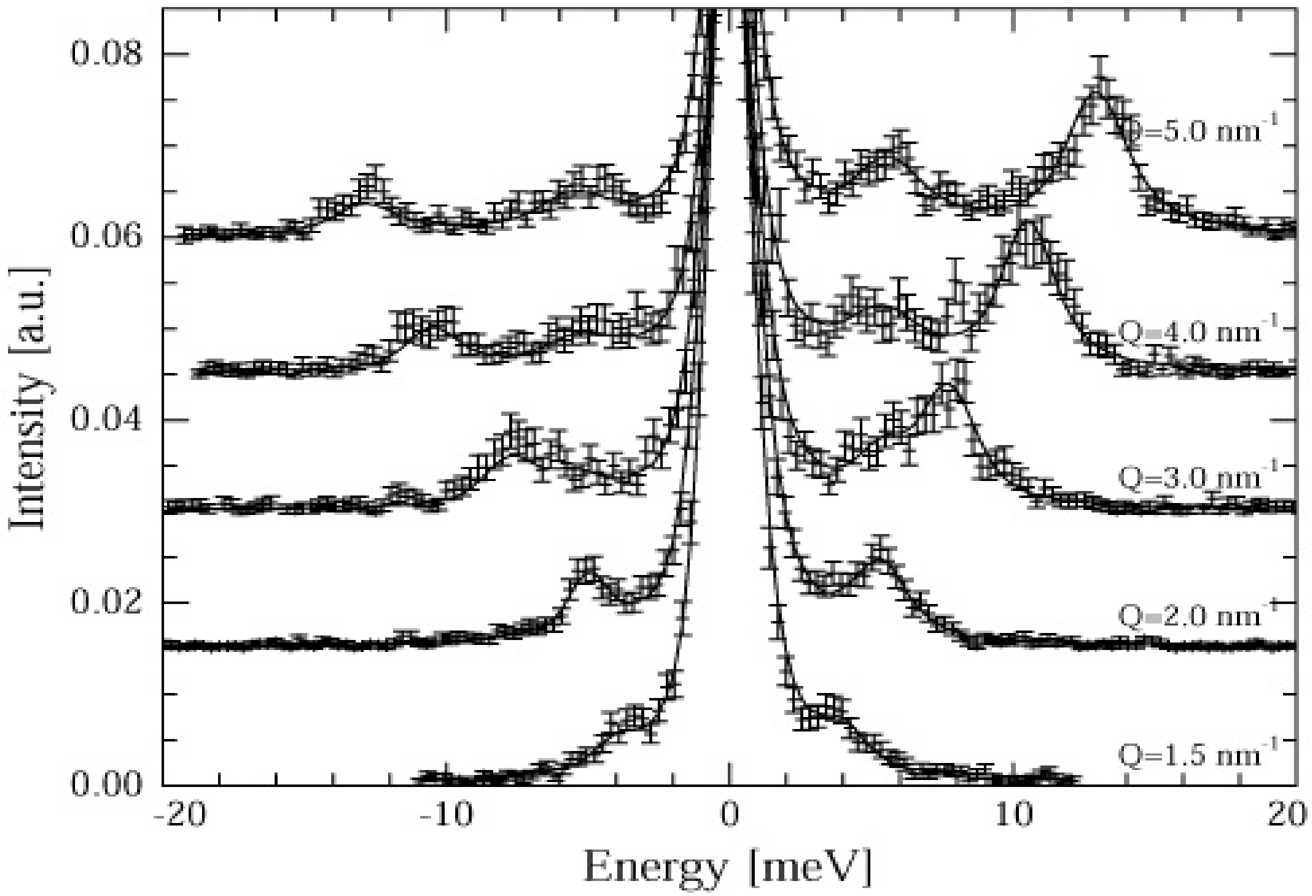

ID28, ESRF

J. Baumert, C. Gutt, V.P. Shpakov, J.S. Tse, M. Krisch, M. Müller, H. Requardt, D.D. Klug, S. Janssen, and W. Press, *Phys. Rev. B* **68**, 174301 (2003)

backscattering

Some math : difference between
particles (neutrons) and
radiation (X-rays)

