Applications of *Ab Initio* Random Structure Searching

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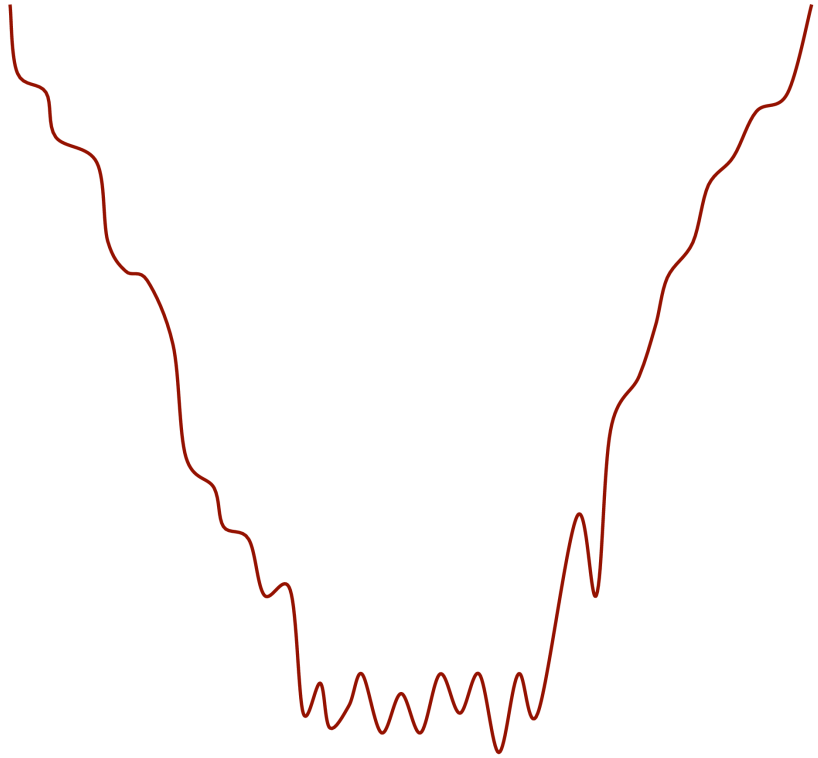
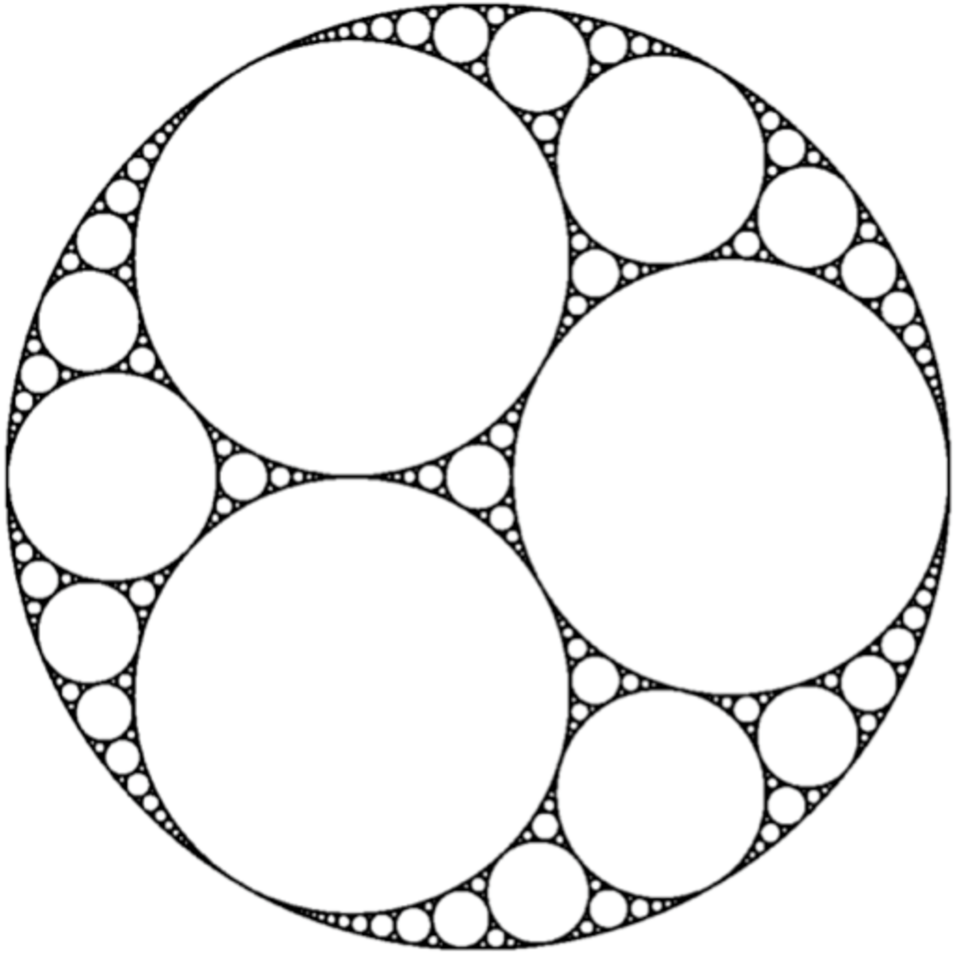
QMC in the Apuan Alps 2009, Vallico Sotto, Italy, 25 July – 1st August 2009

Energy landscape



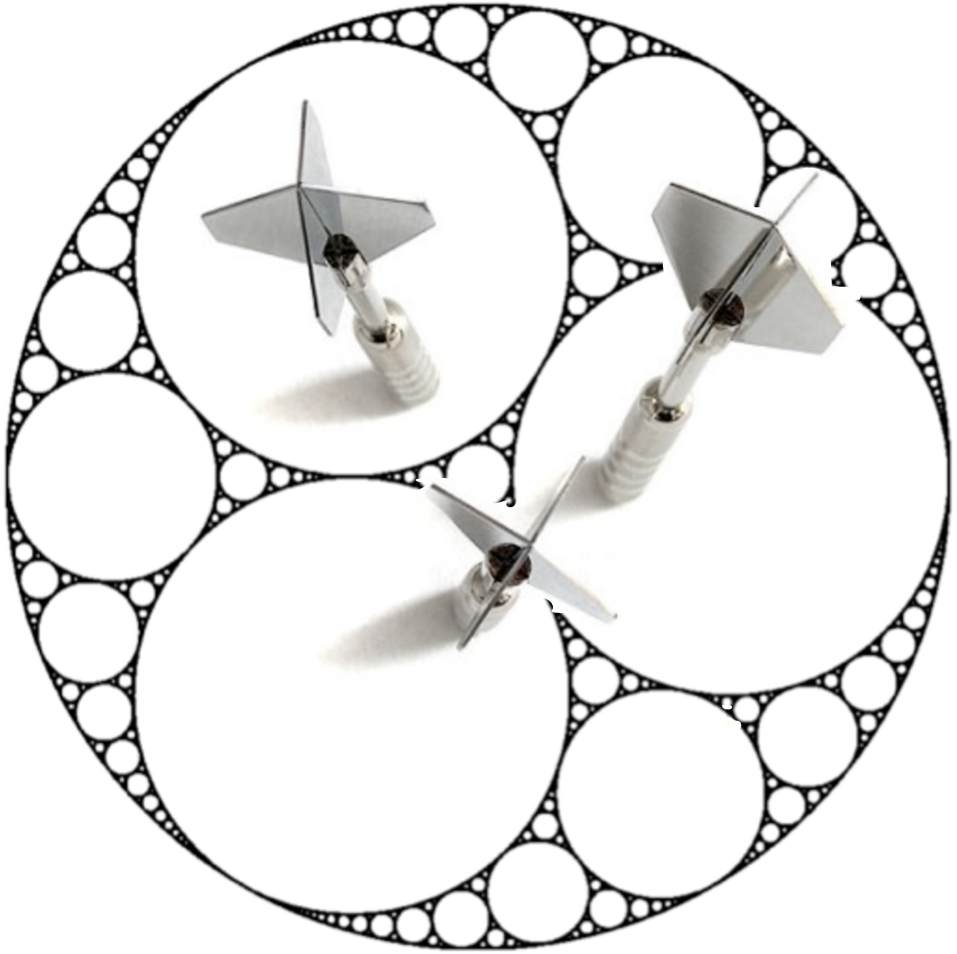
Minima at low energies, could have multiple funnels

