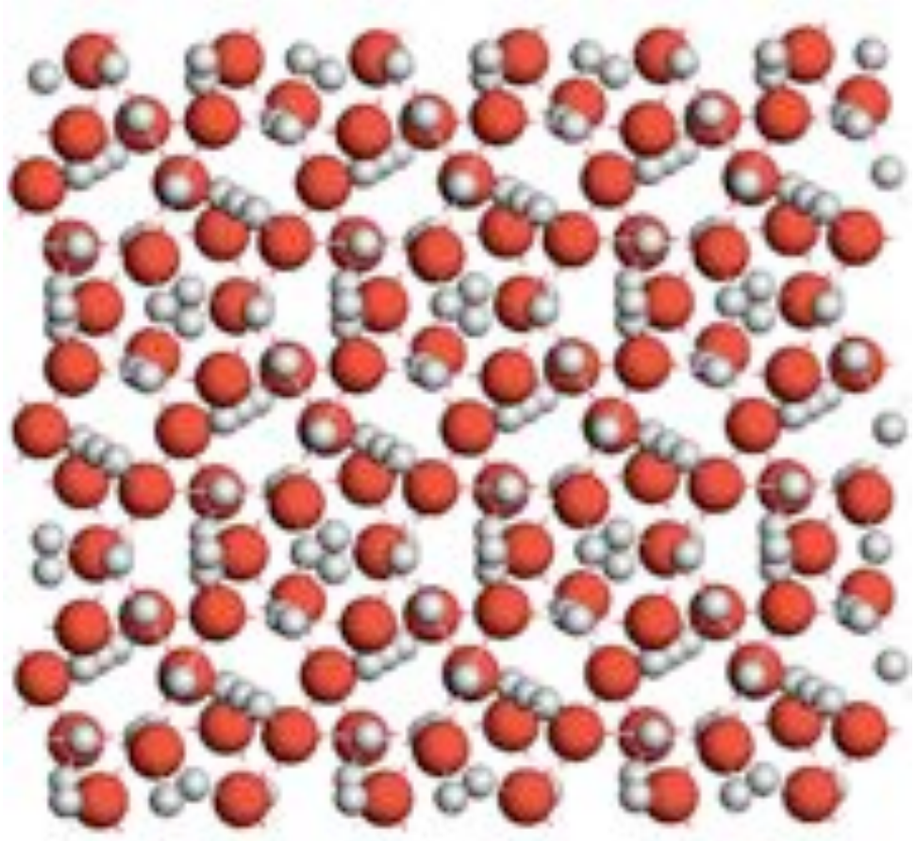
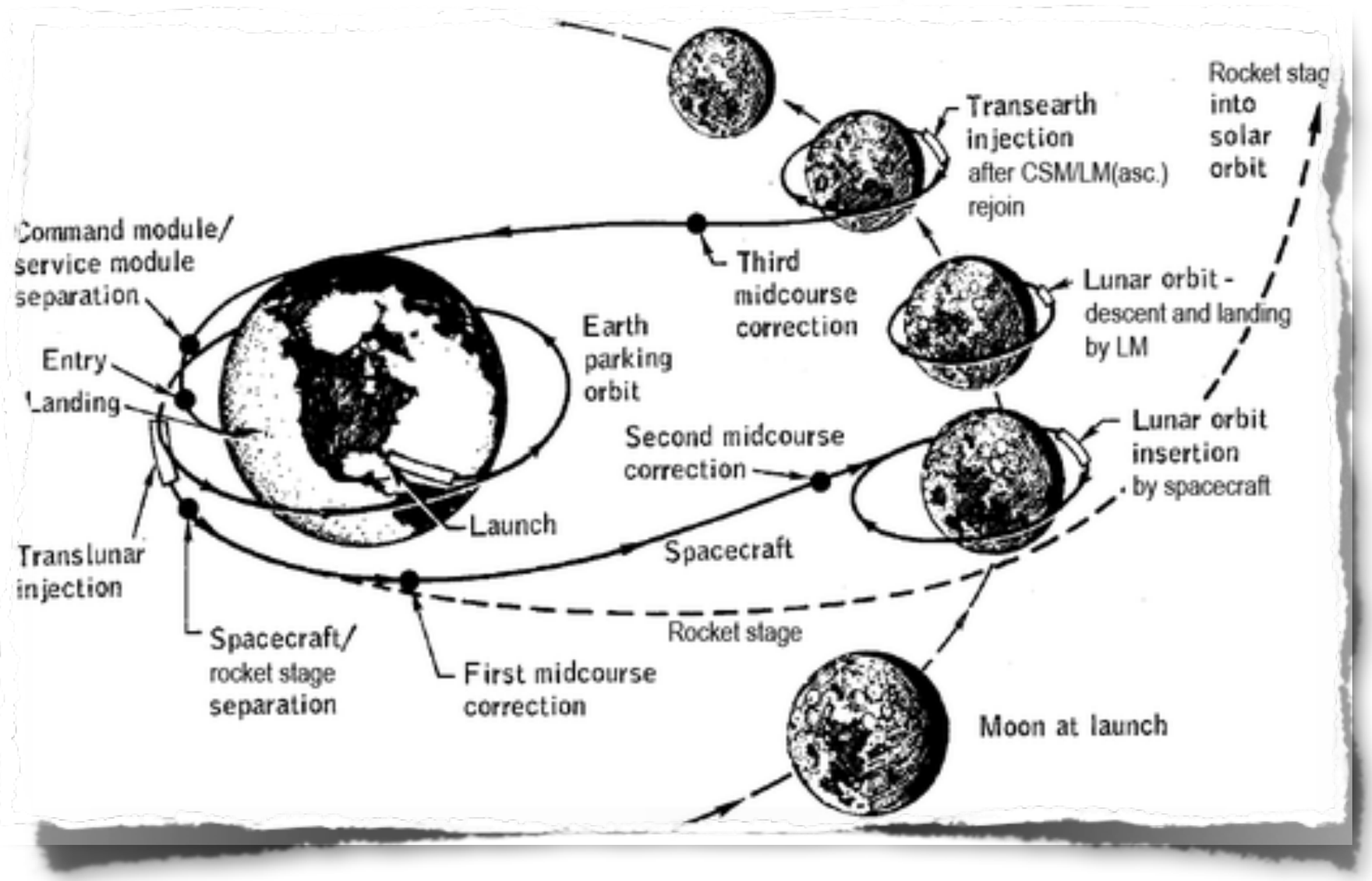
Random search: a tool for discovery and the end of water?

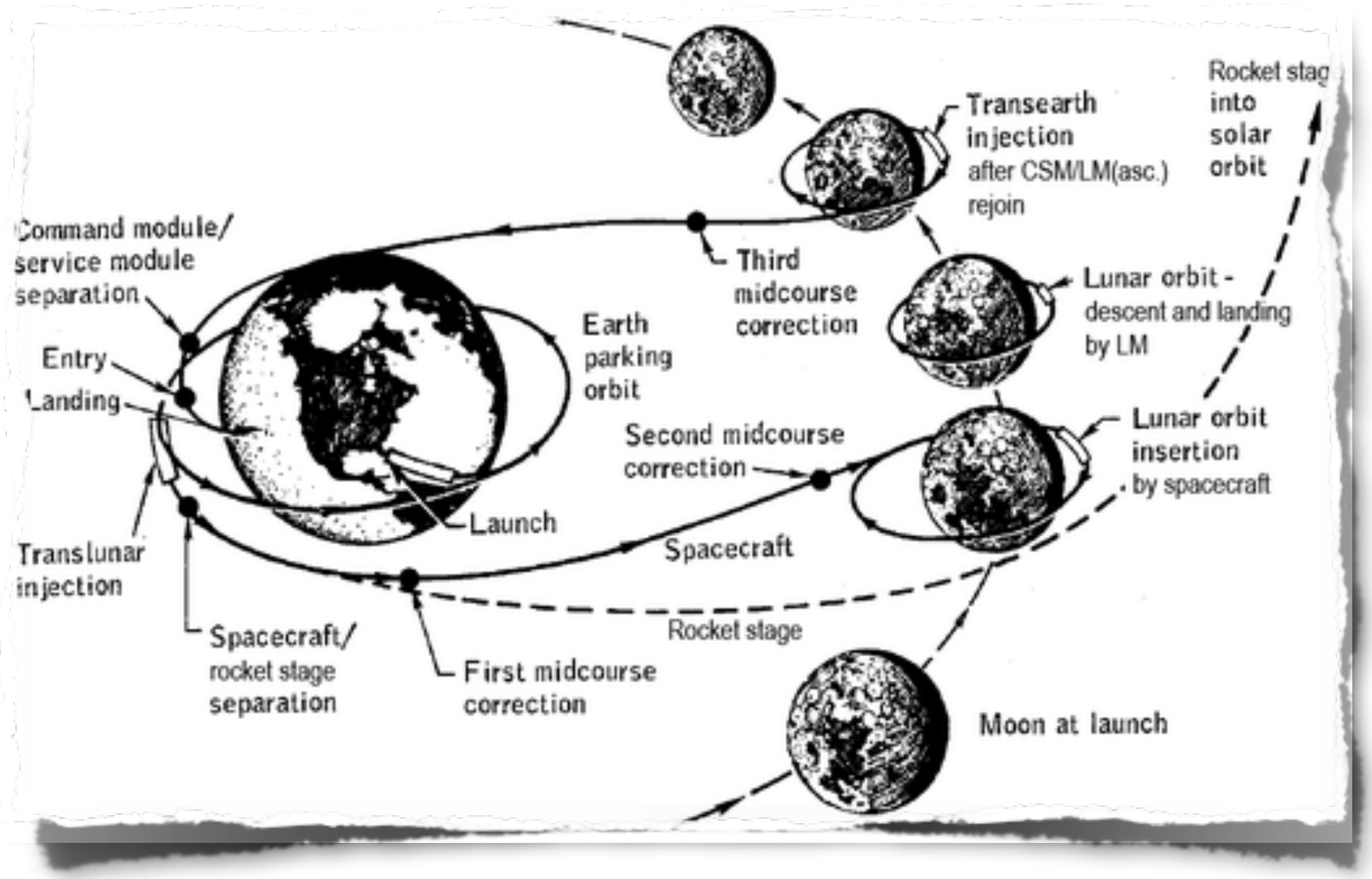


Chris J Pickard
University College London
&
London Institute for Mathematical Sciences

Moon Shot


Command module/
service module
separation
Entry
Landing
Translunar
injection
Spacecraft/
rocket stage
separation
Earth
parking
orbit
Launch
First midcourse
correction
Second midcourse
correction
Third
midcourse
correction
Transearth
injection
after CSM/LM(asc.)
rejoin
Spacecraft
Rocket stage
Lunar orbit -
descent and landing
by LM
Lunar orbit
insertion
by spacecraft
Rocket stag
into
solar
orbit
Moon at launch