$2d \sin\Theta = \lambda$

$2d\Delta\cos\Theta = \Delta\lambda$

$\Delta\lambda / \lambda = 2d \cot\Theta\Delta\Theta$

$\Theta \sim 90°$

$E_{ph} \sim k \sim 1/\lambda$

$E_{neutr} \sim k^2$

Phonon Dispersion

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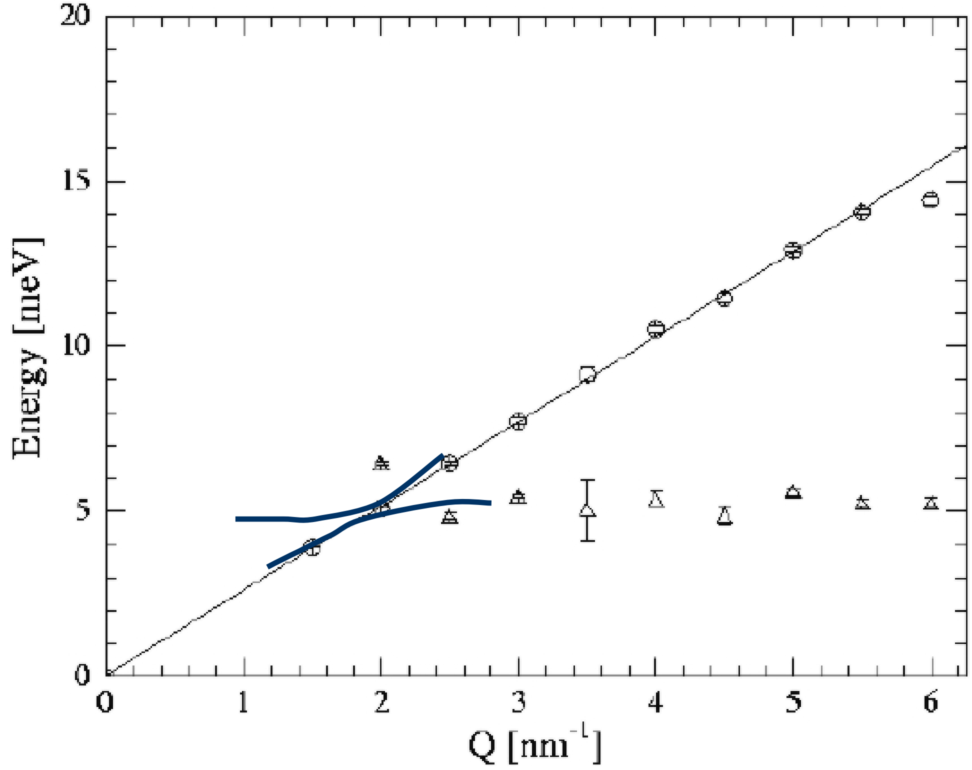
$CH_4 - H_2O$ @ 100K

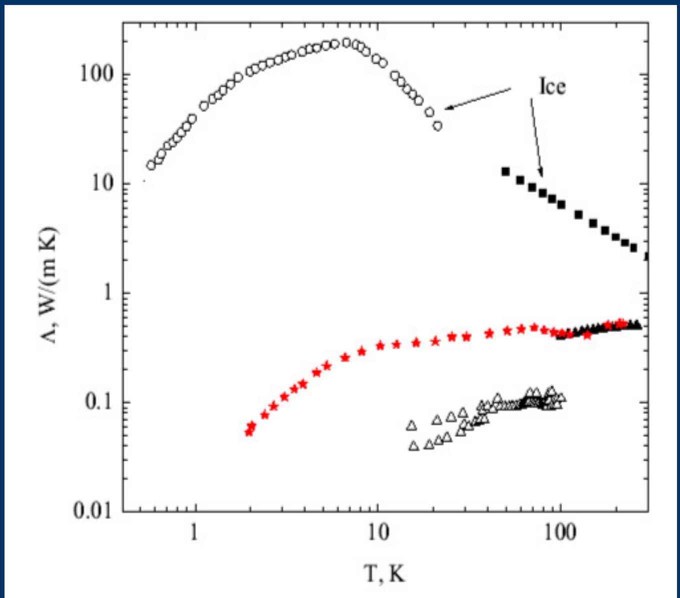


Velocity of Sound: 3900 ± 50 m/s

Other related work:

Thermal conductivity: A. Krivchikov et al
JCP 2005

^{83}Kr nuclear resonant scattering: J.Tse et al
Nature Mat. Dec 2005



„RT-coupling" rotation J = 0 - 1

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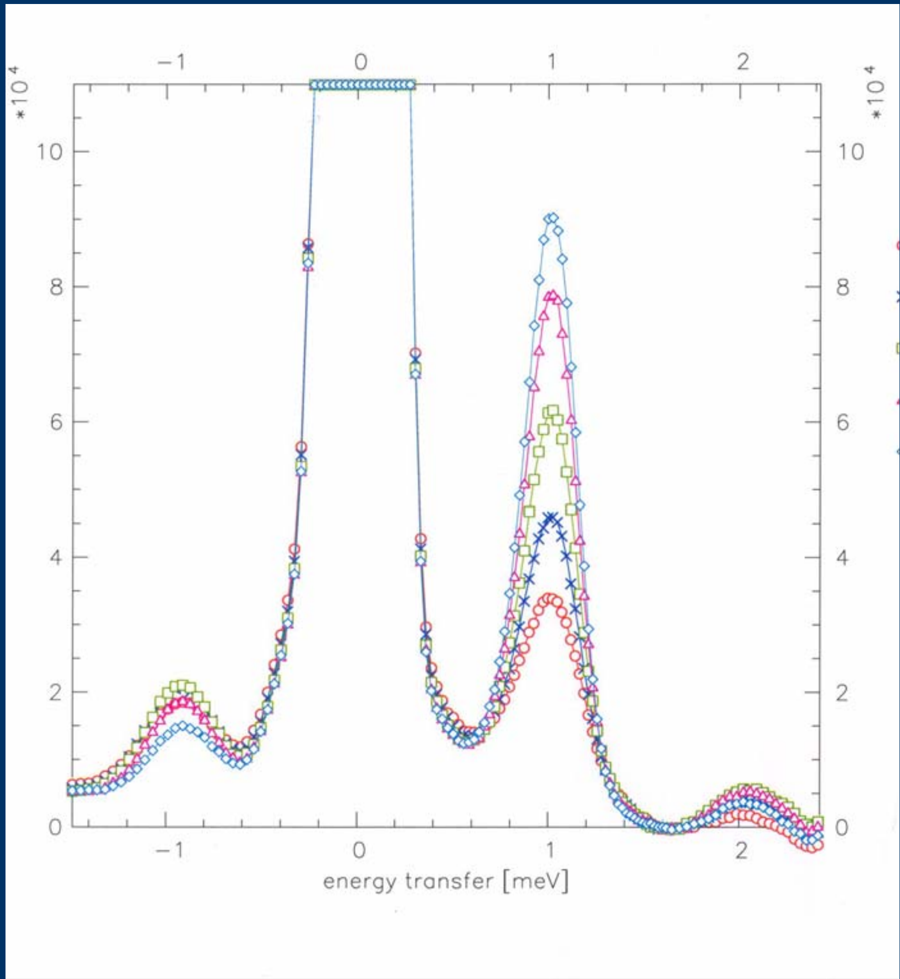