Energy Landscape



Doye and Massen, *PRE*, **71**, 016128, 2005

Energy Landscape



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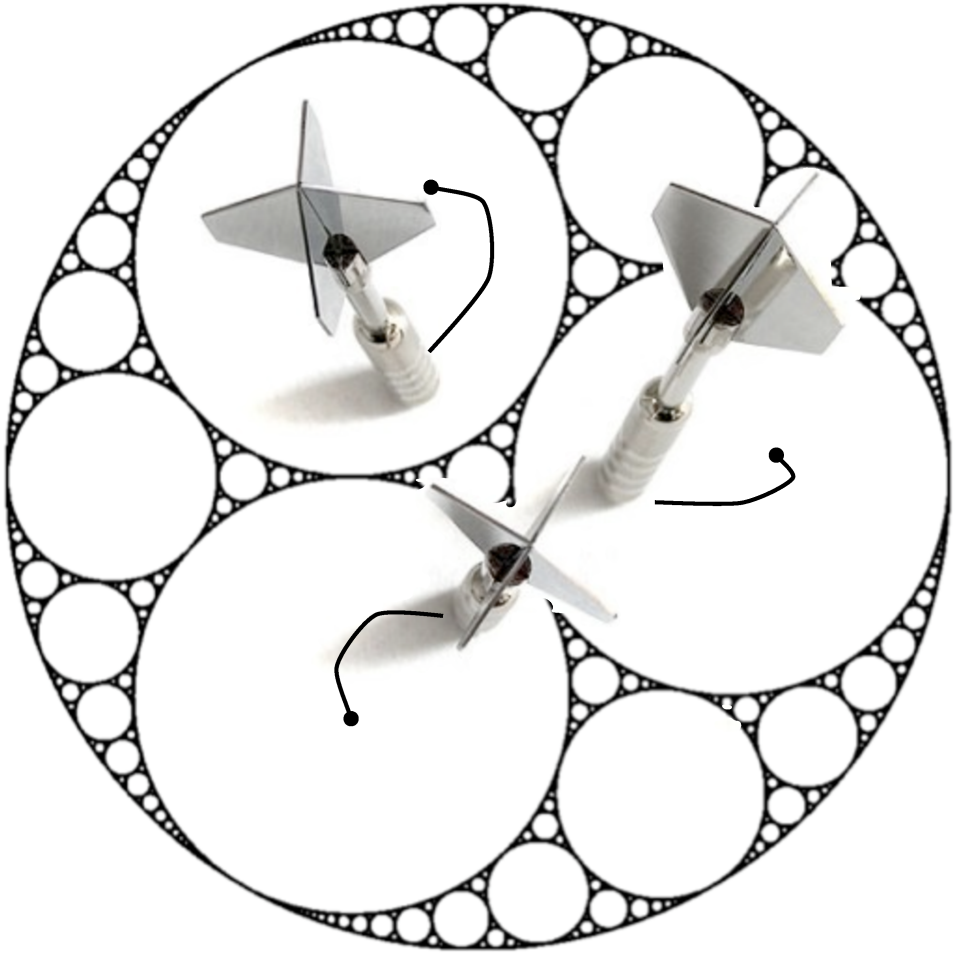
Energy Landscape