Moon Shot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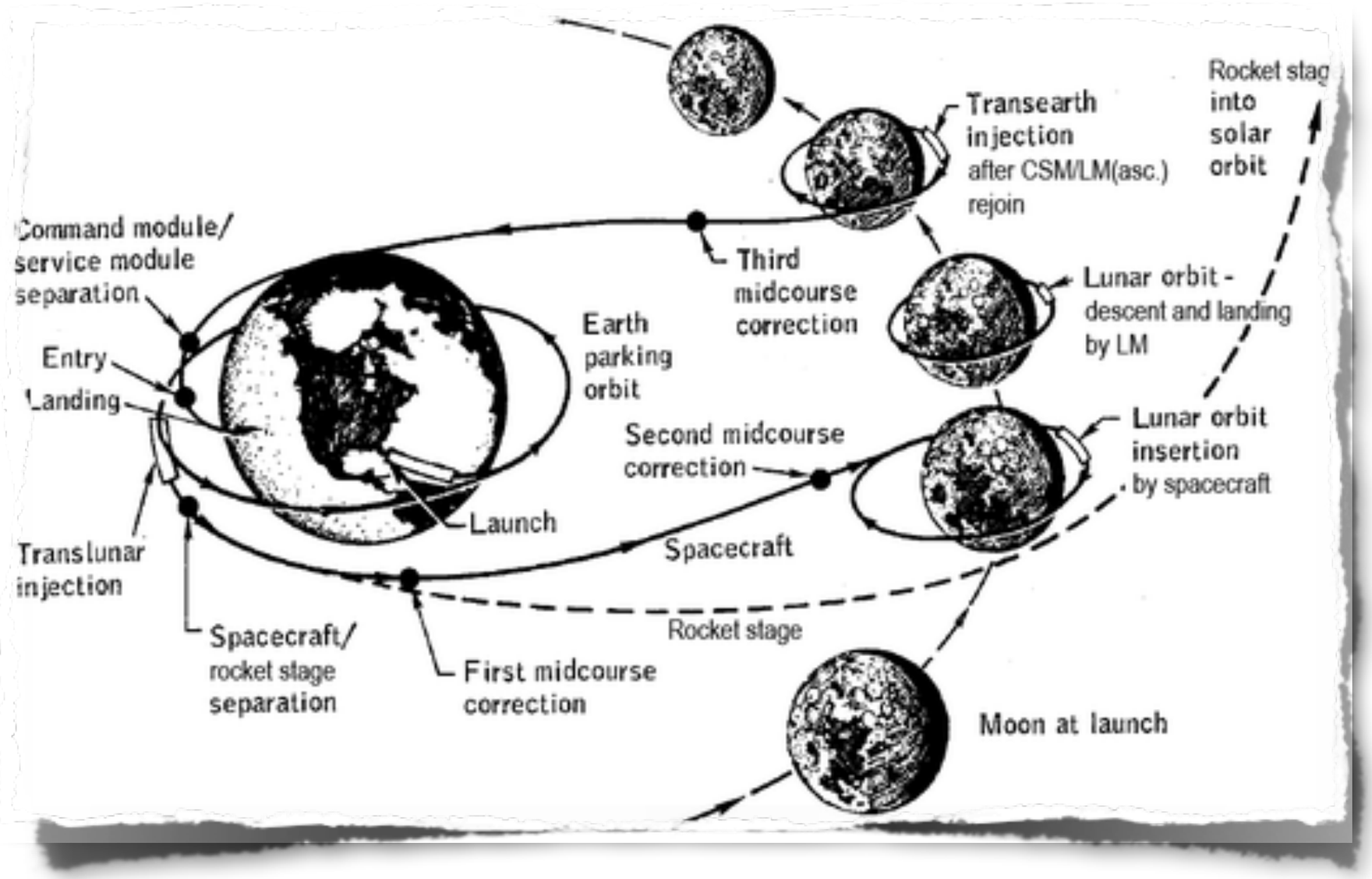
Moon Shot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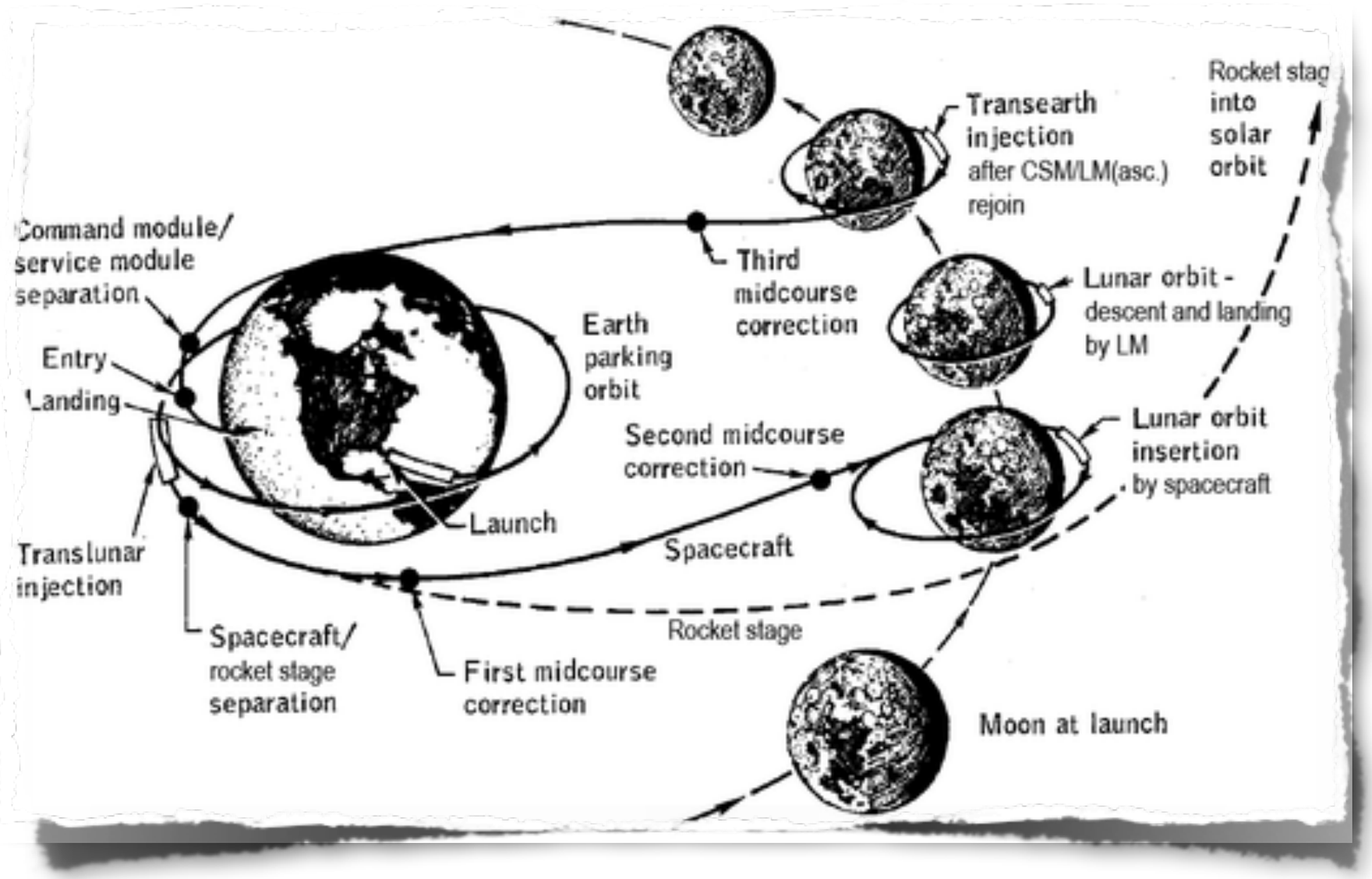
Moon Shot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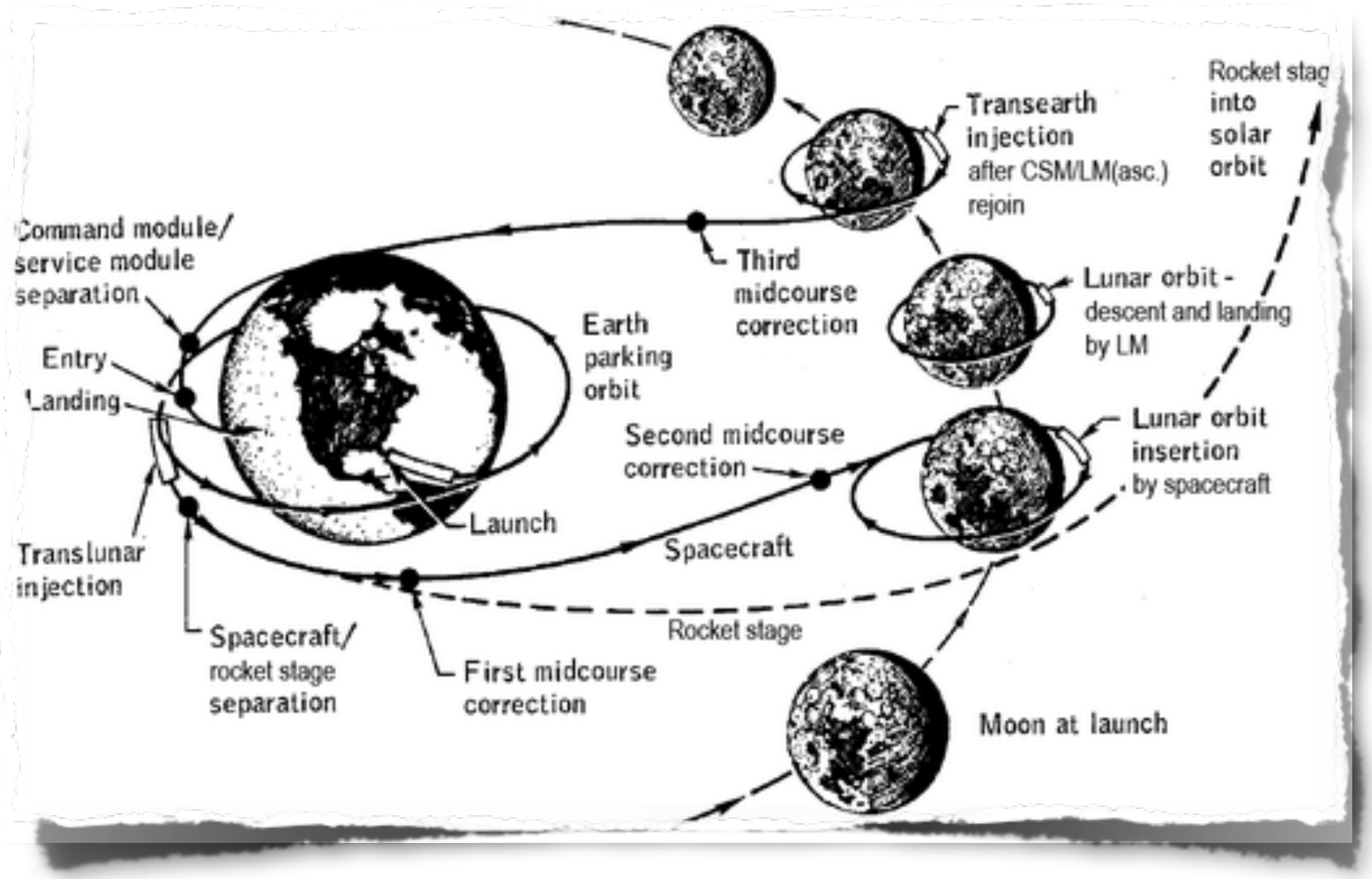
Moon Shot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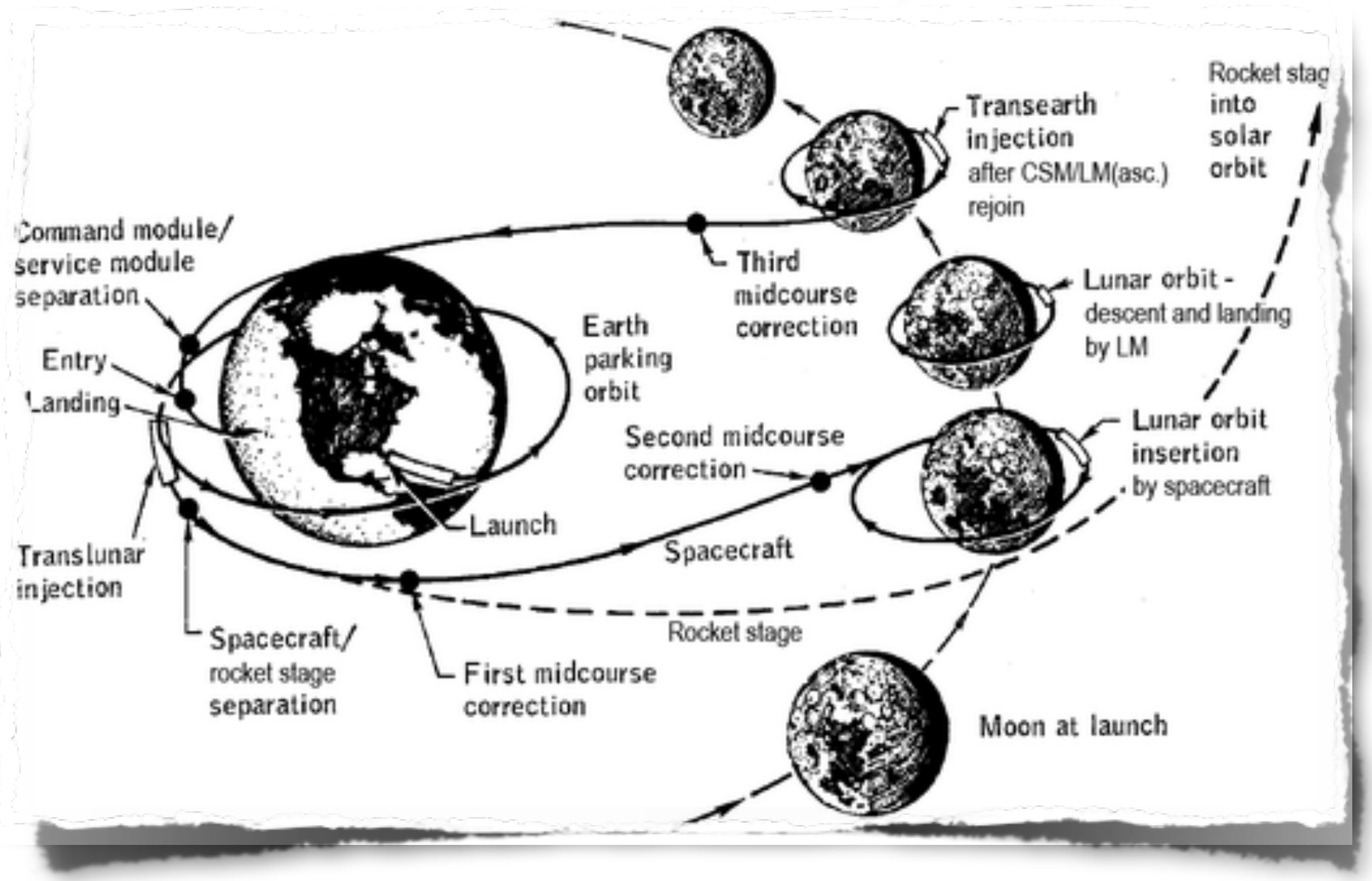
Moon Shot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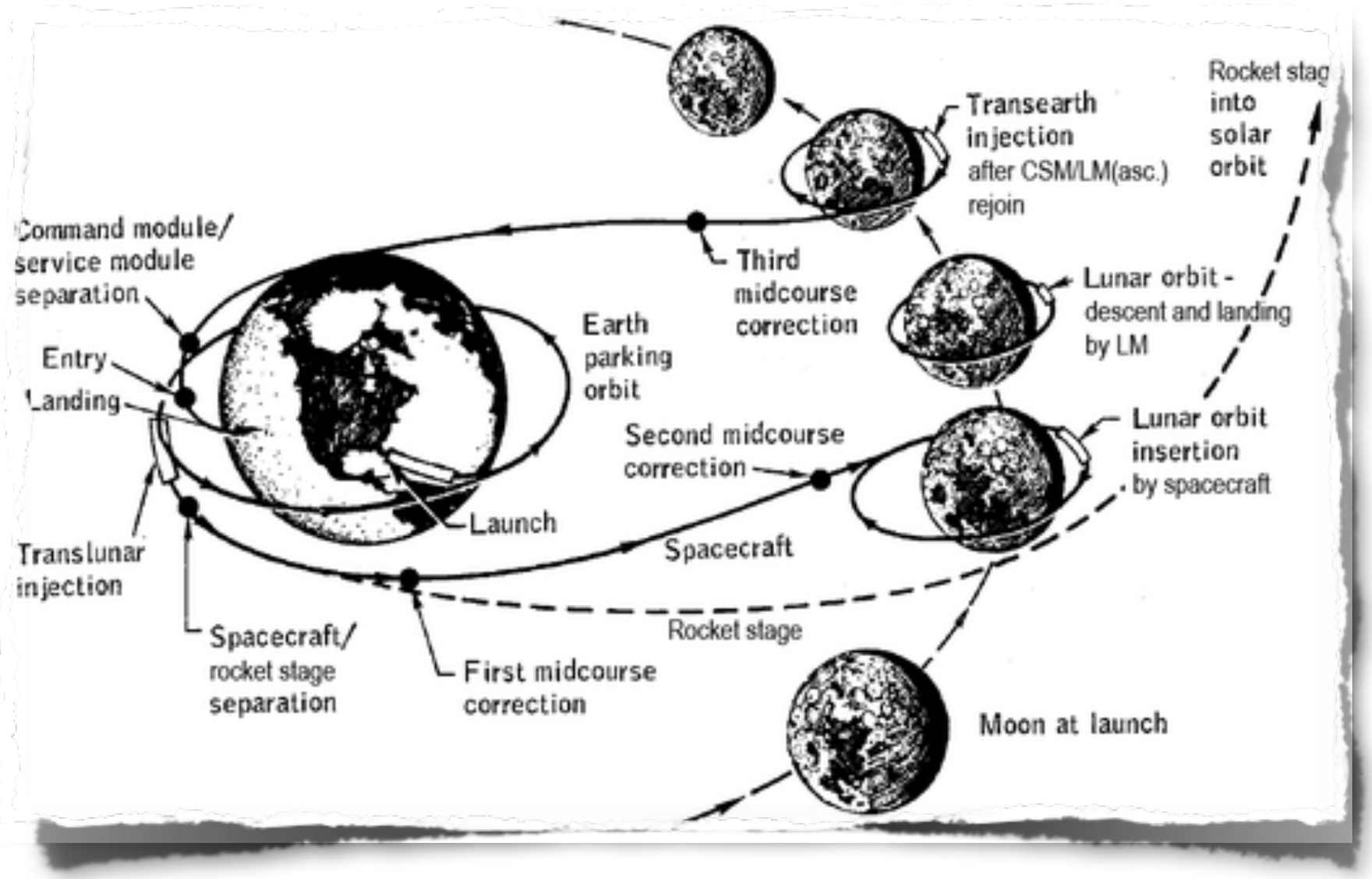
Moon Shot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Lunar orbit
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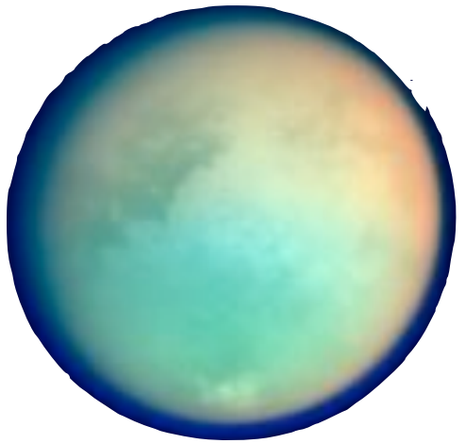
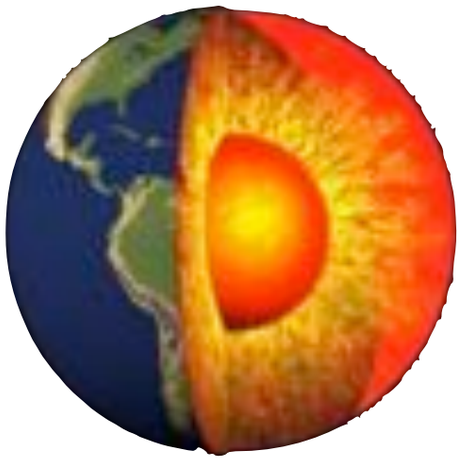
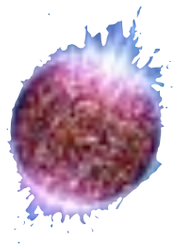
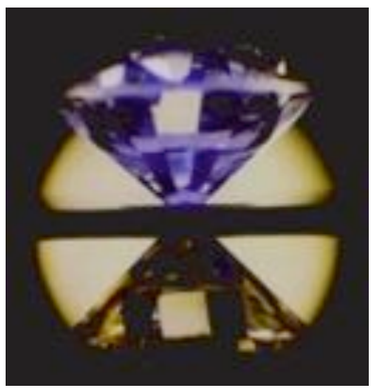
Spacecraft
Rocket stage
Moon at launch

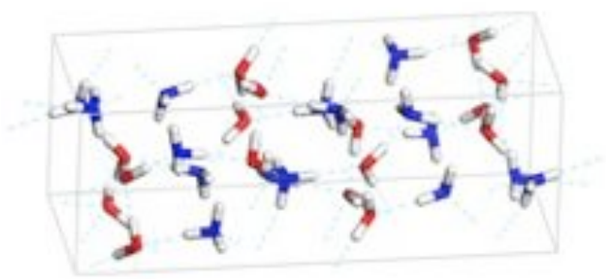
Condensed matter!