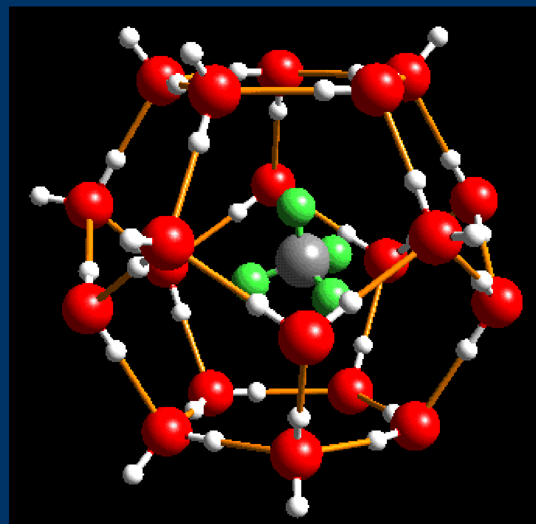
TOF SV29 FRJ2 Juelich

Nuclear spin conversion

$\Psi = \Phi_{rot} \chi_{spin}$

from rotat. thermometer

4K < T_{rot} < 14K



Quantum rotations + translational "rattling" motion

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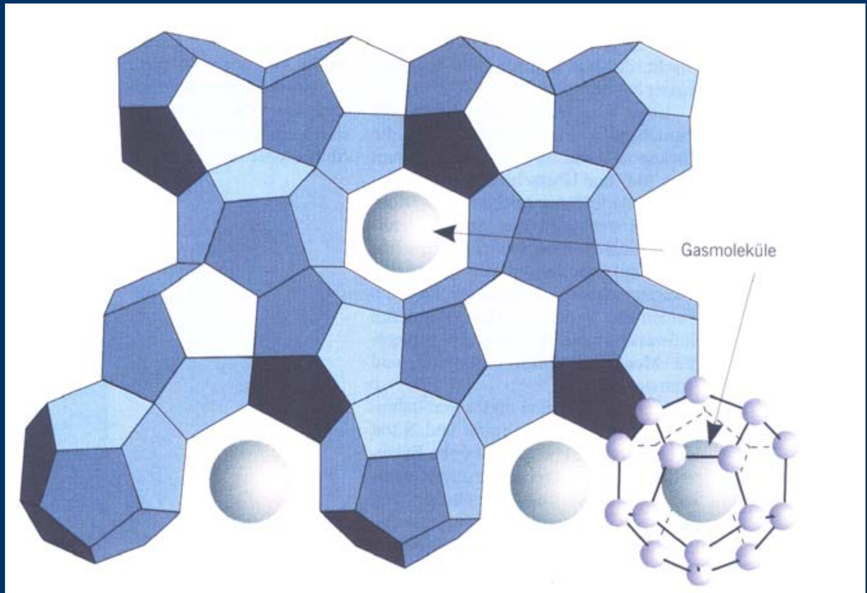