Doye and Massen, *PRE*, **71**, 016128, 2005

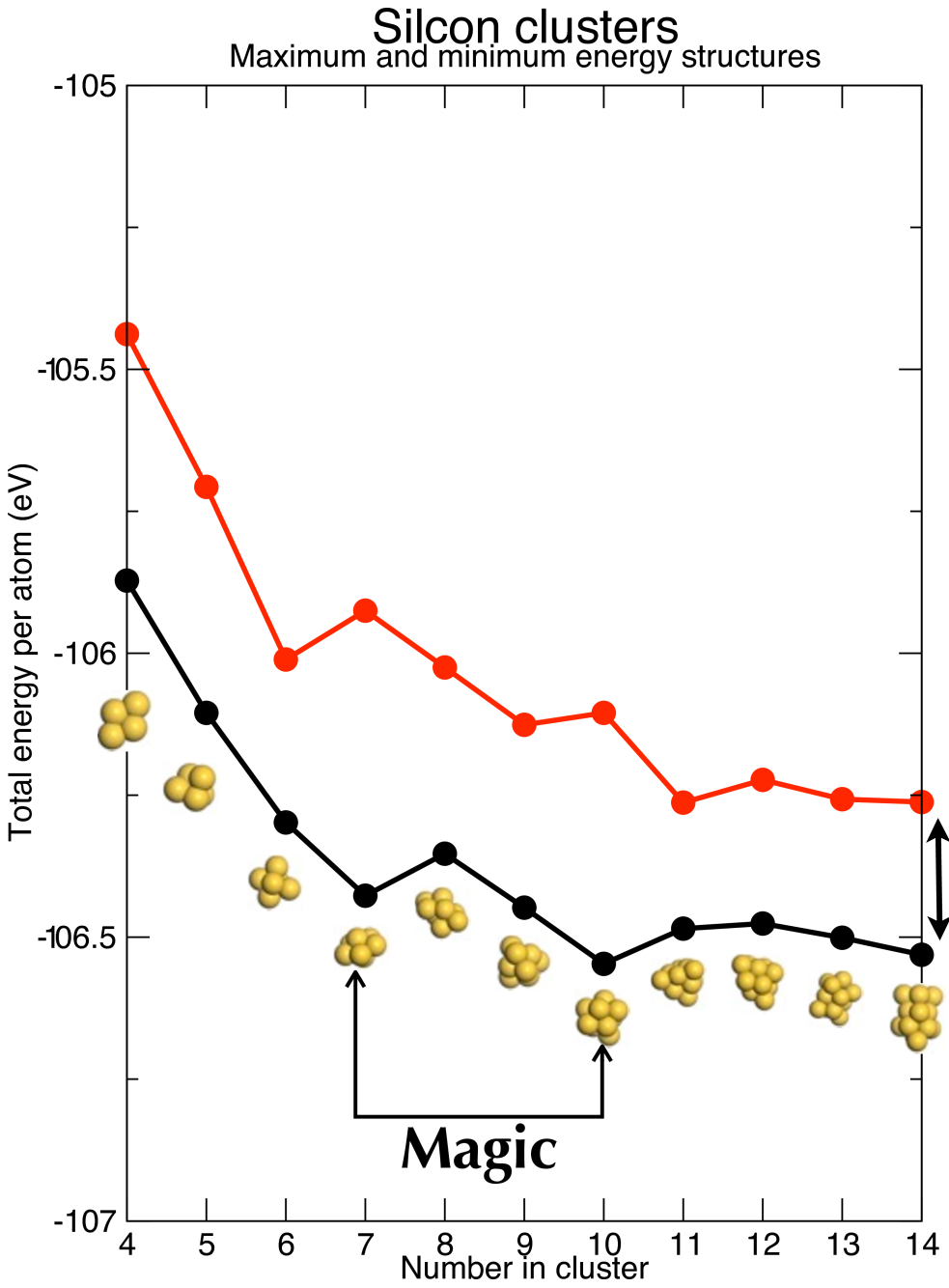
Ab Initio Random Structure Searching

- Make a random unit cell
- Throw the required numbers of each atom type into the cell at random
- Relax under the quantum mechanical forces and stresses
- Repeat until happy or computing credits run out
- Look at lowest-energy or other interesting structures

Pickard and Needs, Phys Rev Lett 97, 045504 (2006)

Ab Initio Random Structure Searching

- Easy to understand
- Easy to do
- Unbiased
- Teaches you chemistry
- Loves modern computers
- Can do exhaustive searching on $\sim$12 atoms ($\equiv$ 39 degrees of freedom)



Throw atoms randomly into a box (within a bigger box)

Least stable

Most stable

A comparison of searching methods

Average number of relaxations to find the global minimum-energy structure

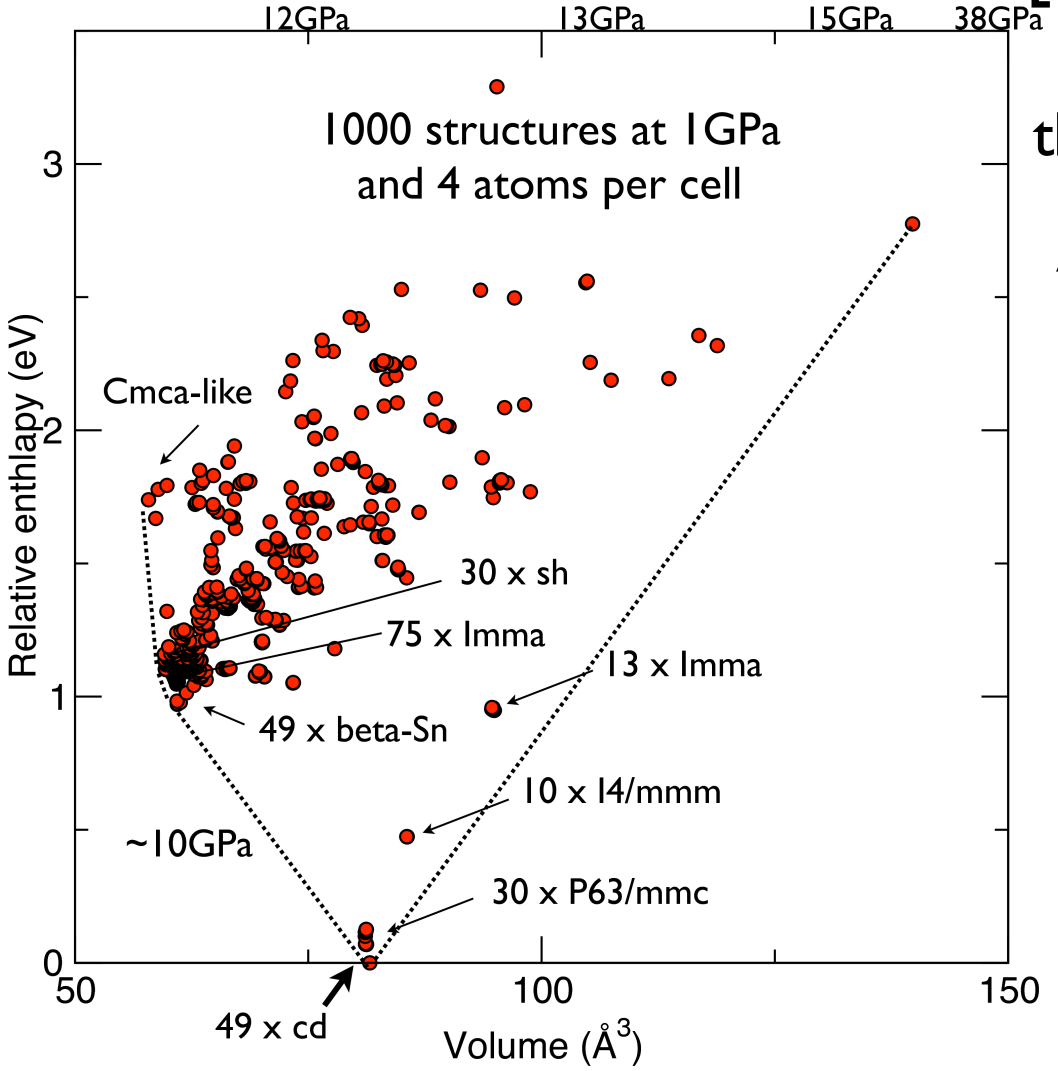
Method	LJ 26	LJ 38	LJ 55
Minima Hopping	96	1190	190
Evolutionary Algorithm	56	1265	100
Random Searching	190	12560	9846

Minima Hopping and Evolutionary Algorithm data from:
Schönborn *et al.* J Chem Phys 130, 144108 (2009)