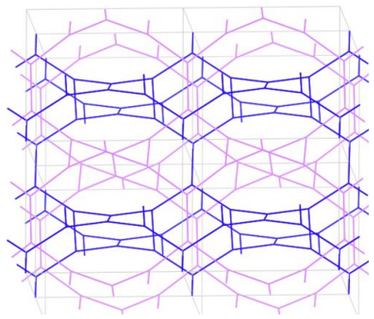








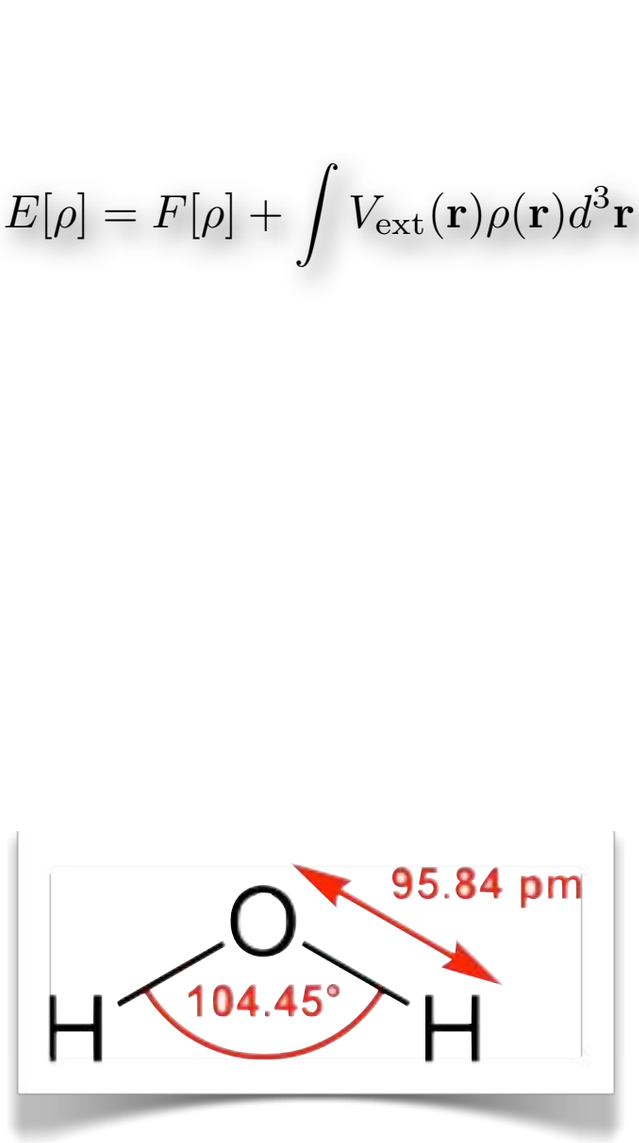




?

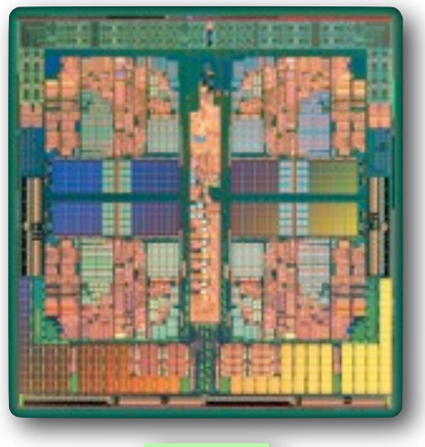
Theory

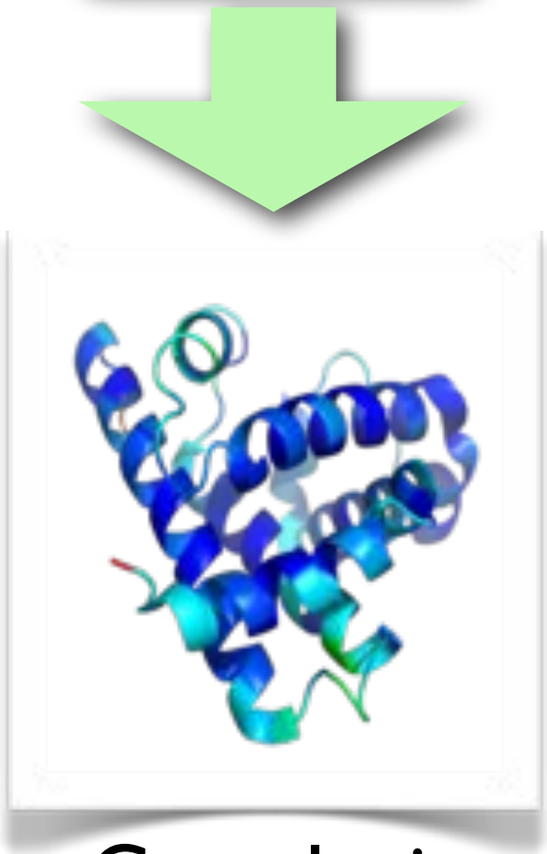
$$E[\rho] = F[\rho] + \int V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d^3\mathbf{r}$$