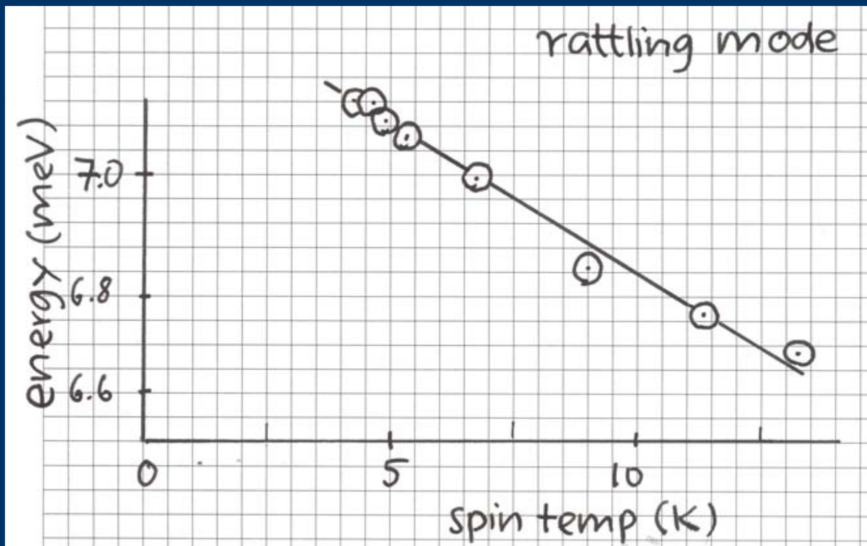
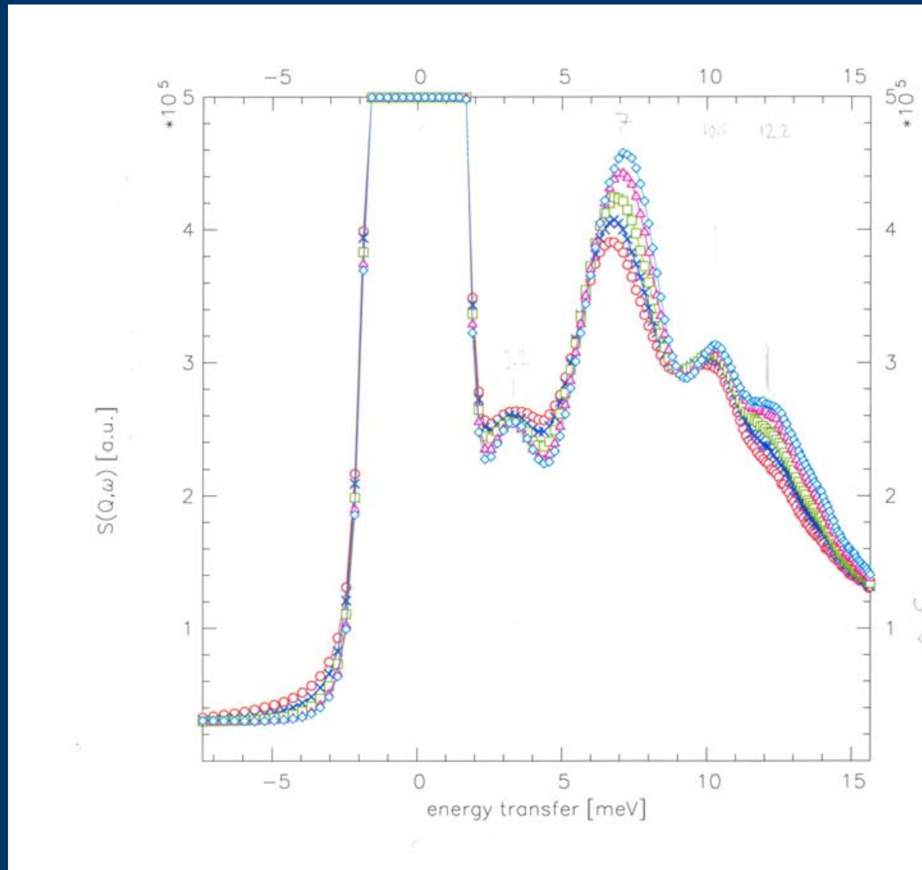


Frequency of rattling depends on rotational state





Skutterudites XFe_4Sb_{12}

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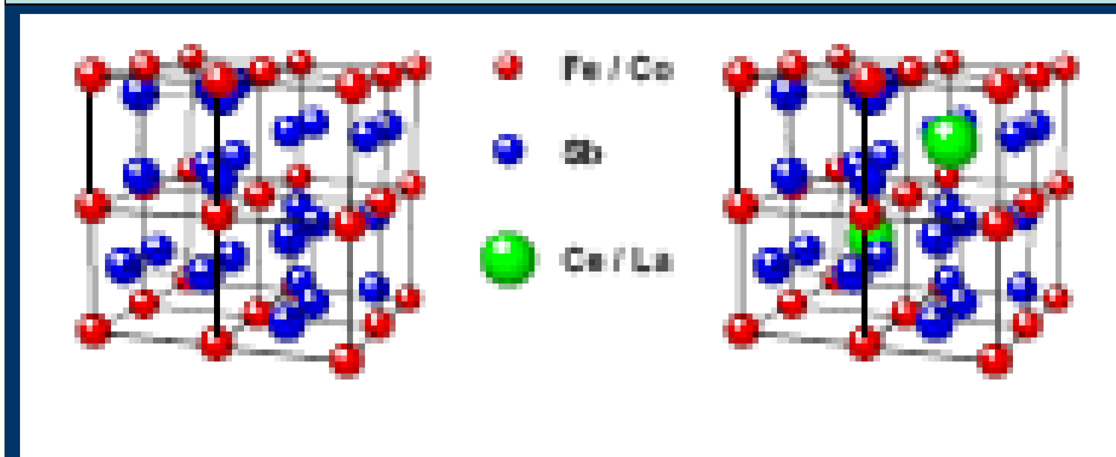
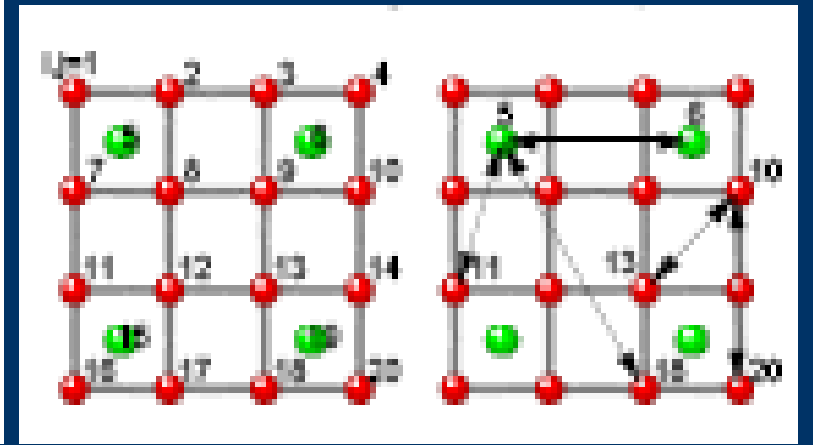