LJ 38 using random structure searching with "relax-and-shake" $\sim$1000

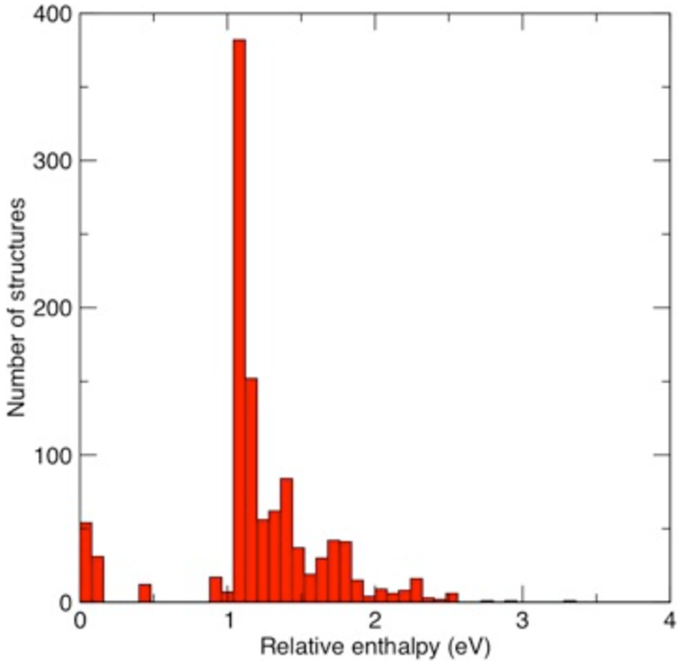
Example: silicon

cd - beta-Sn - Imma - sh - [Cmca] - hcp - fcc



A single run at 1 Gpa gets all the phases up to about 40 GPa

At least 1/4 of the structures have been observed



Philosophy

- When you don't know anything, select structures from a uniform random distribution

- When you know something for sure impose it directly, when you think something is likely to be true bias the search towards it

- Impose chemical ideas through constraints on the initial structures - chemical units, coordination number

- Use experimental data as constraints

- Impose symmetry

Density Functional Theory Calculations

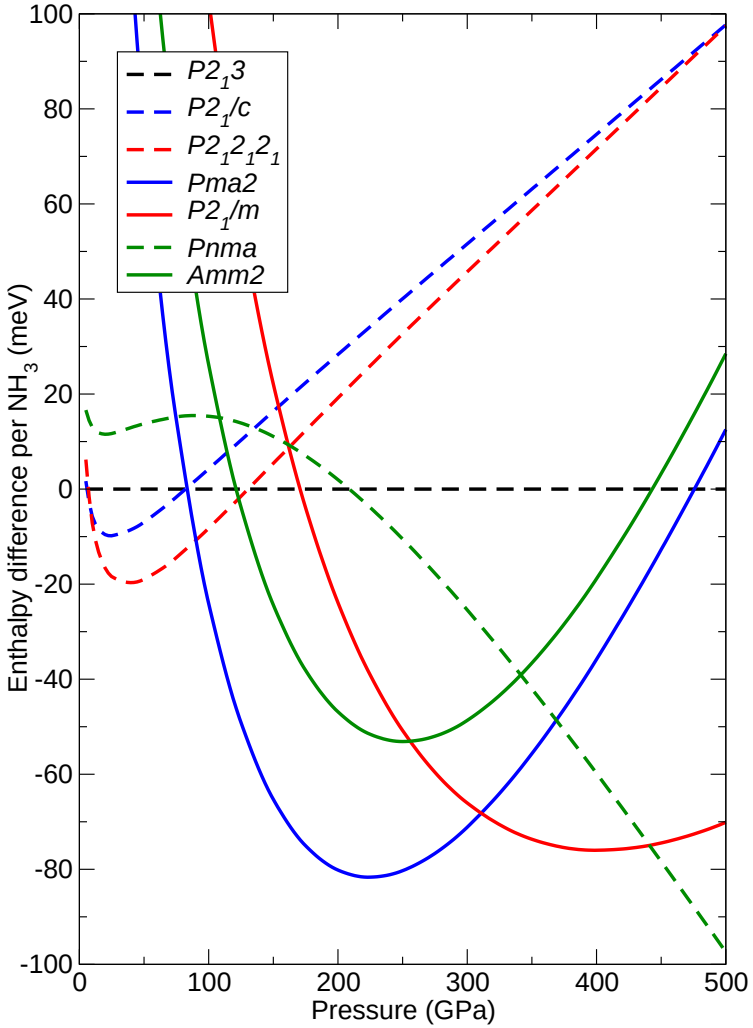
CASTEP code

Plane wave basis set

Ultrasoft pseudopotentials

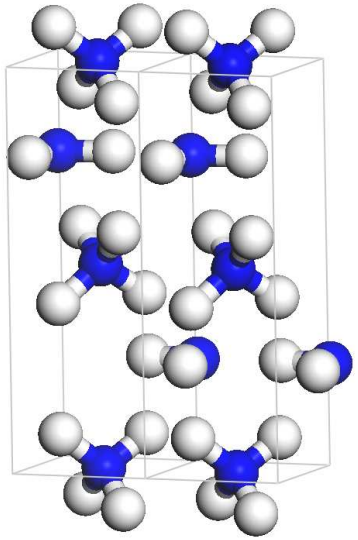
Perdew-Burke-Ernzerhof Generalized Gradient Approximation (PBE-GGA)

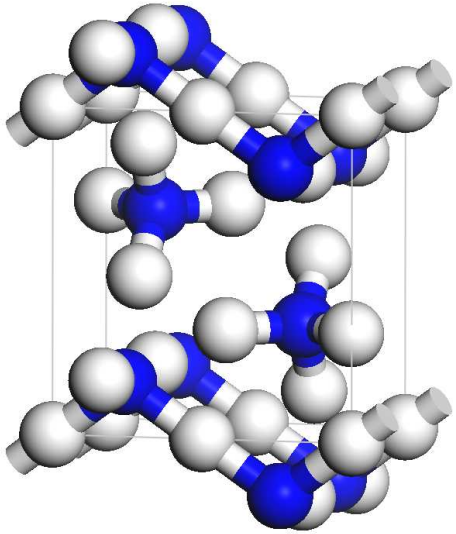
Ammonia NH_3 - Enthalpy versus Pressure

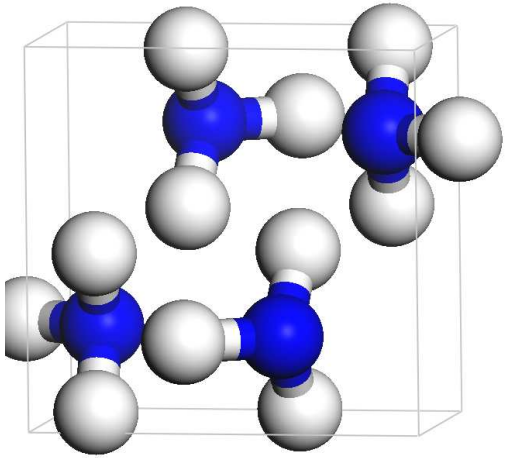


Dashed lines: Molecular Phases
Solid lines: Ionic Phases

Ammonia NH_3 - Structures







$Pma2$	$P2_1/m$	$Pnma$
Ionic	Ionic	Molecular
90-311 GPa	311-440 GPa	$>$440 GPa

Pickard and Needs *Nature Materials* **7**, 775 (2008)