Precision

Computation

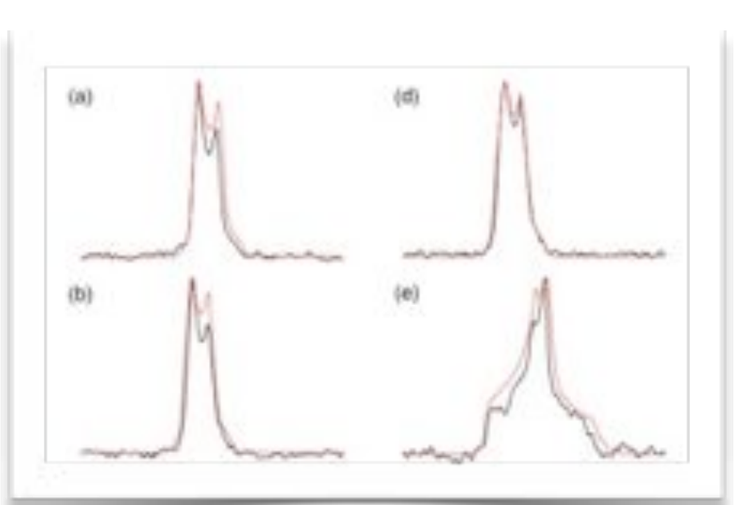




Complexity

Software

ion_atom.F90



Properties

Computers

4

12

5,680

90,112

705,024

A real challenge

Many small calculations

```
top - 11:05:21 up 134 days, 22:42,  2 users,  load average: 8.17, 8.30, 8.20
Tasks: 412 total,   9 running, 403 sleeping,   0 stopped,   0 zombie
Cpu(s): 98.7%us,  1.0%sy,  0.0%ni,  0.0%id,  0.0%wa,  0.0%hi,  0.3%si,  0.0%st
Mem:  16443812k total, 15781456k used,   662356k free,  1897328k buffers
Swap: 52428116k total,      196k used, 52427920k free,  9785668k cached

  PID USER      PR  NI  VIRT  RES  SHR S %CPU %MEM    TIME+  COMMAND
30546 cjp       25   0  200m 107m 6444 R 100.2  0.7   6:42.44 castep-serial
30618 cjp       25   0  219m 125m 5632 R 100.2  0.8   1:44.42 castep-serial
30941 cjp       25   0  175m  81m 5620 R 100.2  0.5   0:54.65 castep-serial
30584 cjp       25   0  203m 110m 6496 R 99.9  0.7   6:25.01 castep-serial
30779 cjp       25   0  201m 107m 5680 R 99.9  0.7   2:08.21 castep-serial