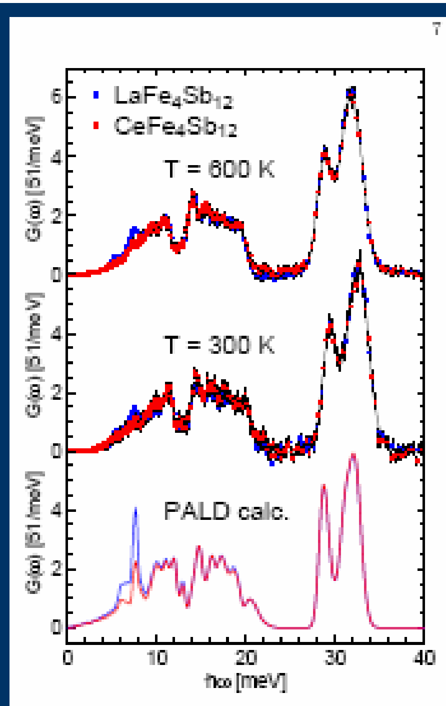


Spacegroup $Im\bar{3}$ ~ bcc cages a_0 ~ 10Å

Filled skutterudites

What is new? electrical conductivity!

Thanks to
Marek Koza
Raphael Herrman



Skutterudites & Si,Ge - clathrates

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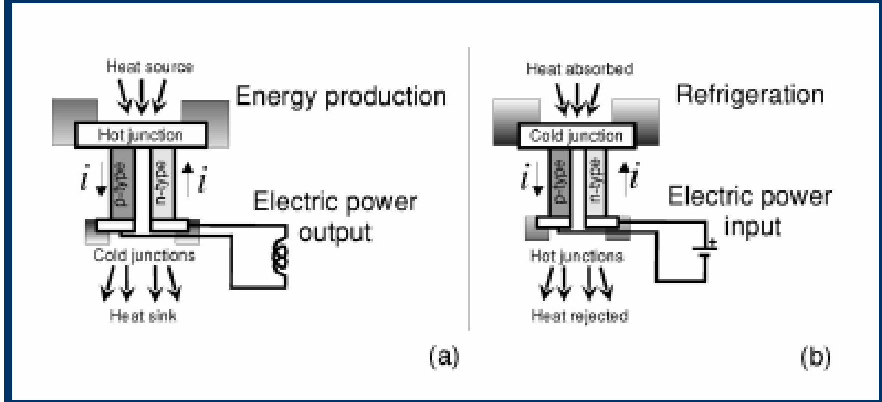
$\vec{j} = L(\nabla T)$



Thermoelectrical effect
gradT, gradU = E

Seebeck (conversion of therm. to
Peltier electric)

No dissipation: good electrical conductivity σ
Large thermal gradient: κ_{th} low
„electron crystal & phonon glass"

Recommended reference for further reading:
R.P.Herrman et al Am. J. Phys. 73, 110-118 (2005)