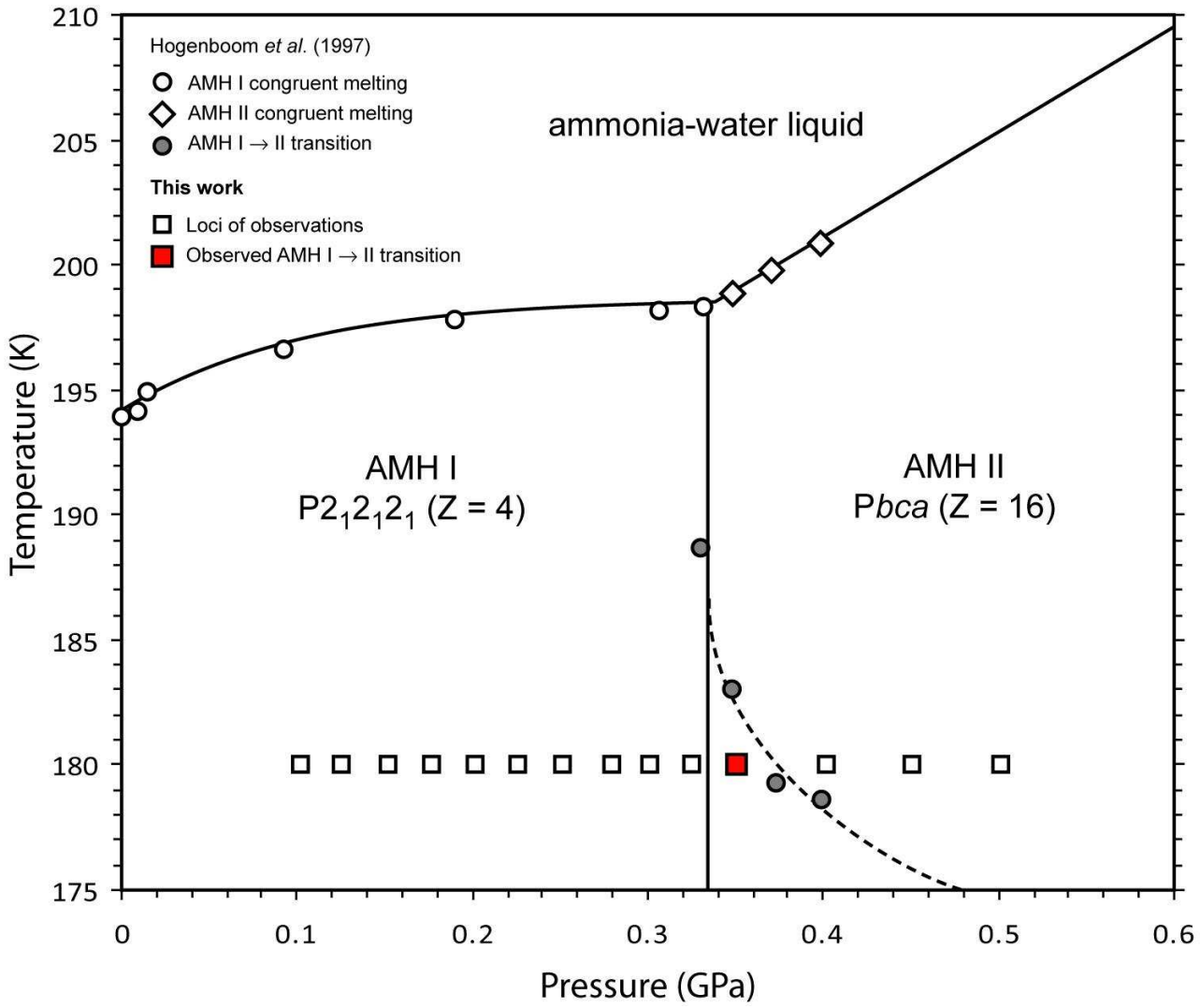
Gas-Phase Proton Transfer Energies for NH_3 and H_2O

$$
\begin{aligned}
2NH_3 &\rightarrow NH_2^- + NH_4^+ && \text{costs} \quad 8.8\,\text{eV} \\
2H_2O &\rightarrow OH^- + H_3O^+ && \text{costs} \quad 9.8\,\text{eV} \\
NH_3 + H_2O &\rightarrow NH_2^- + H_3O^+ && \text{costs} \quad 10.3\,\text{eV} \\
NH_3 + H_2O &\rightarrow OH^- + NH_4^+ && \text{costs} \quad 8.1\,\text{eV}
\end{aligned}
$$

- Gain in electrostatic energy from bringing point + and − charges from ∞ to a separation of 2.5 Å is 5.8 eV
- Packing of ions compared with molecules
- DFT study by Fortes *et al. J. Chem. Phys.* **115**, 7006 (2001) predicted a transition from $NH_3 + H_2O$ to $OH^- + NH_4^+$ at 5 GPa