30653 cjp       25   0  235m 141m 6432 R 99.5  0.9   4:03.64 castep-serial
30695 cjp       25   0  181m  87m 5620 R 99.5  0.5   1:24.95 castep-serial
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```
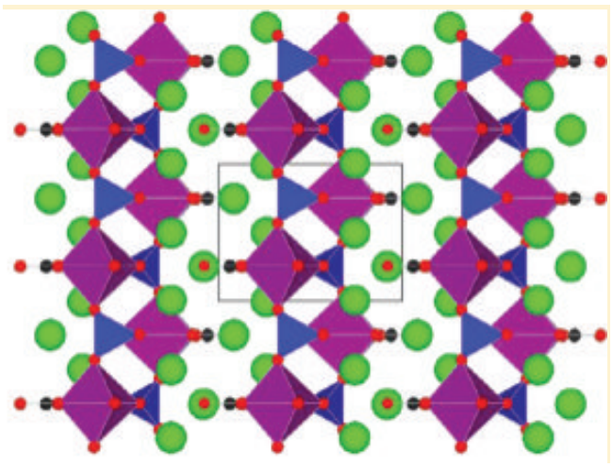

Lots of data

Materials science as search

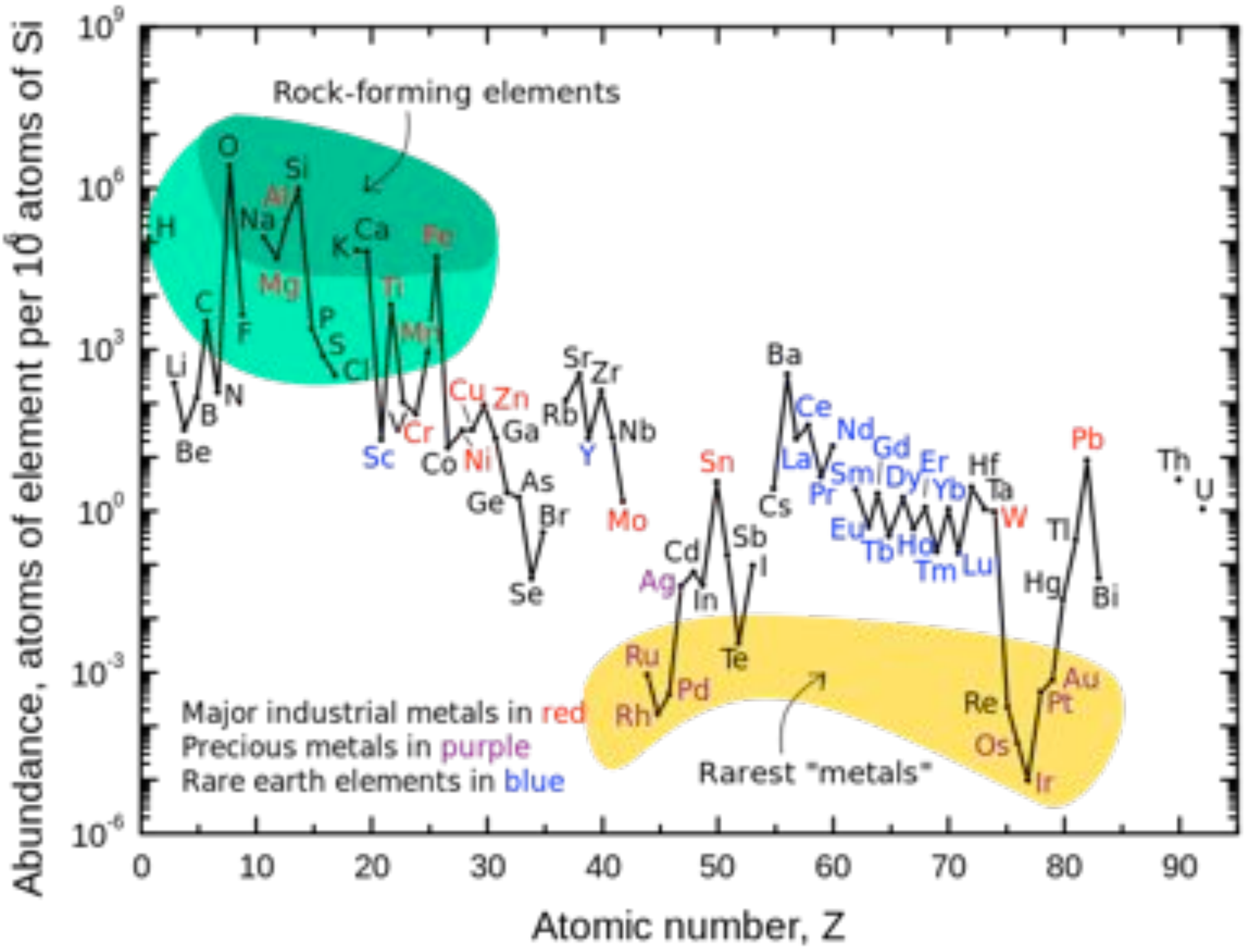


Gerd Ceder's Materials Project, MIT

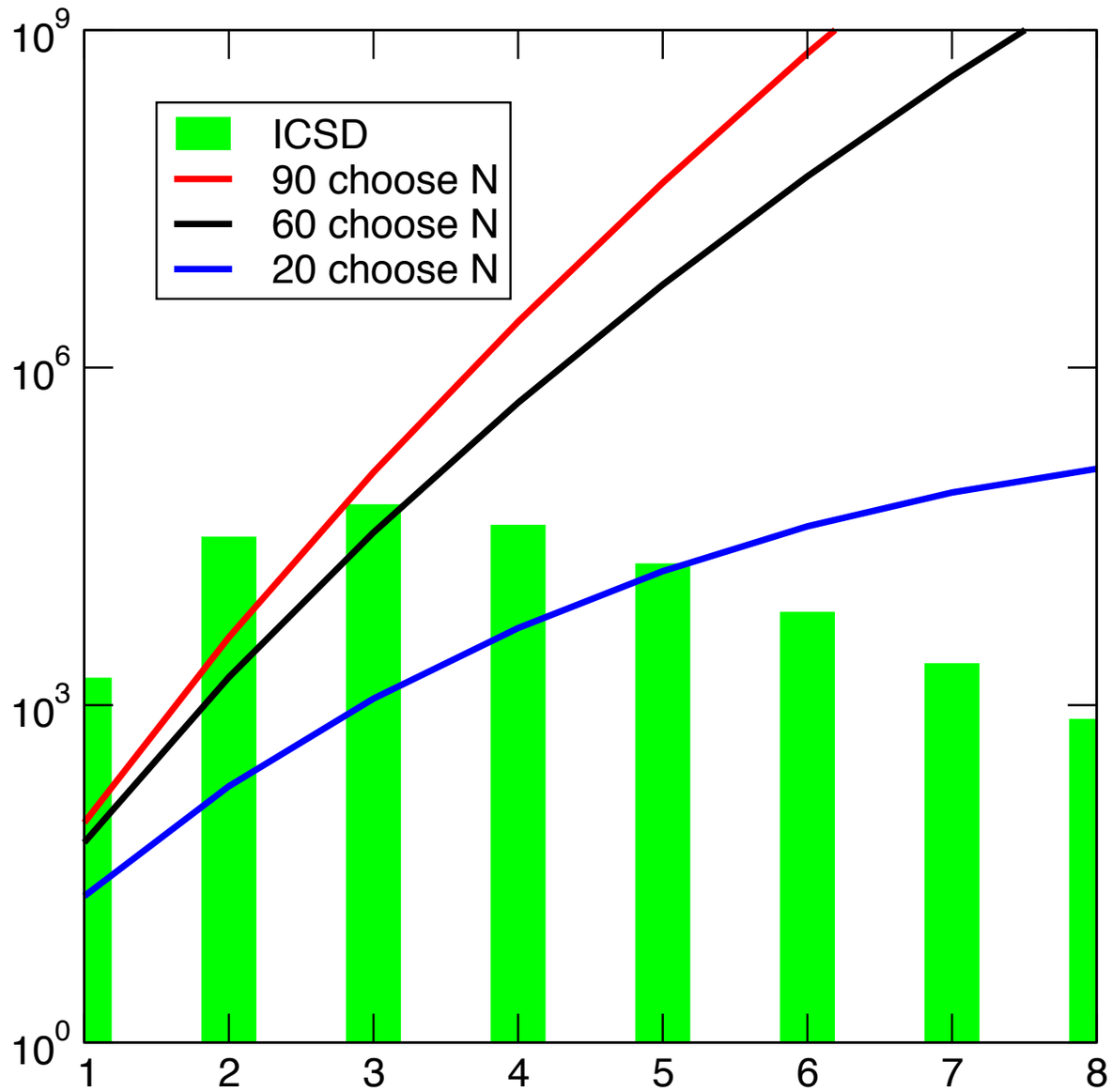
Materials Genome Initiative: A Renaissance of American Manufacturing

$100M to accelerate materials discovery

The elemental palette

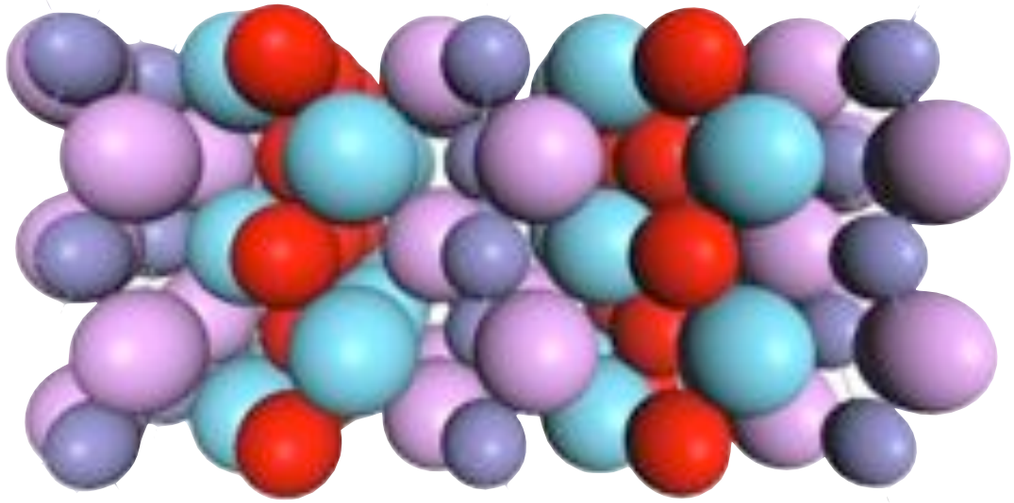


Is the ICSD empty?



A very important problem

What structure will a collection of atoms adopt? What will they do?



Material

Typically answered by experiment

AIRSS

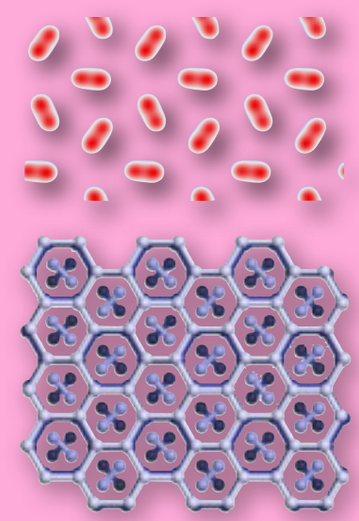
Ab initio random structure searching

Pickard & Needs, PRL 2006 and JPCM 2011

Discovery through virtual experiments

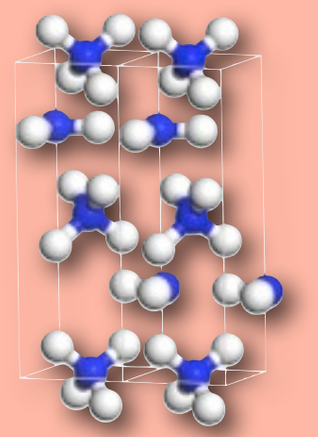
Hydrogen is polar and "graphene"

Nature Physics, 2007