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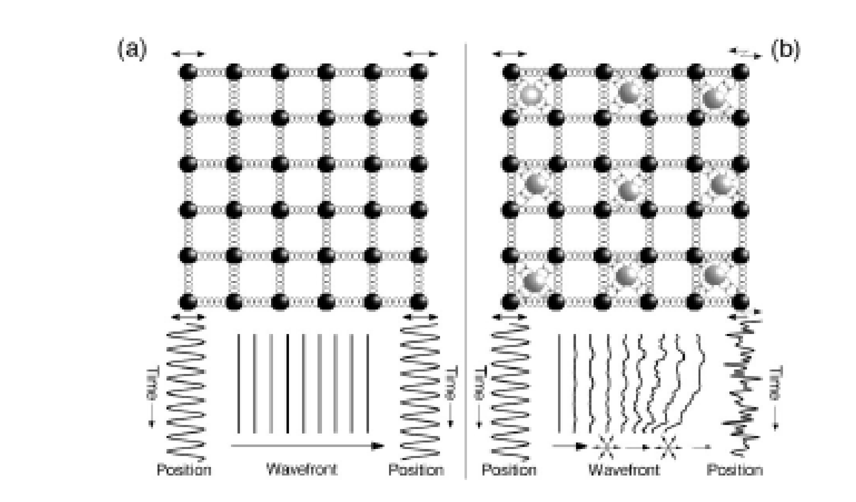
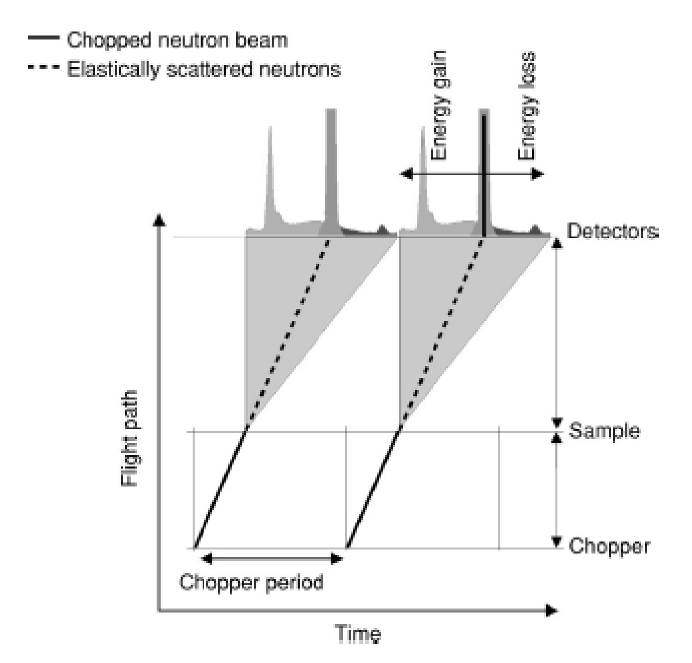
Einstein-type motion (low-lying optical mode, not Debye-behaviour !)

by itself fascinating ....





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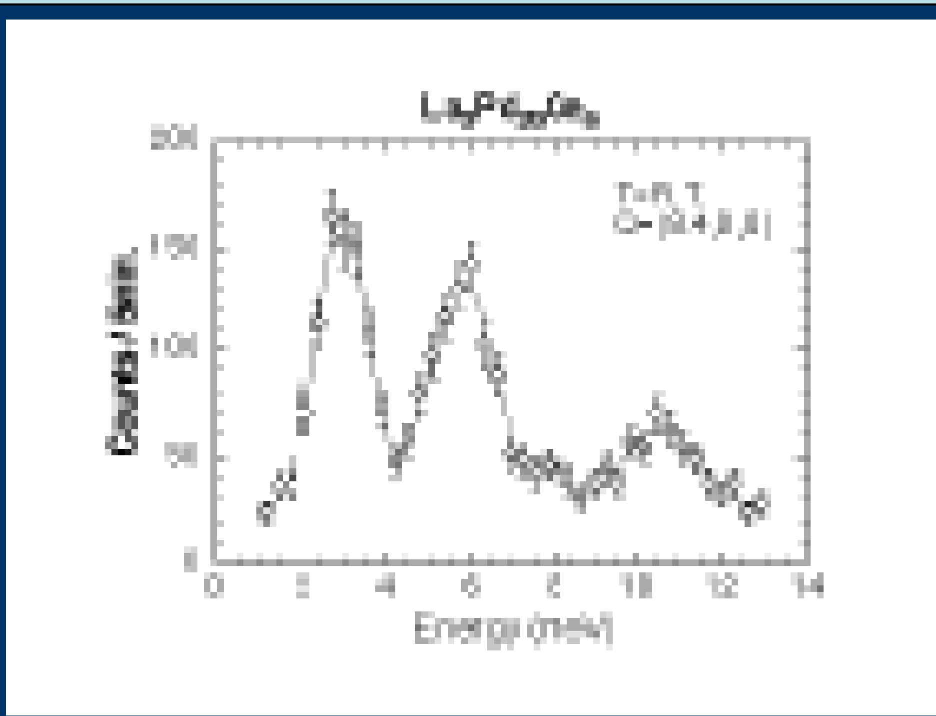