Ammonia Monohydrate

A component of the outer planets and their larger satellites



Fortes, Suard, Lemé-Cailleau, Pickard and Needs, unpublished

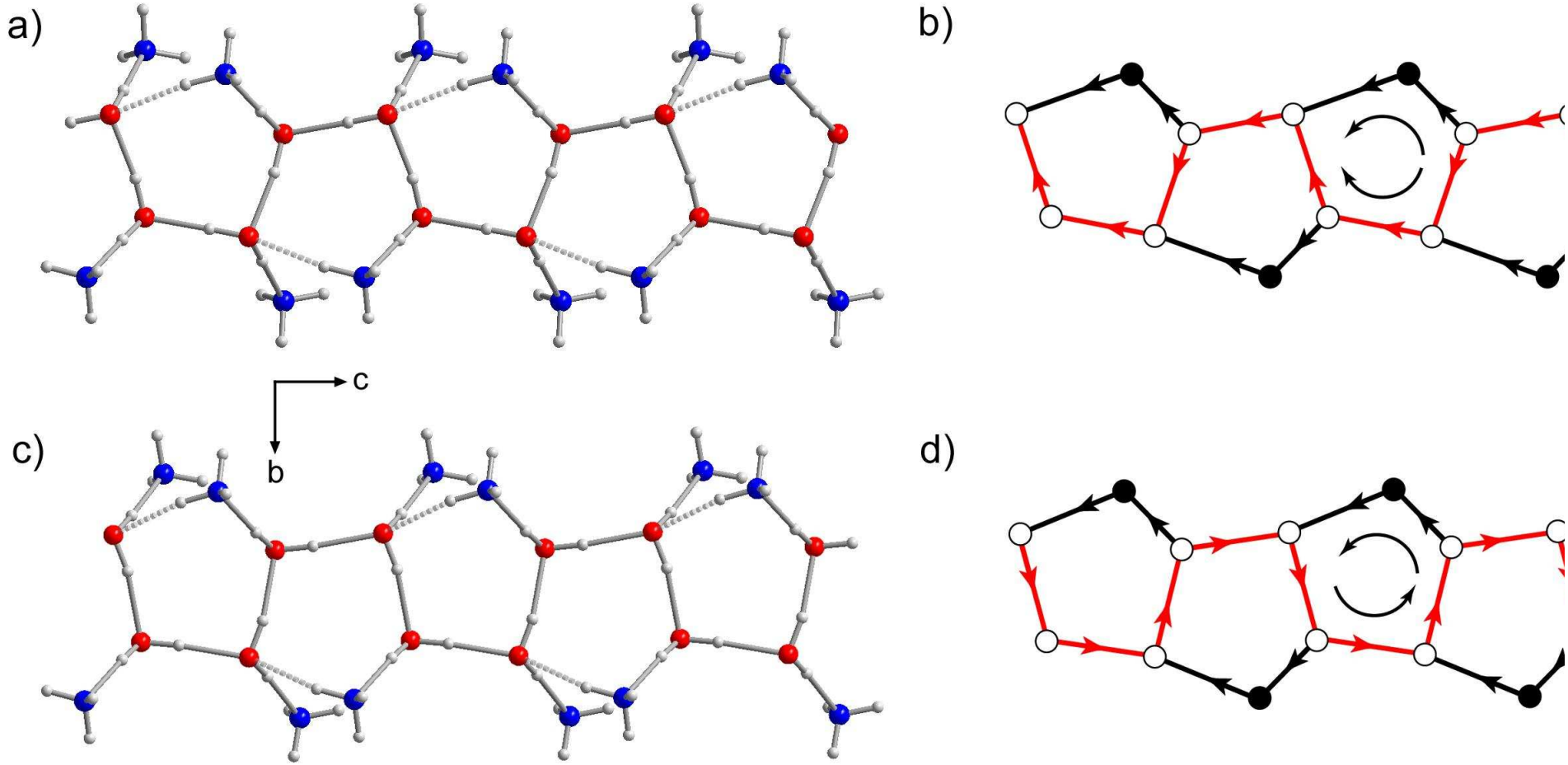
Structure of Phase II of Ammonia Monohydrate

• 2003: Neutron diffraction experiment by Fortes $et\ al.$ on ammonia dihydrate which decomposed under pressure into ammonia monohydrate and water ice. No structure could be obtained, but unit cell has $Z = 16$ (112 atoms) with possible space groups $Pcca$, $Pnca$, or $Pbca$

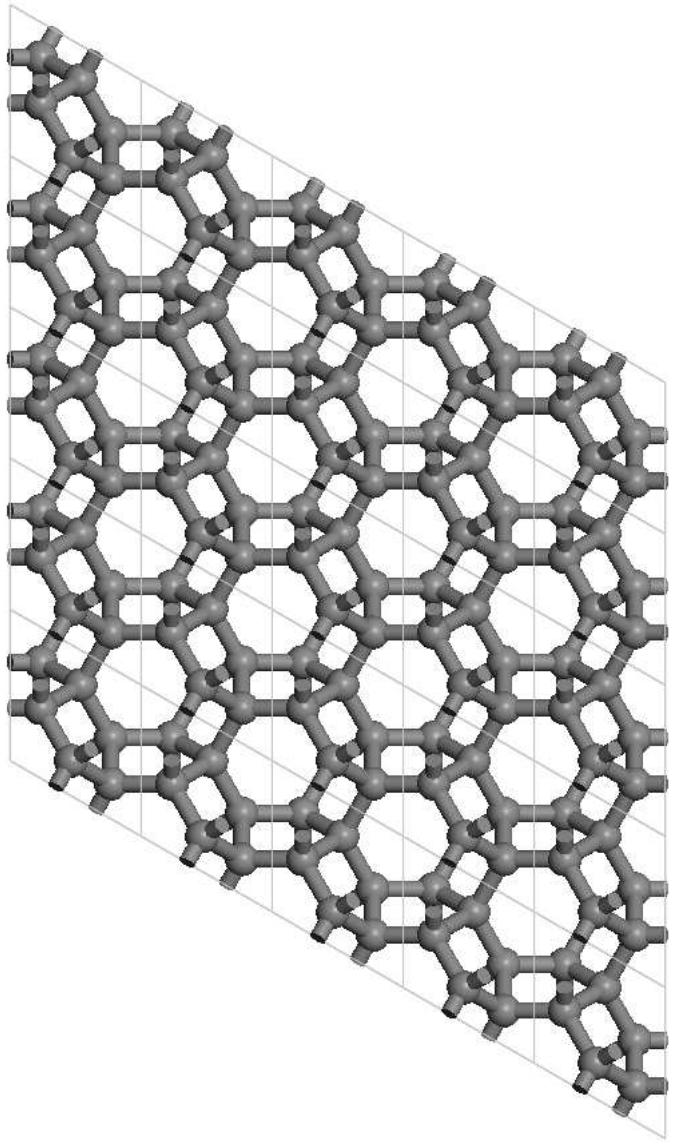
• 2008: DFT calculations using experimental unit cell, inserting 16 $\mathrm{H_3N \cdot \cdot H \cdot OH}$ units, assuming $Pcca$, $Pnca$, or $Pbca$ symmetry. Lowest enthalpy structure of $Pbca$ symmetry

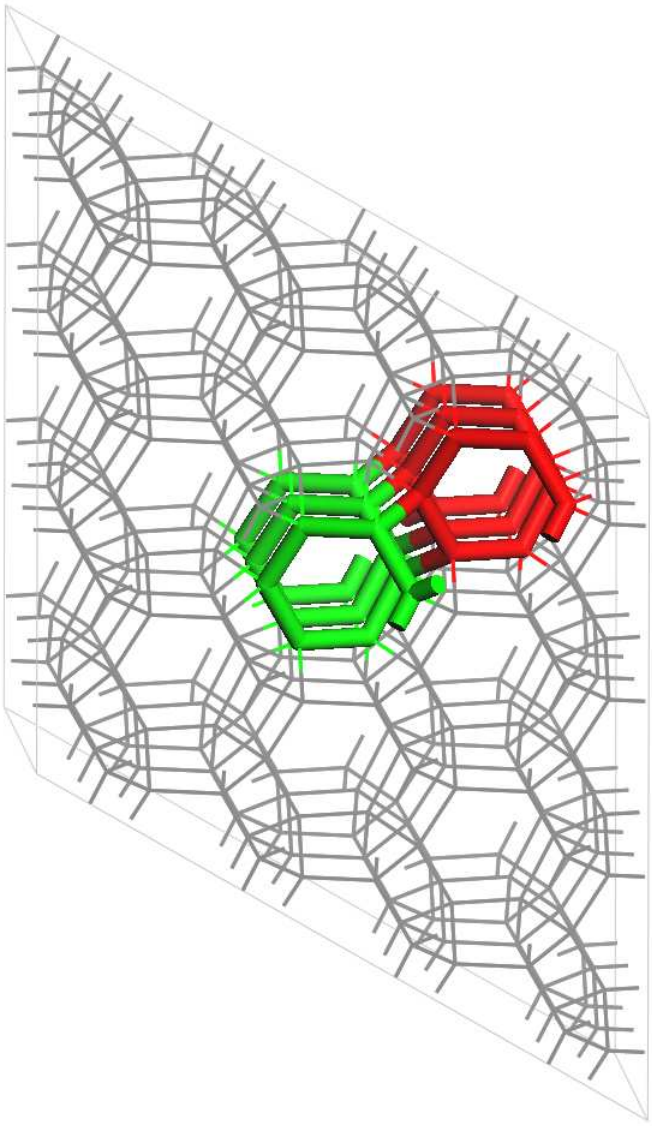
• 2009: Neutron diffraction experiment by Fortes $et\ al.$ on ammonia monohydrate obtains a structure of $Pbca$ symmetry (slightly different from DFT prediction)