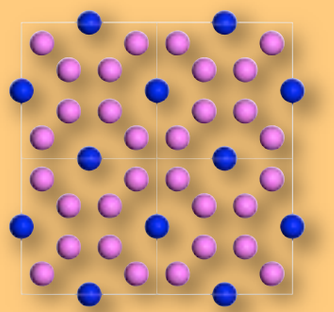
Ammonia is ionic

Nature Materials, 2008



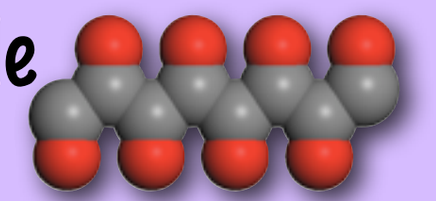
Aluminium is complex

Nature Materials, 2010

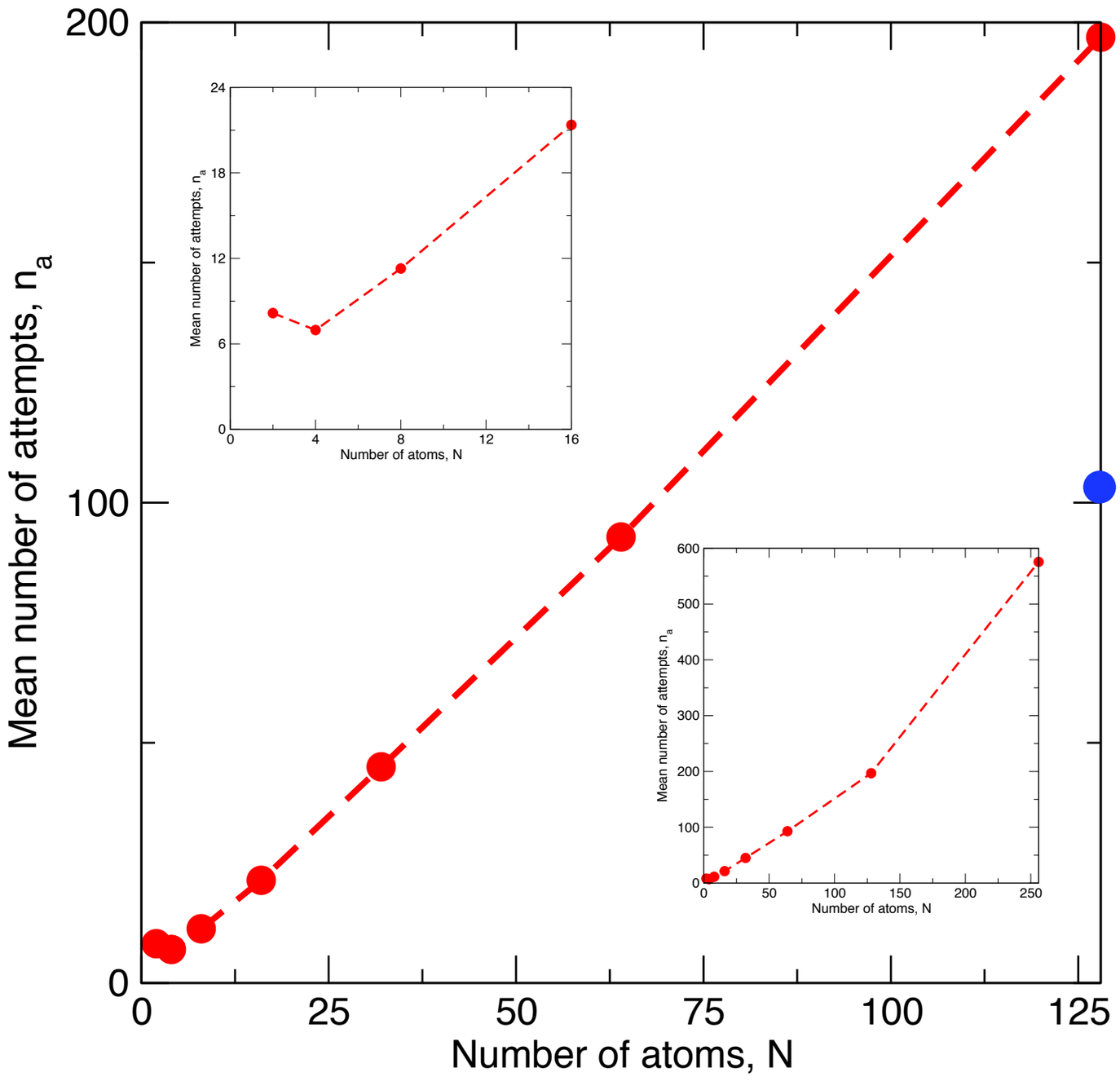


CO is not a molecule

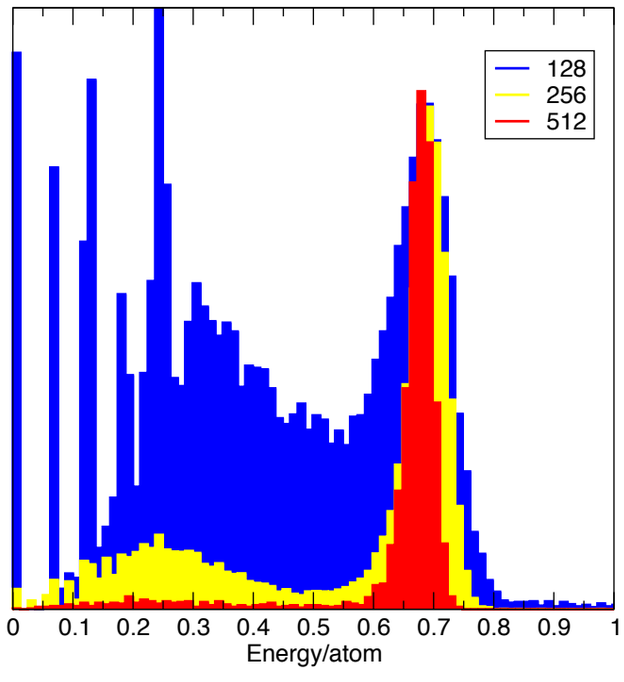
Physical Review Letters, 2011

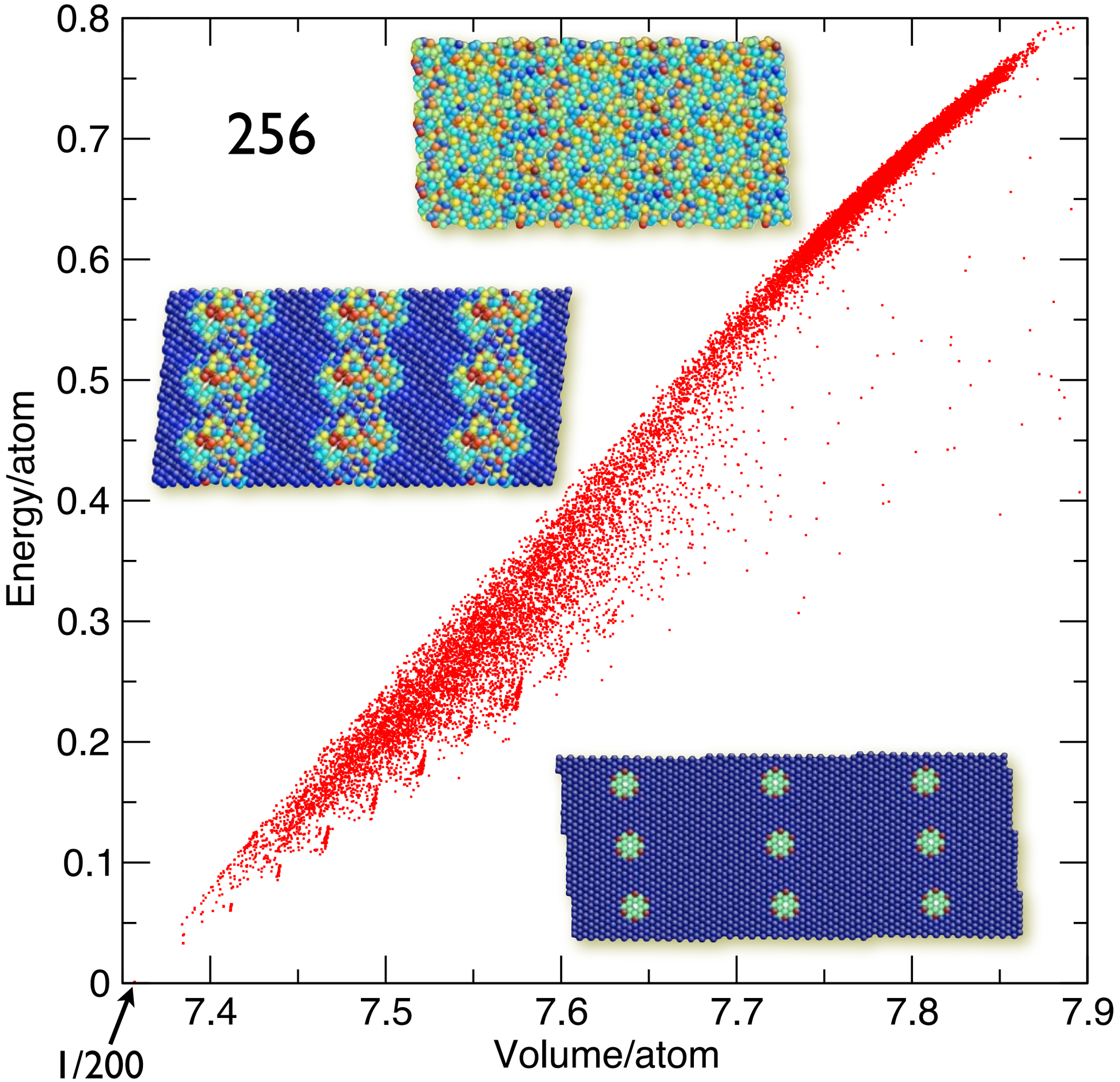


HCP Lennard-Jones Crystal

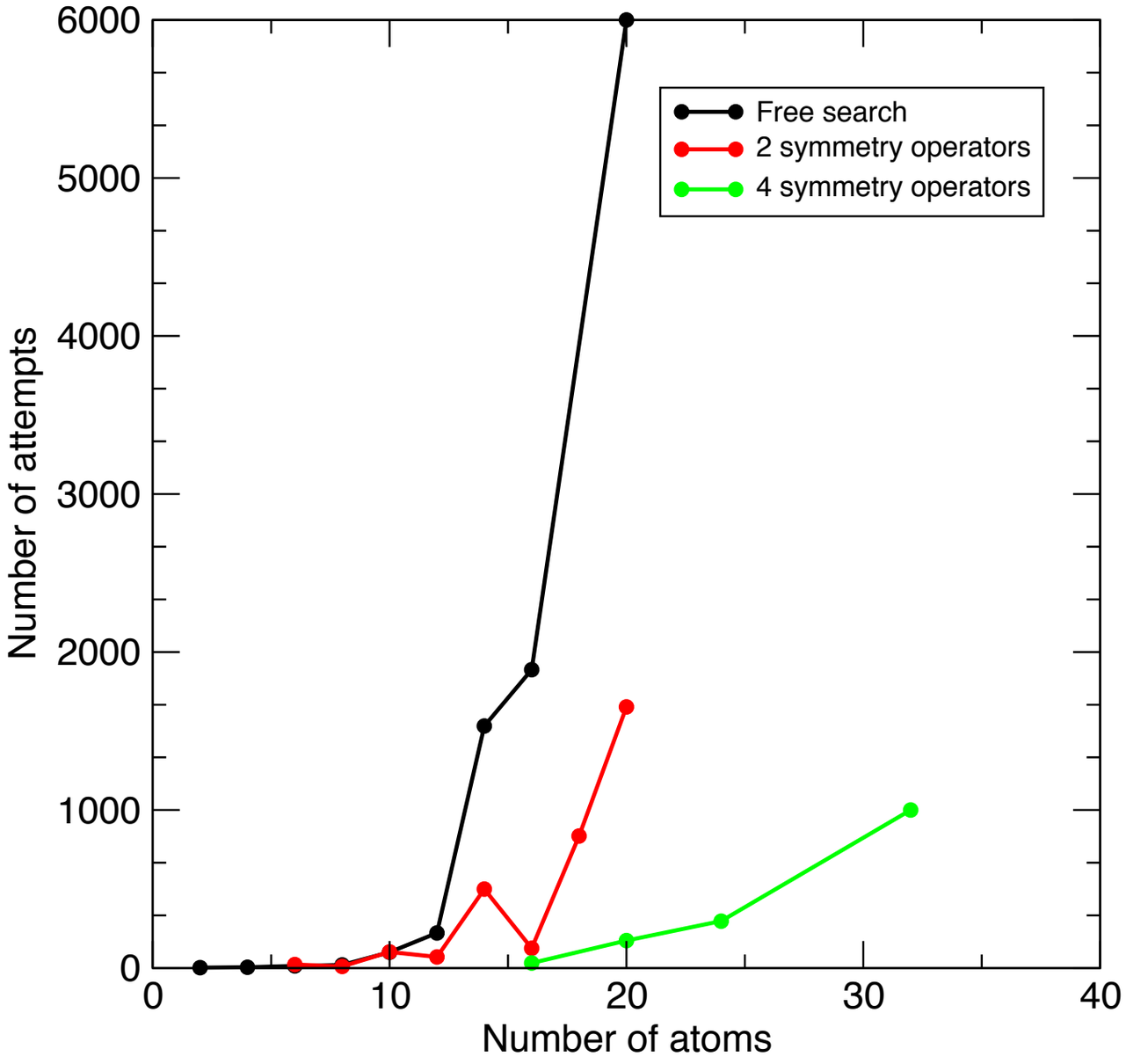


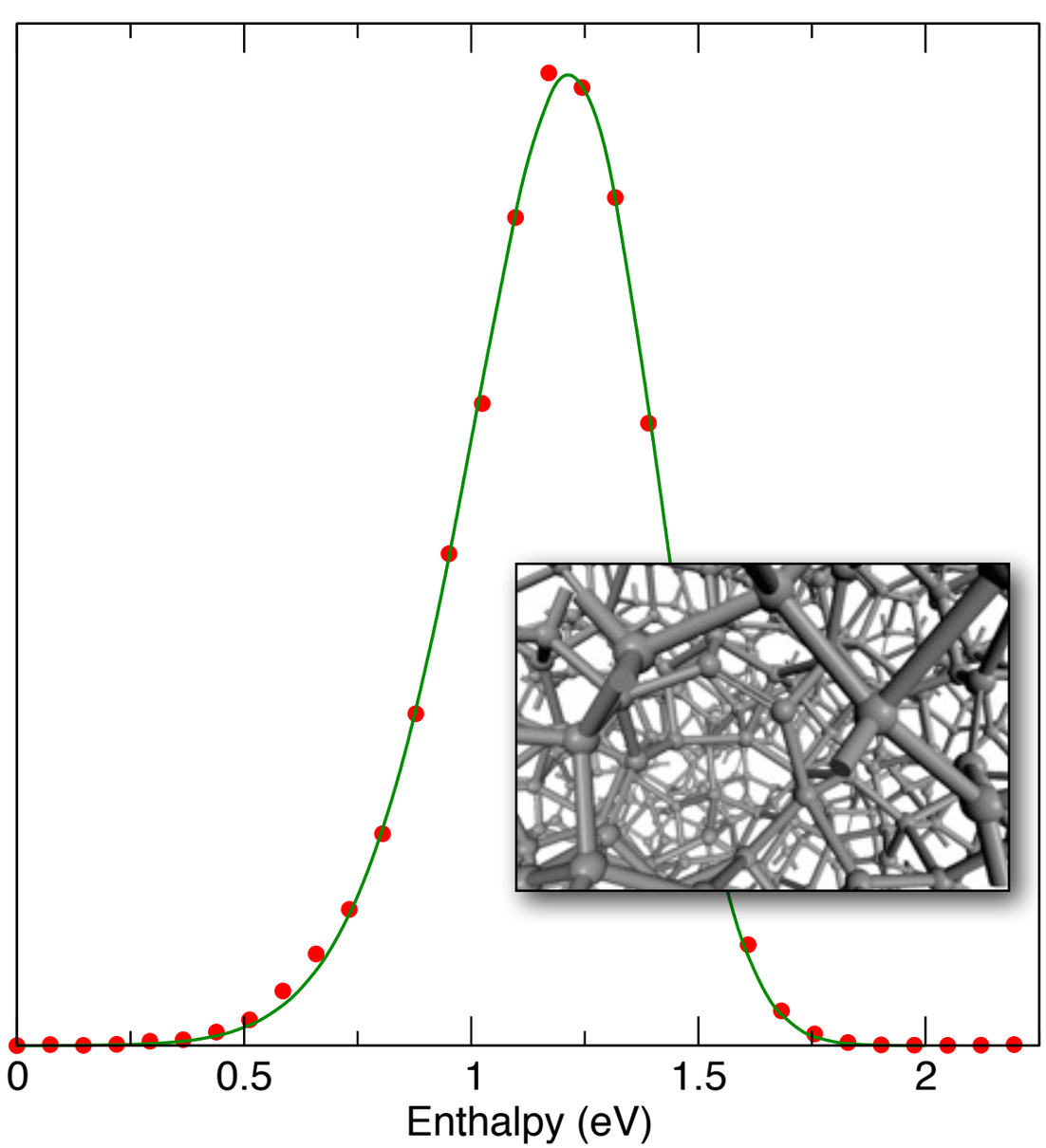
The size of configuration space rapidly increases - but the ground state basin is also growing




256
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Energy/atom
7.4
7.5
7.6
7.7
7.8
7.9
Volume/atom
1/200

A tougher one





20xC@100GPa, 30K structures

Constraints

Hard and soft

Stoichiometry

Symmetry

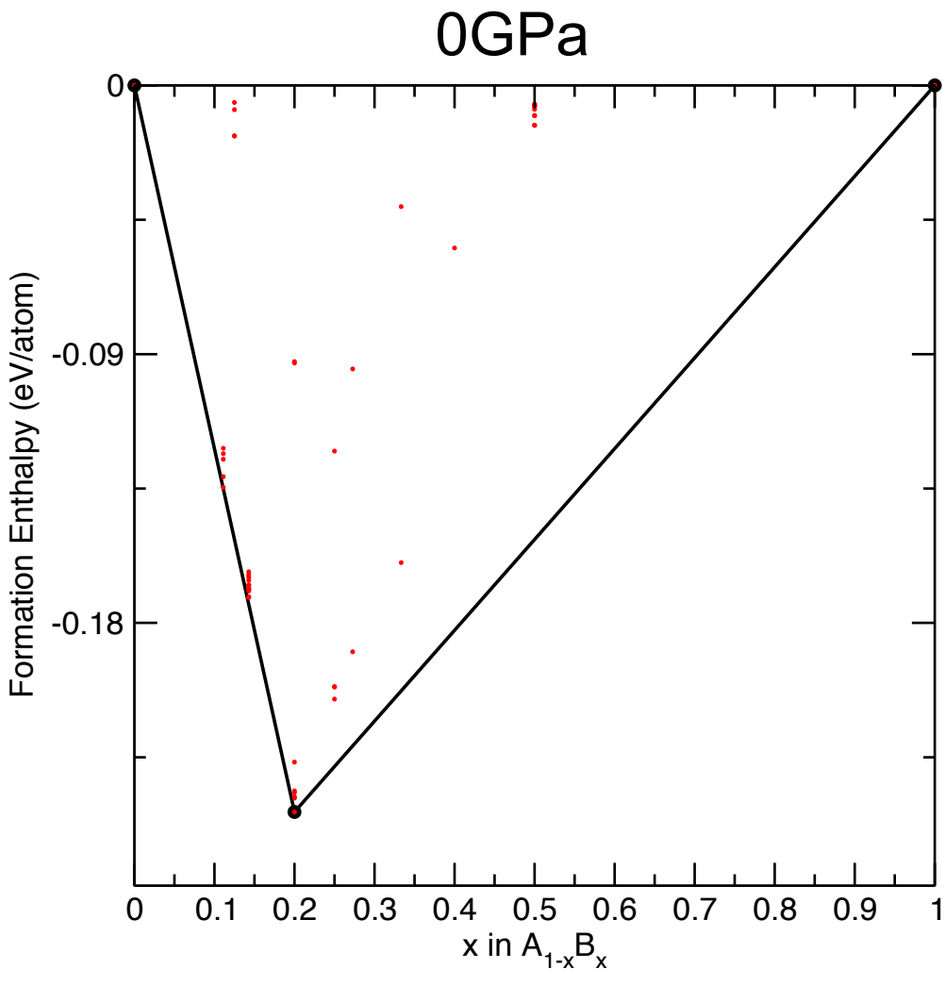
Structural Units

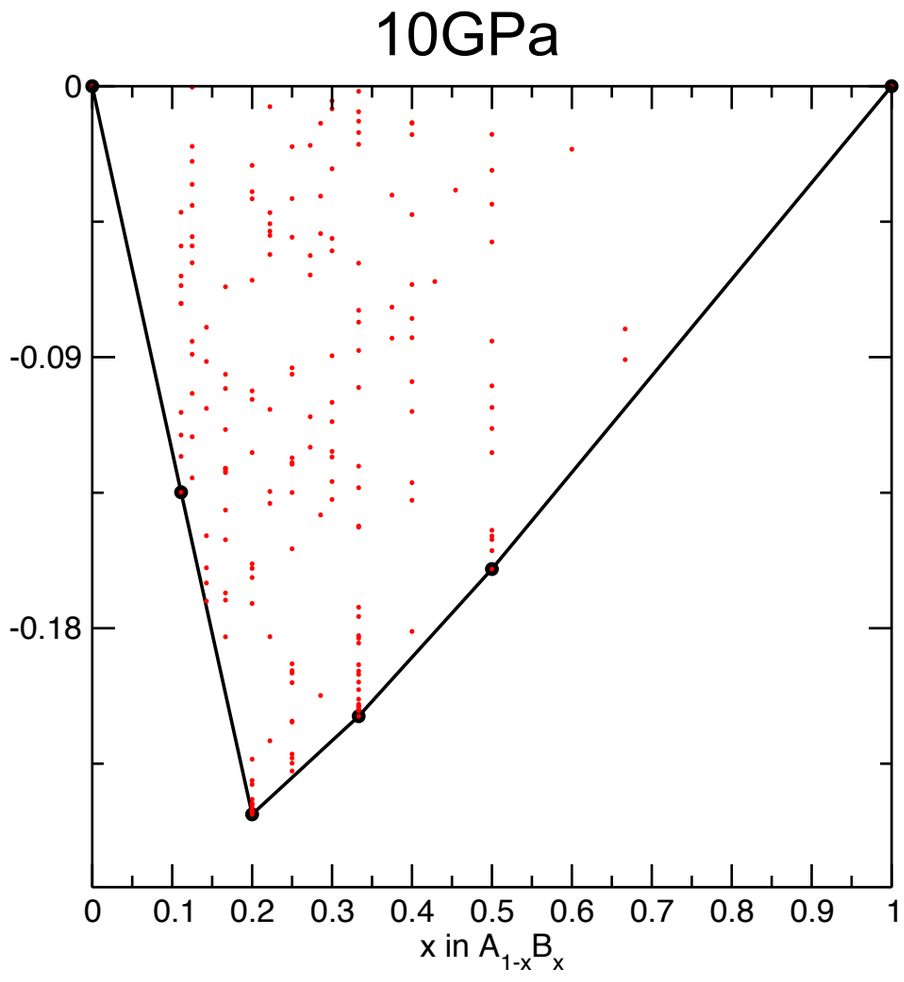
Energy

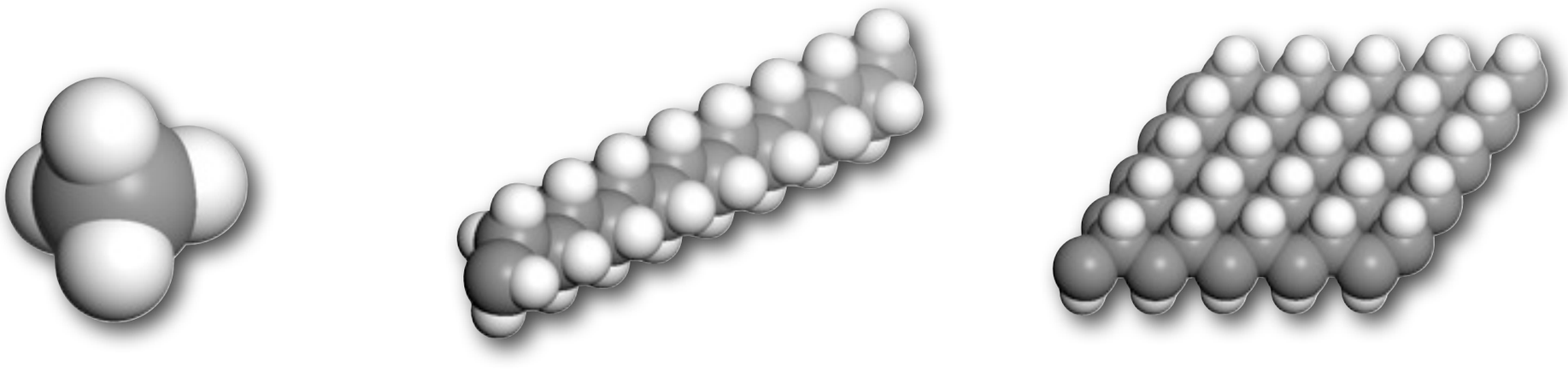
Cell shape

Experiment

Carbon and Hydrogen



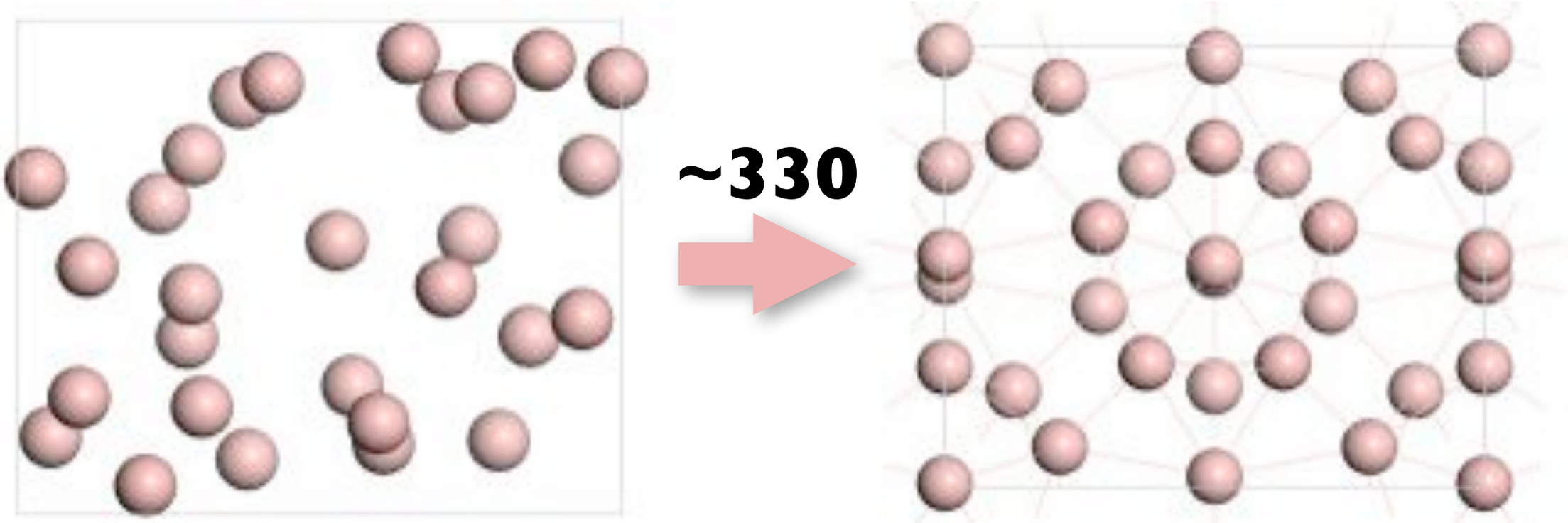