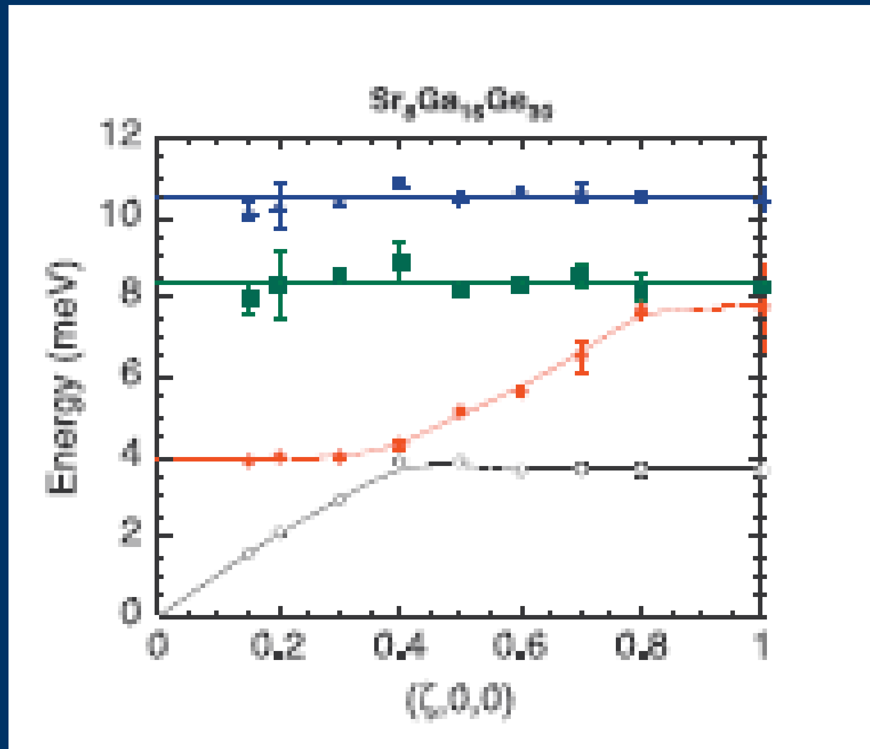

Rattling modes =
Einstein modes of guest atoms

~ single particle translational oscillations
weak coupling (anticrossing, $I_{inel} \neq Q^{**2}$),
anharmonicity

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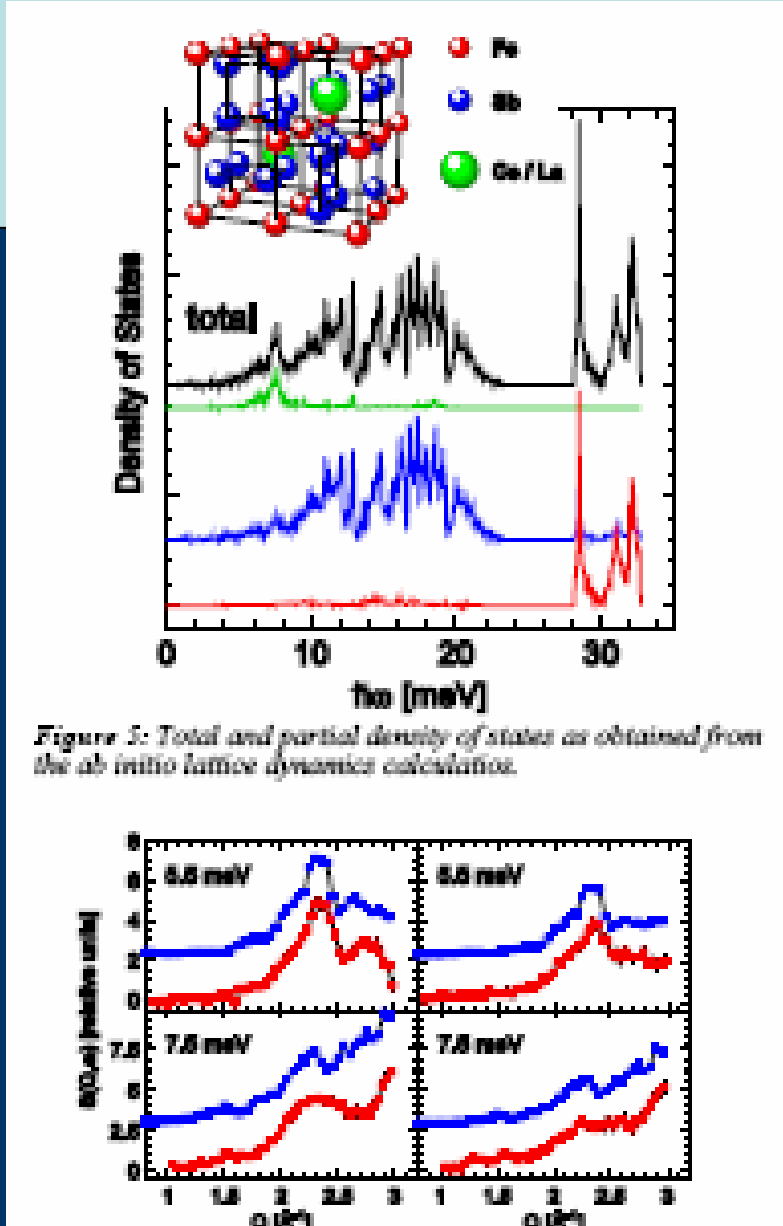

Figure 5: Total and partial density of states as obtained from the ab initio lattice dynamics calculation.

Figure 6: Constant energy slices of the calculated (blue) and measured (red) inelastic intensity of $LaFe_4Sb_{12}$ (left) and $CeFe_4Sb_{12}$ (right) samples. Calculated data are shifted for clarity.

$I(Q) \sim Q^2$ signals
single particle behaviour

Departures !