Structure of Phase II of Ammonia Monohydrate

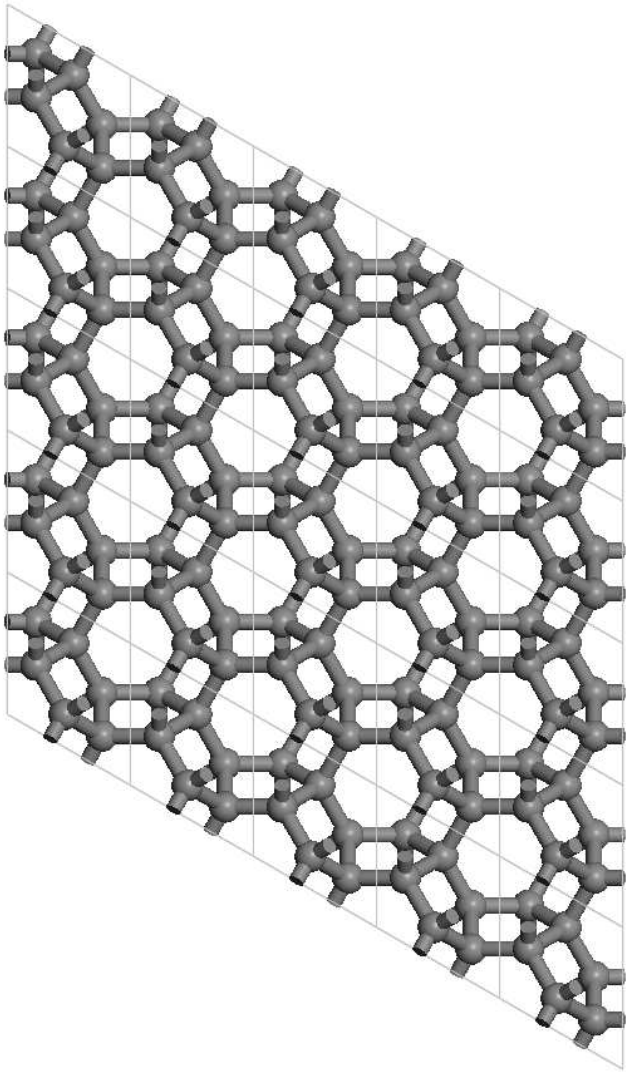


Chiral Framework Structure for C, Si, Ge, Sn





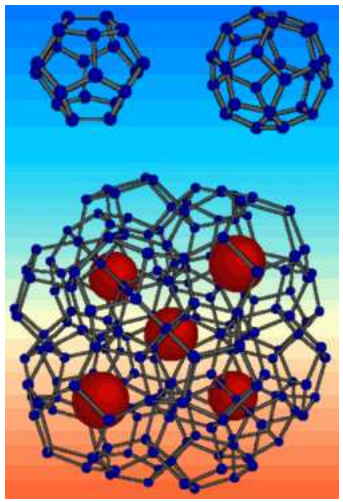
Chiral Framework Structure



CFS and Clathrate II compared with diamond

Element	ΔE_{CFS} (meV)	ΔE_{CII} (meV)	V_{CFS} (Å^3)	V_{dia} (Å^3)
C	112	72	6.2	5.7
Si	53	52	22.1	20.4
Ge	34	26	26.0	24.1
Sn	28	23	39.5	36.8