Graphane - Sofo, Jorge O. et al. (2007)

Cell shape

gamma-Boron 28 atoms



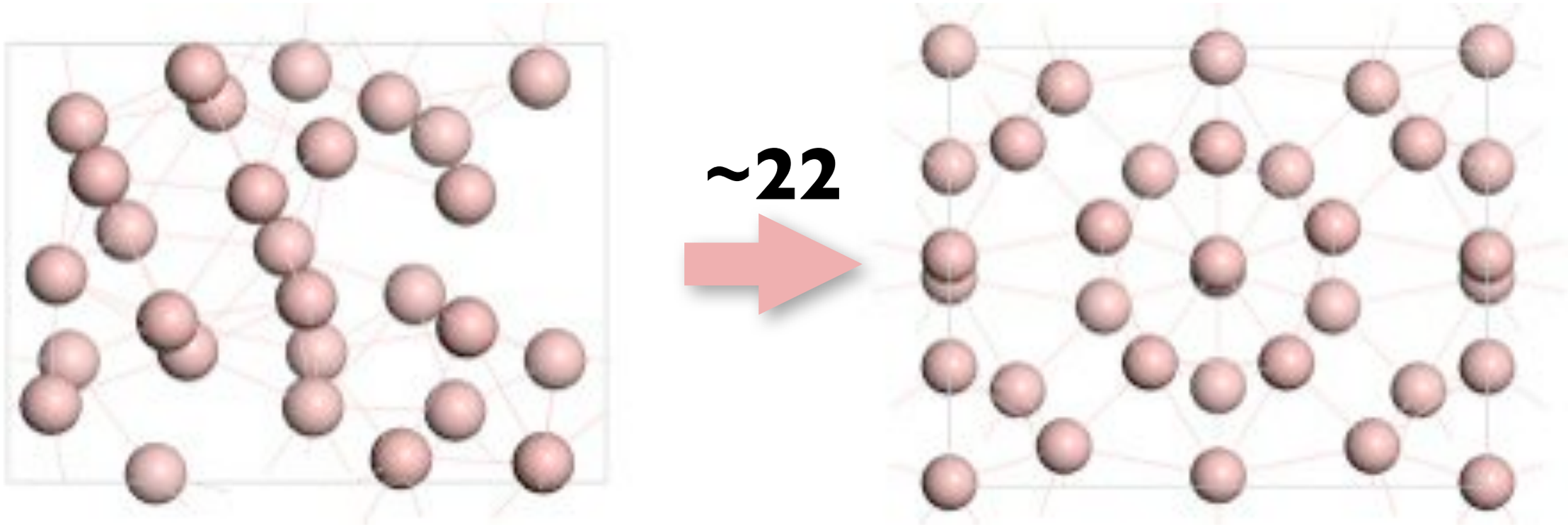
Comparing to EAs

Oganov et al *Nature* 2009 **~550**

Ji, Wang & Ho *PCCP* 2010 **~288**

Units

$2B_{12} + 4B$



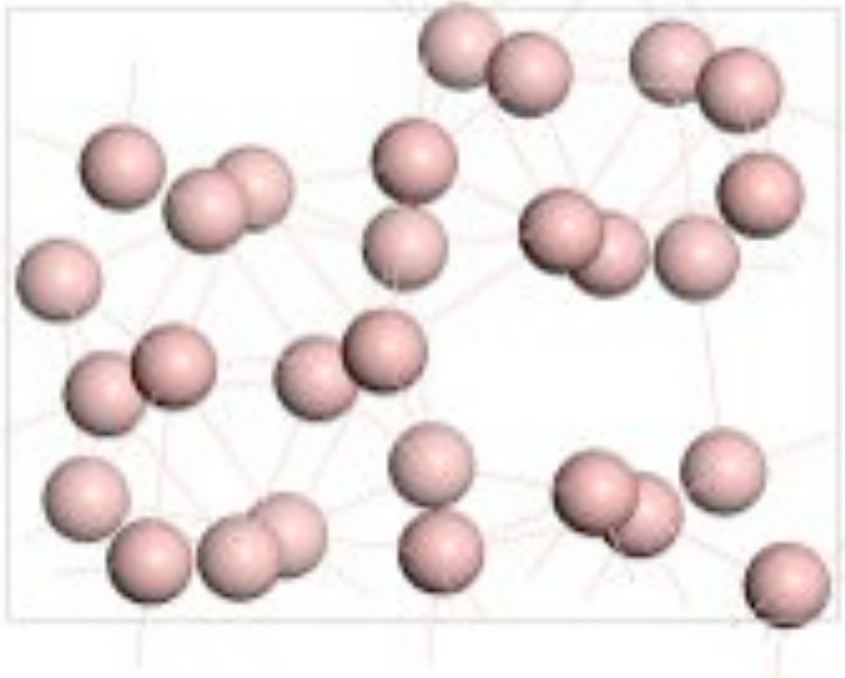
Comparing to EAs

Oganov et al *Nature* 2009 **~550**

Ji, Wang & Ho *PCCP* 2010 **~288**

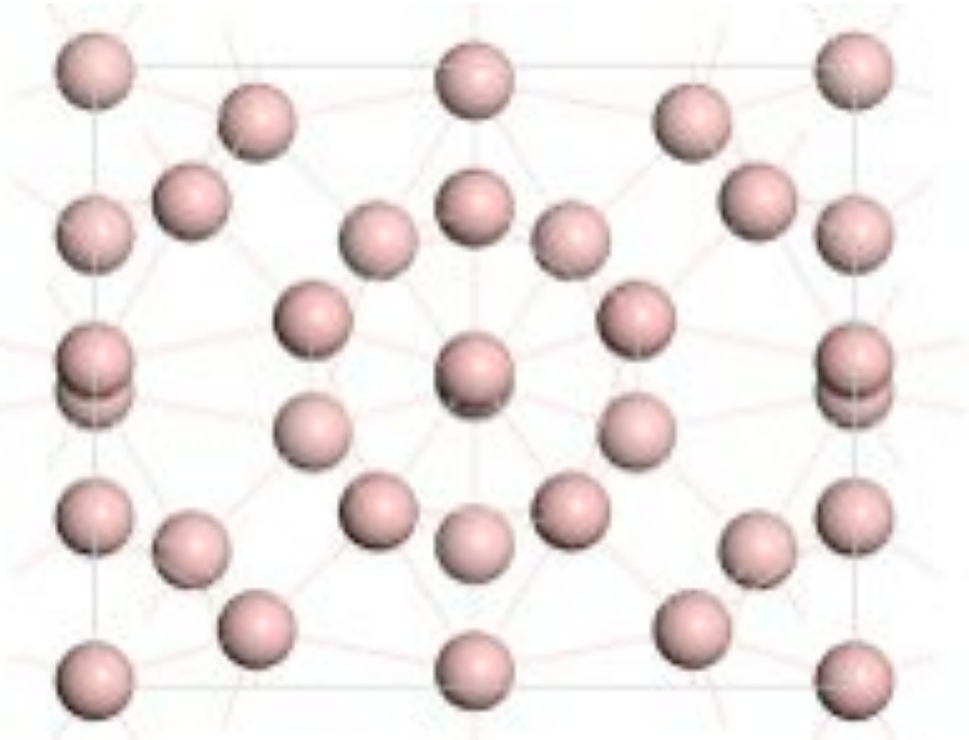
Symmetry

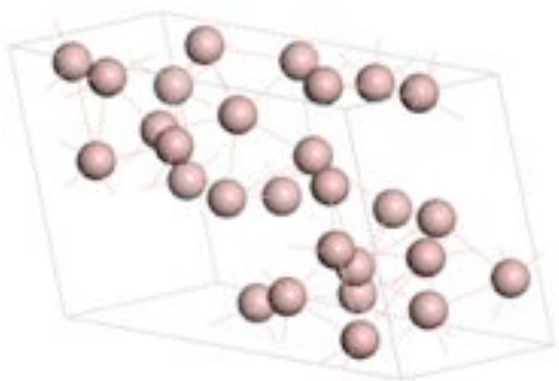
B_{12} + 2B, 2 symm ops



~12

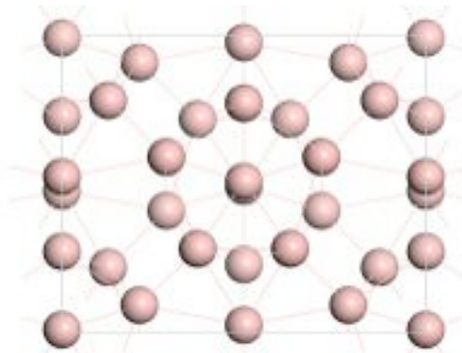
Fixed cell





~108

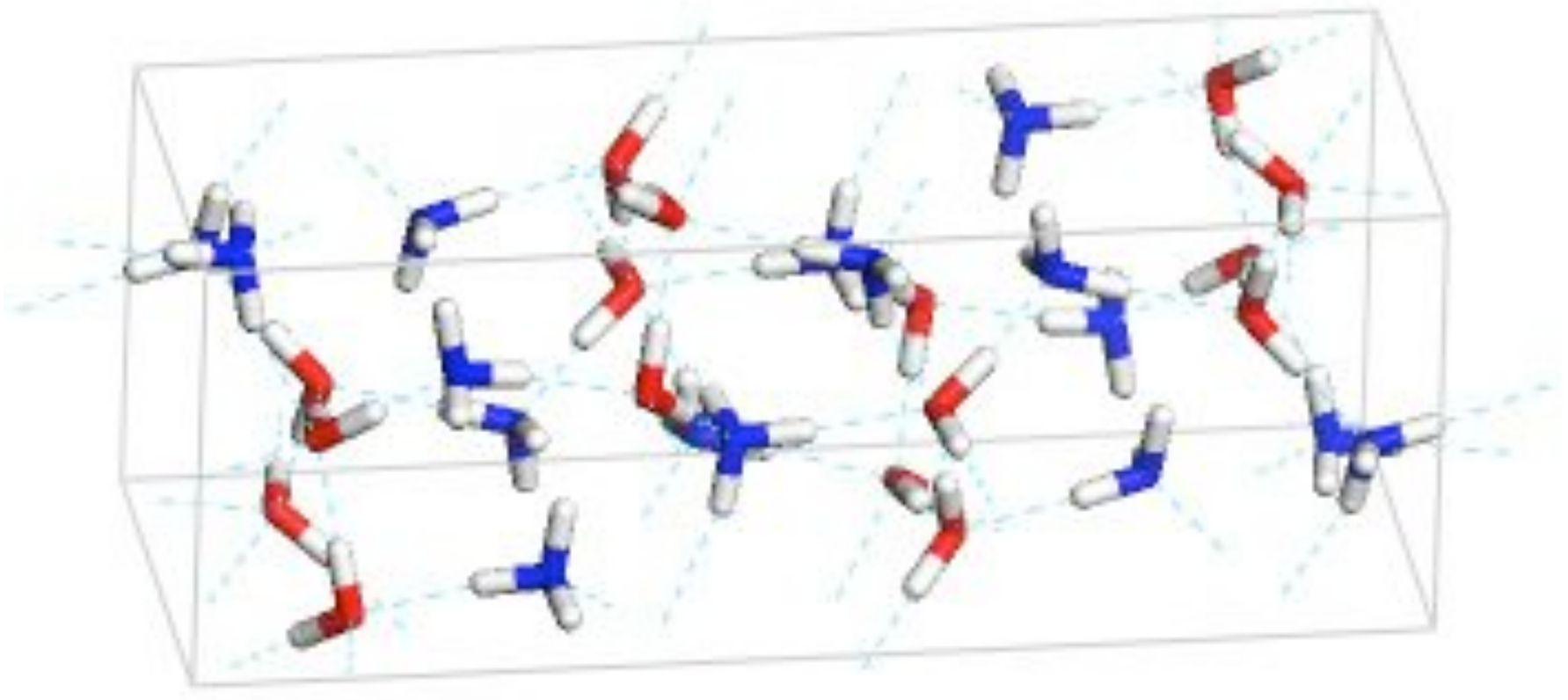
Free cell



Experiment

Ammonia monohydrate

JACS, 2009 with Dom Fortes

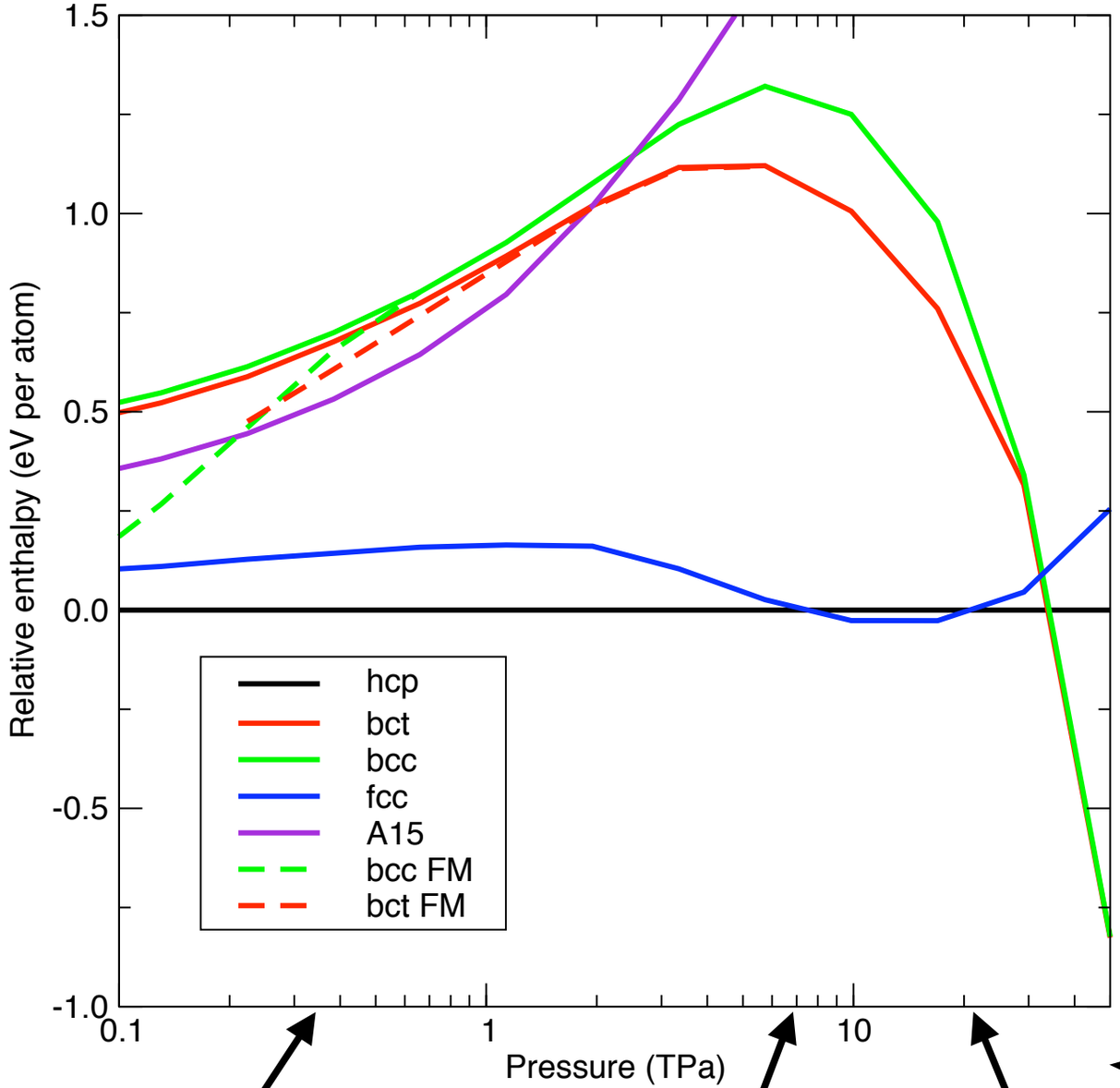


Input lattice parameters and density

Output solved crystal structure containing 112 atoms

"easy experiment, easy theory - new science"

Iron at extremes



You need good PSPs
but DFT should be fine ...

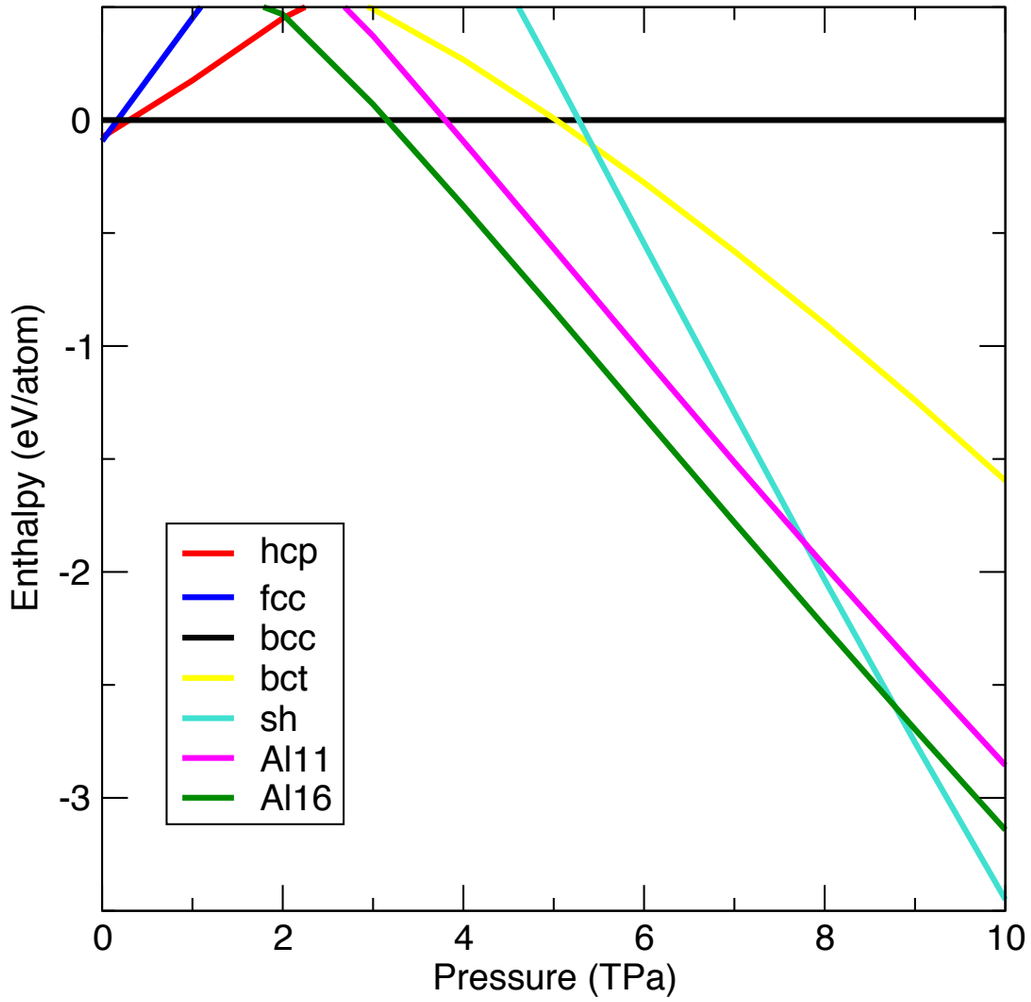
Packing fractions:
fcc/hcp 74.05%
bcc 68.01%

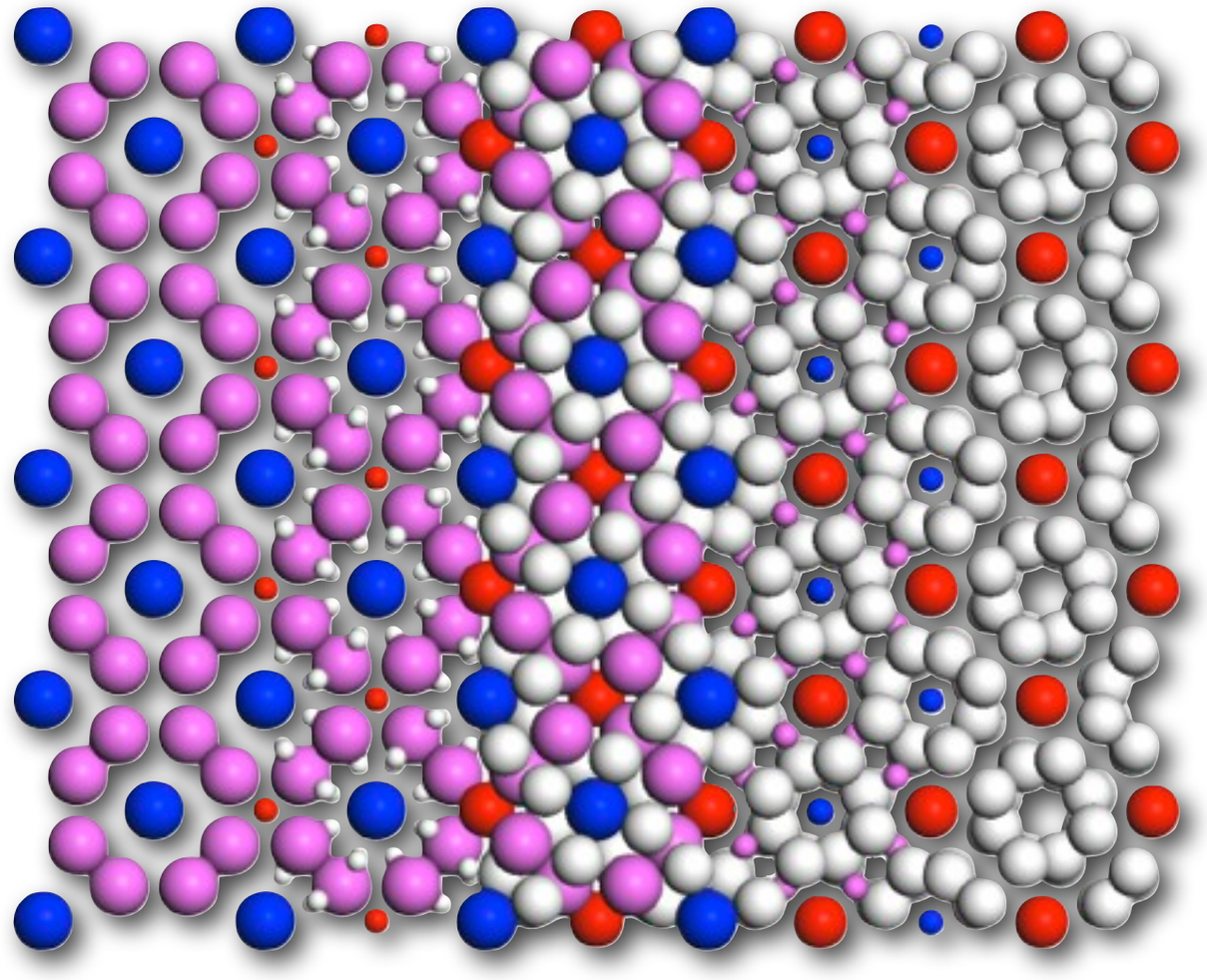