Data from time-of-flight
IN6, IN4 at ILL
M. Koza et al, 2006

Methane hydrate (burning ice)

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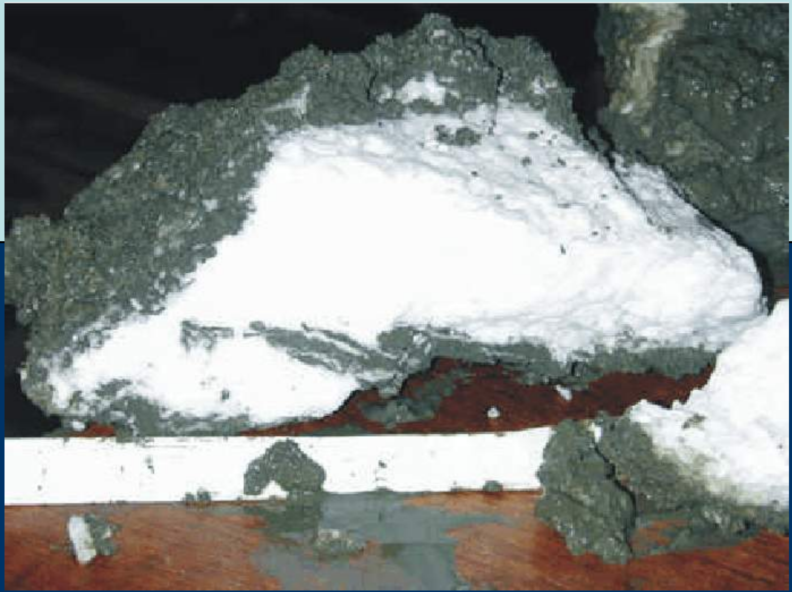
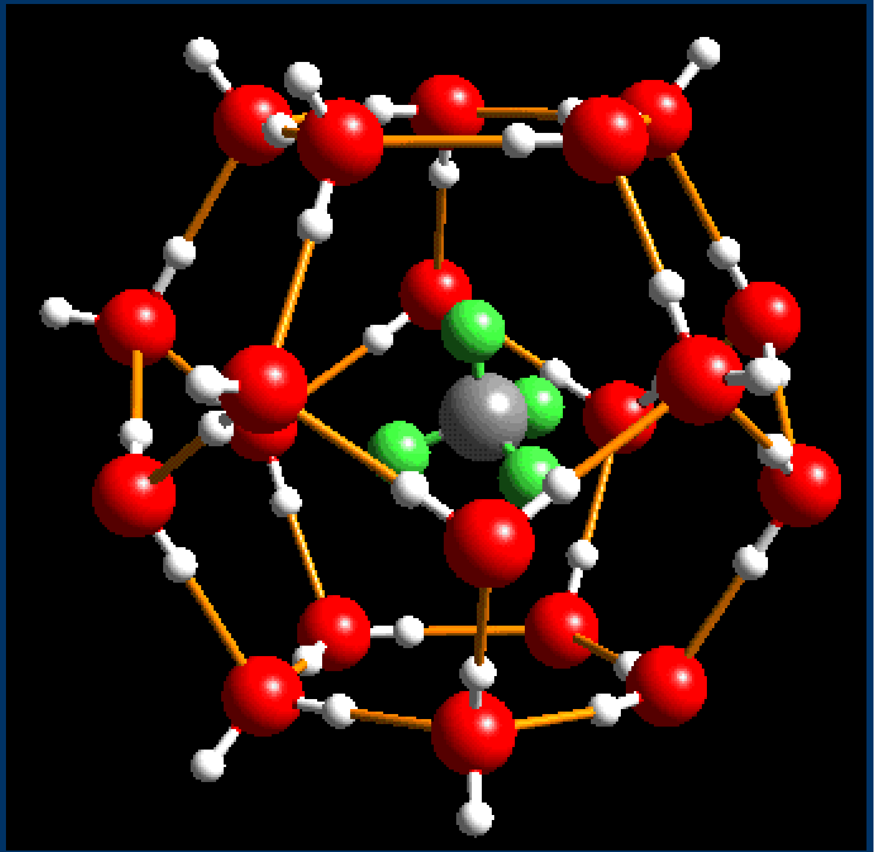


Macroscopic (from Pacific)

←

→

Microscopic (hydrate cage)



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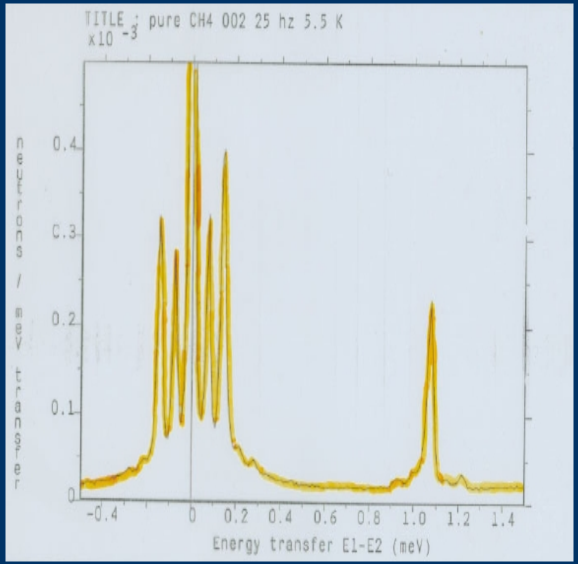
Open
Marine research needs macroscopic features
Thermal conductivity not fully understood
Hamiltoniam $H = H_{Trans} + H_{Rot} + H_{RT}$
(even H_{Trans})

CH4 II   Rotational Excitations



Yet many surprising features
and even some model character

Fin