Pickard and Needs, unpublished

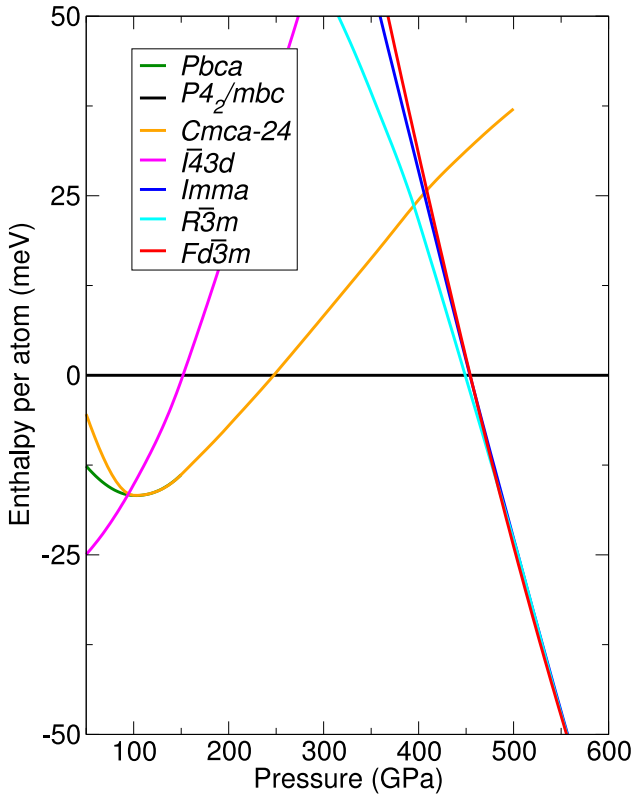


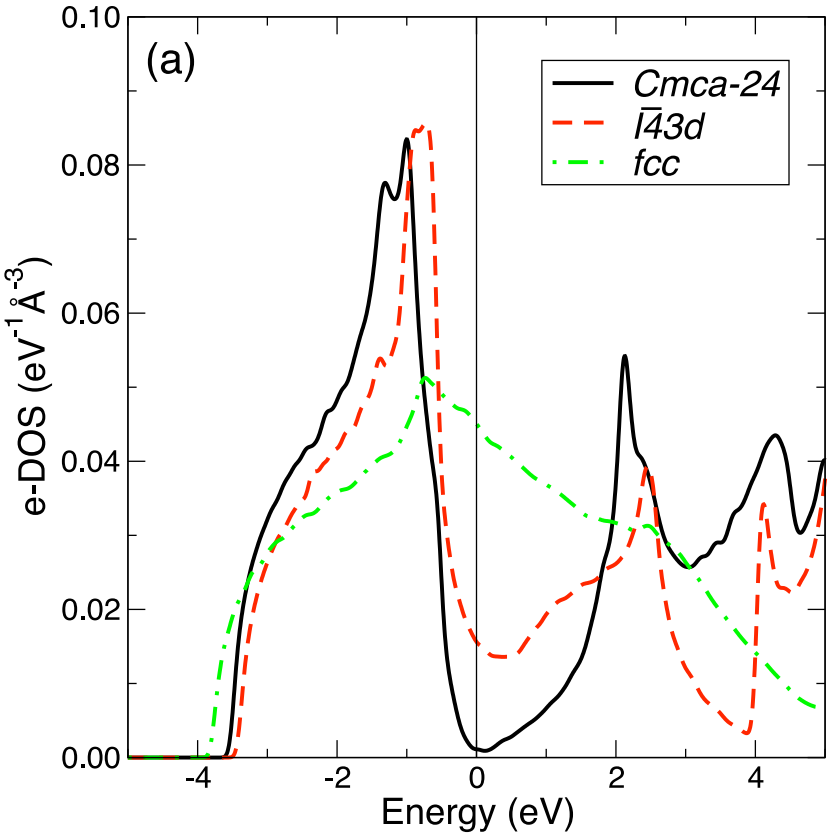
Clathrate II structure

High-Pressure Phases of Lithium

FCC (12-fold) $\Rightarrow$ $I\bar{4}3d$ 40 GPa (3-fold) $\Rightarrow$???? 70 GPa

High pressure phases are "Elemental electrides" (Anions are electrons)

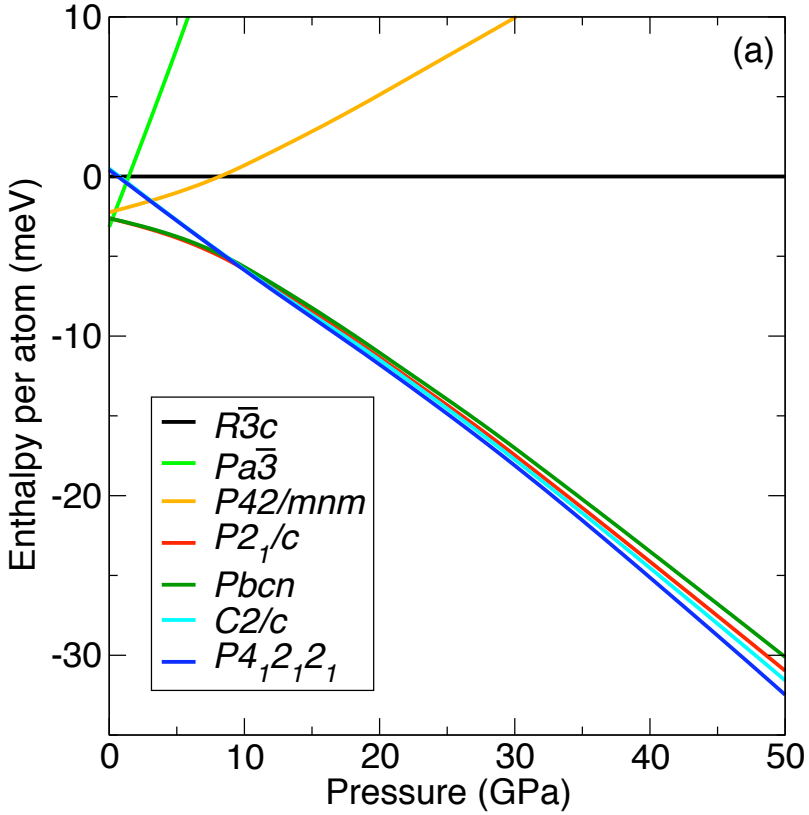


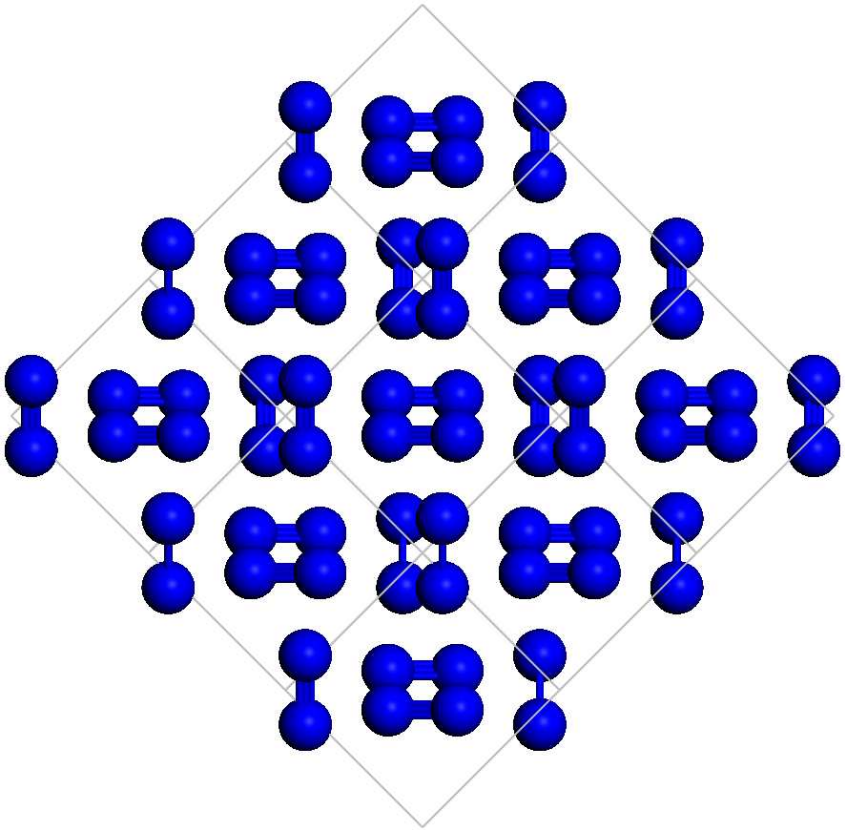


Pickard and Needs, Phys Rev Lett 102, 146401 (2009)

High-Pressure Phases of Nitrogen

Structures of the higher-pressure molecular phases

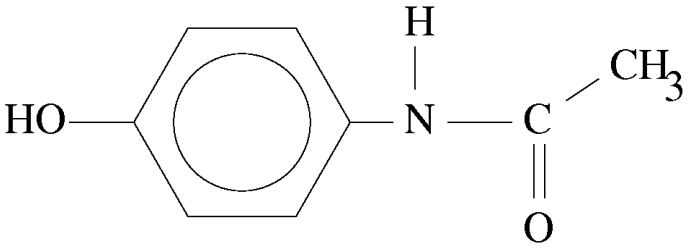




Pickard and Needs, Phys Rev Lett 102, 125702 (2009)

Crystal Polymorph Prediction

Can we predict the crystal structure(s) of paracetamol?



"Layered approach"

Empirical potentials
DFT
QMC

"As it's your first day we're going to start you on something easy"

Conclusions

It's all really quite fun!