s-d transfer

Earth Jupiter Exoplanets Neutron stars

Pickard & Needs, *JPCM*, 2009

Aluminium at Terapascals



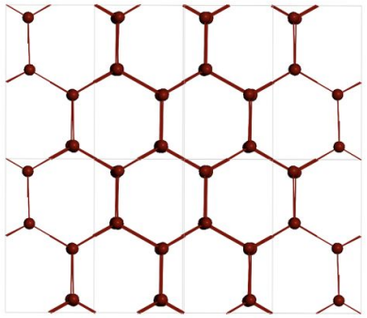


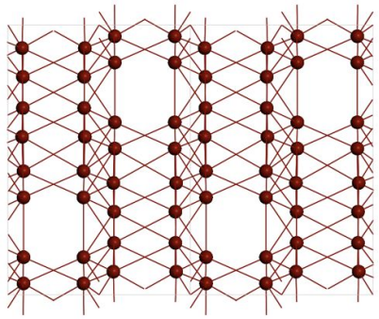
Ba-IV and Rb-IV united

fcc - hcp - bcc - Ba-IV - sh - .....

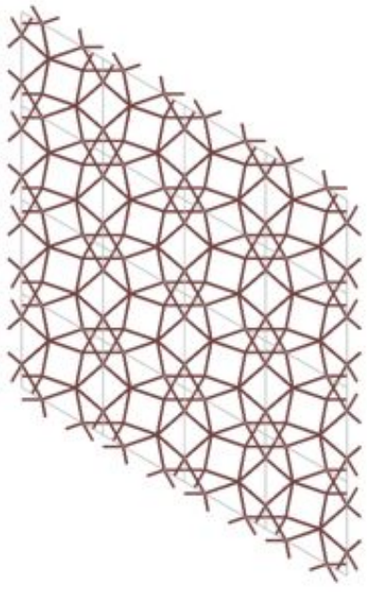
Pickard & Needs, *Nature Materials*, 2010

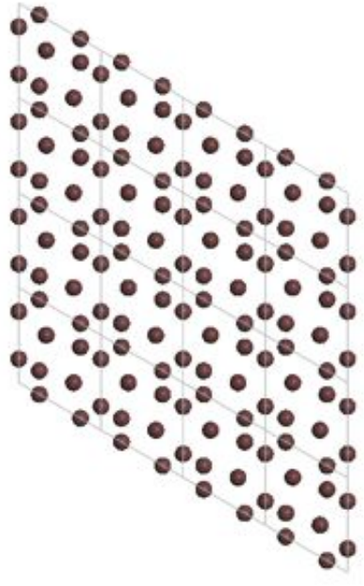
Boron



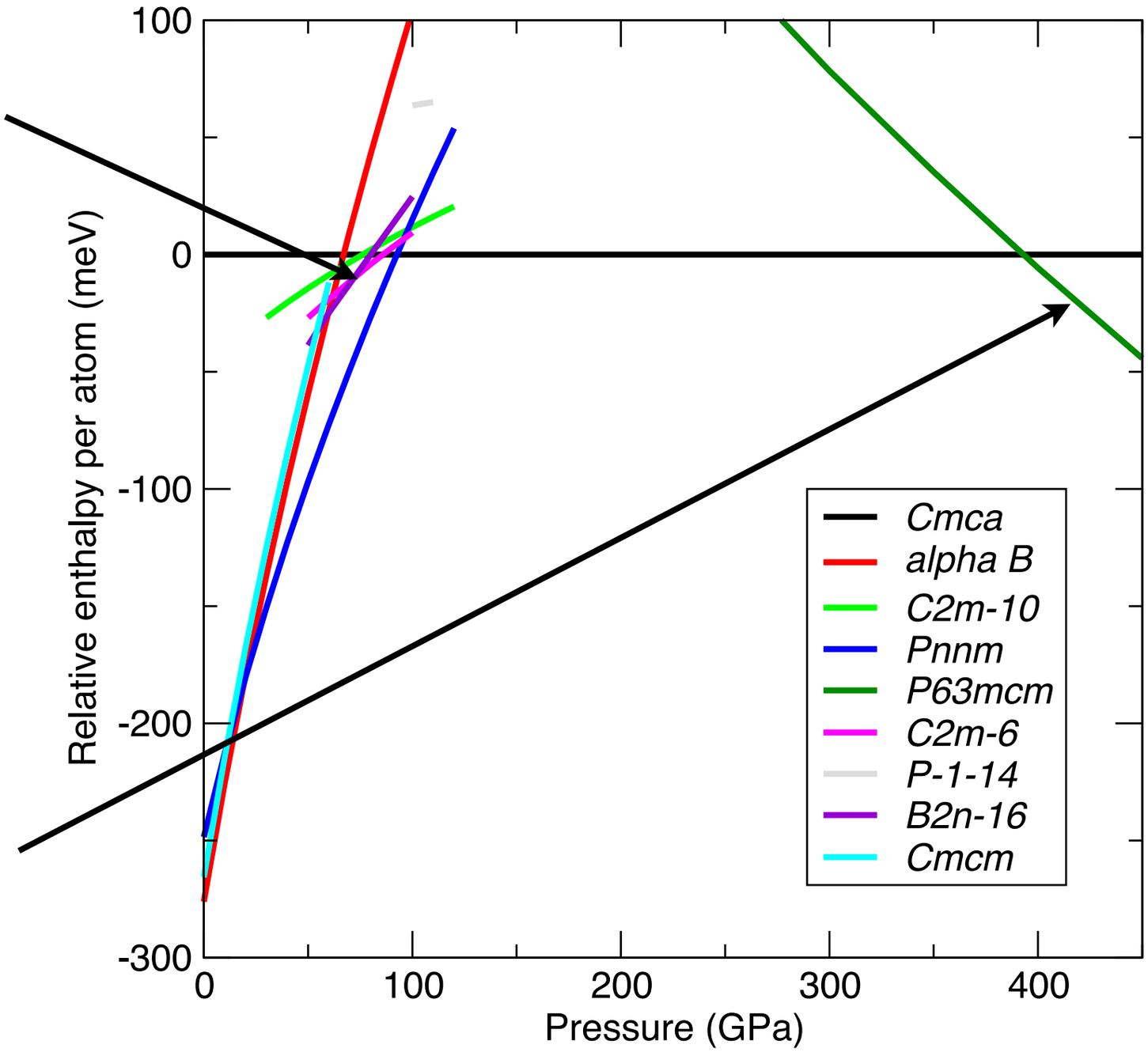


C2/m



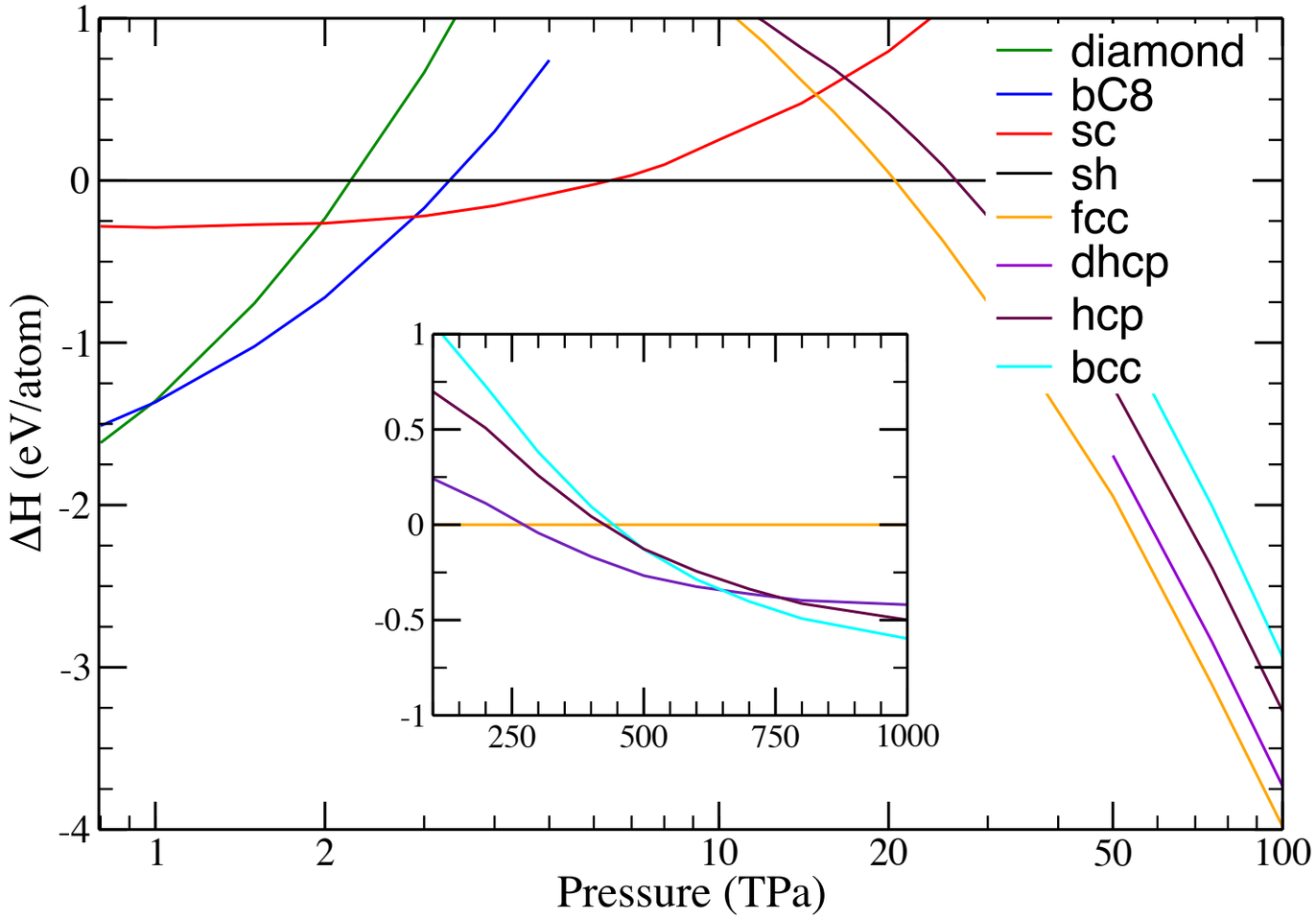


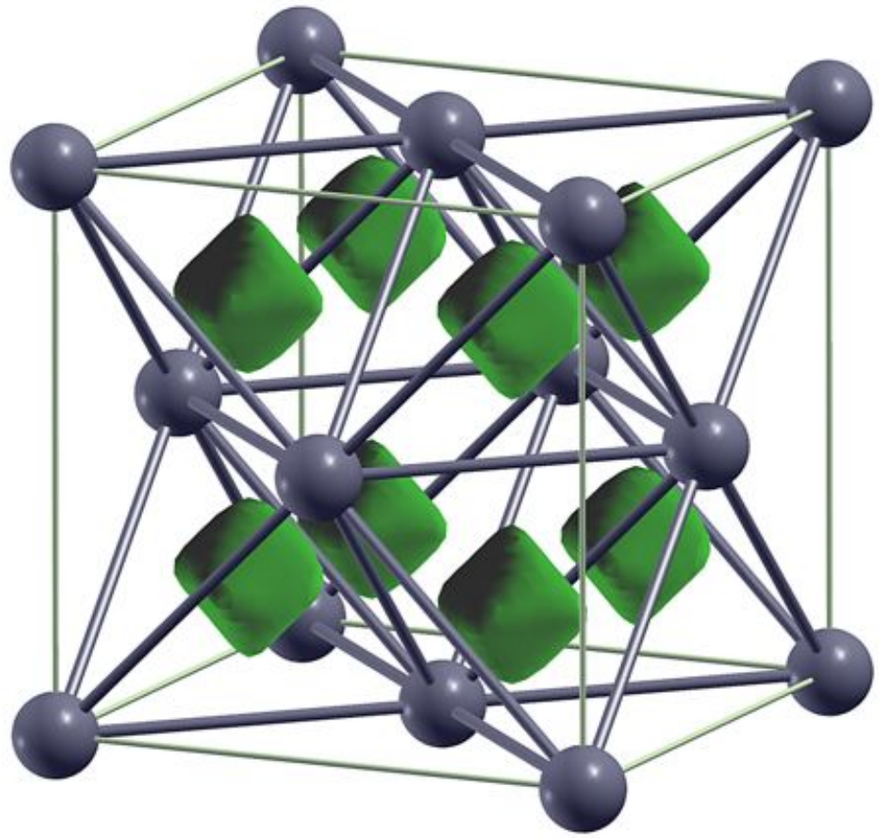
$P6_3/mcm$

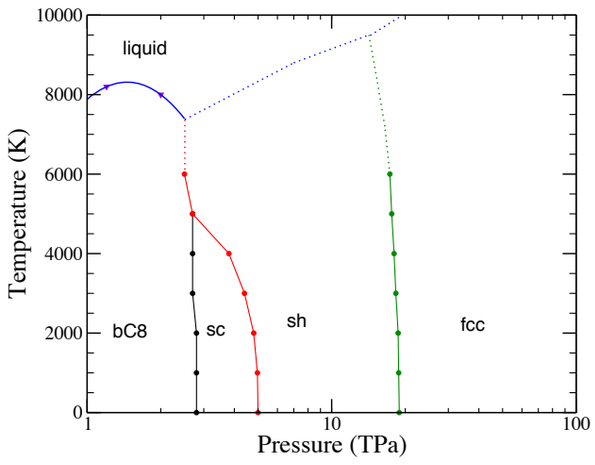


Pickard and Needs, JPCM, 2011

Carbon to PPa



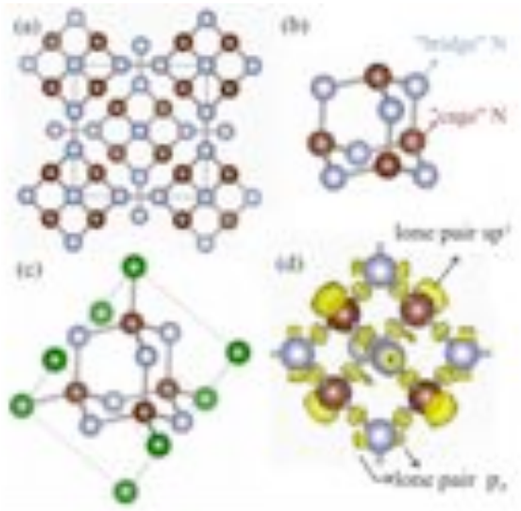




The fcc phase is an electride (CaF_2)

Miguel Martinez, CJP & RJN, *PRL*,2012

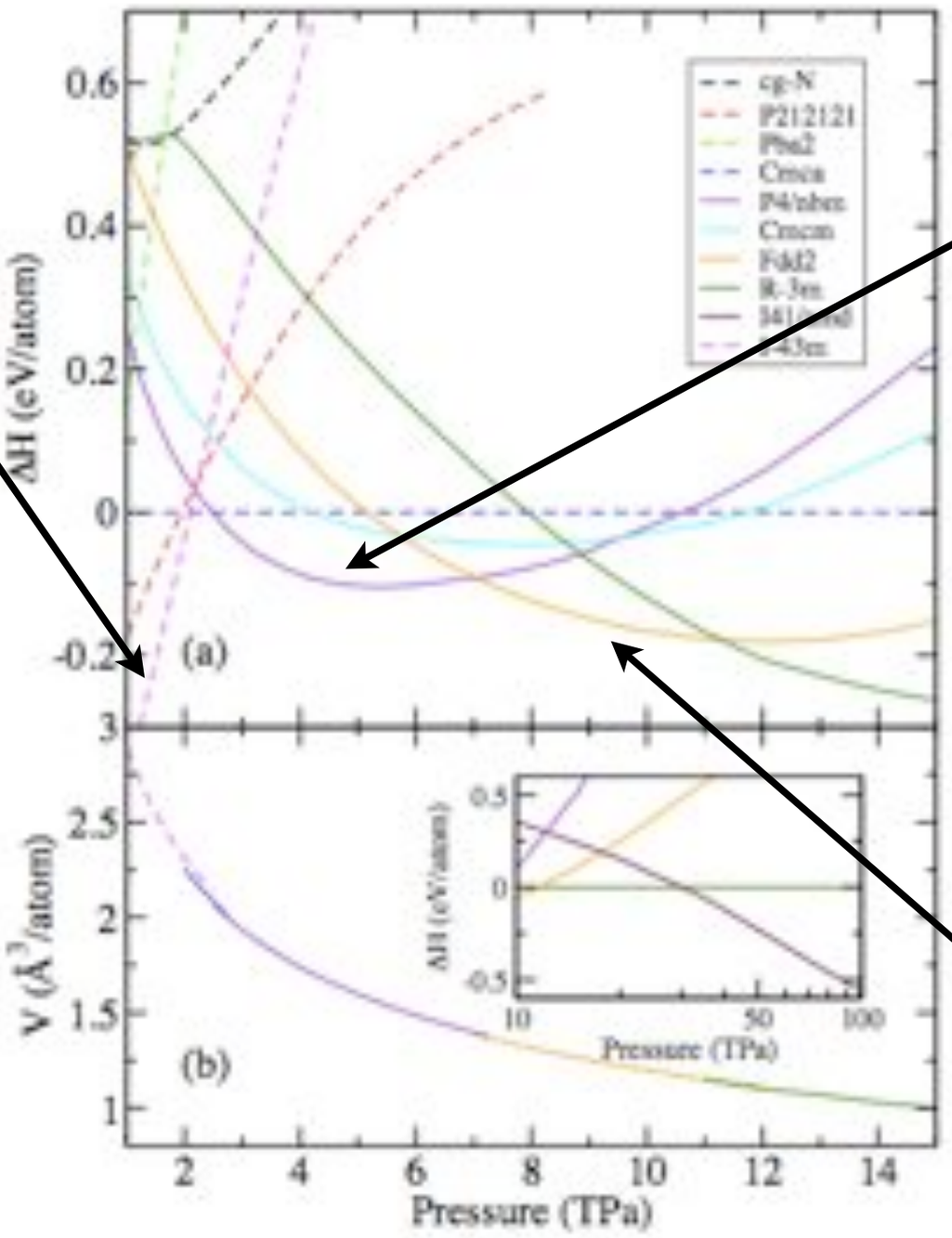
Nitrogen: from cages to salt to waves

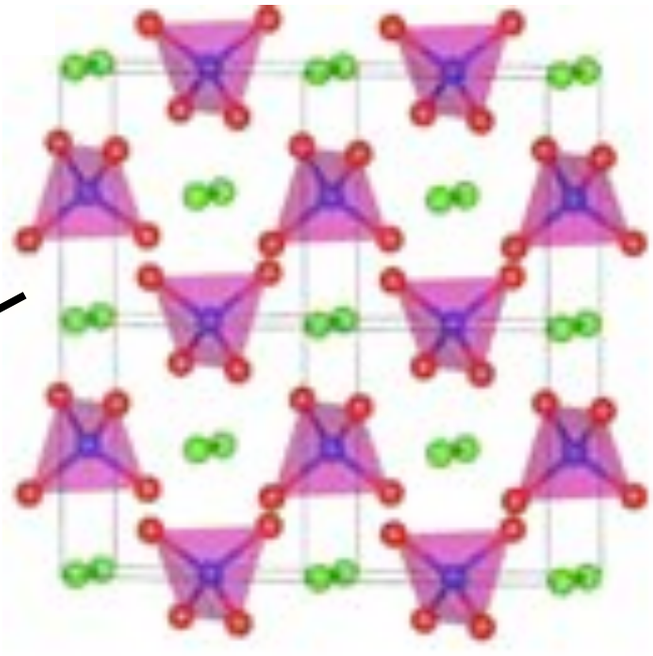


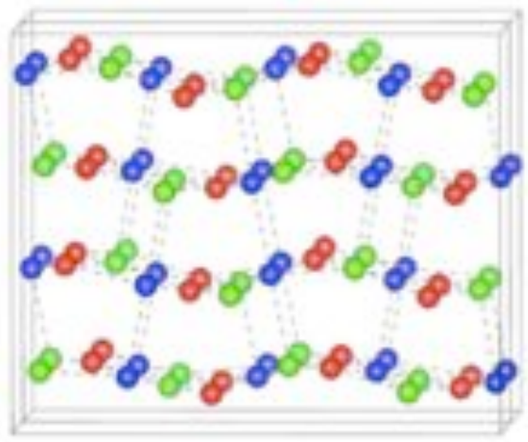
Diamondoid Nitrogen

Wang *et al*, PRL, 2012

Remarkably rich behaviour at terapascals

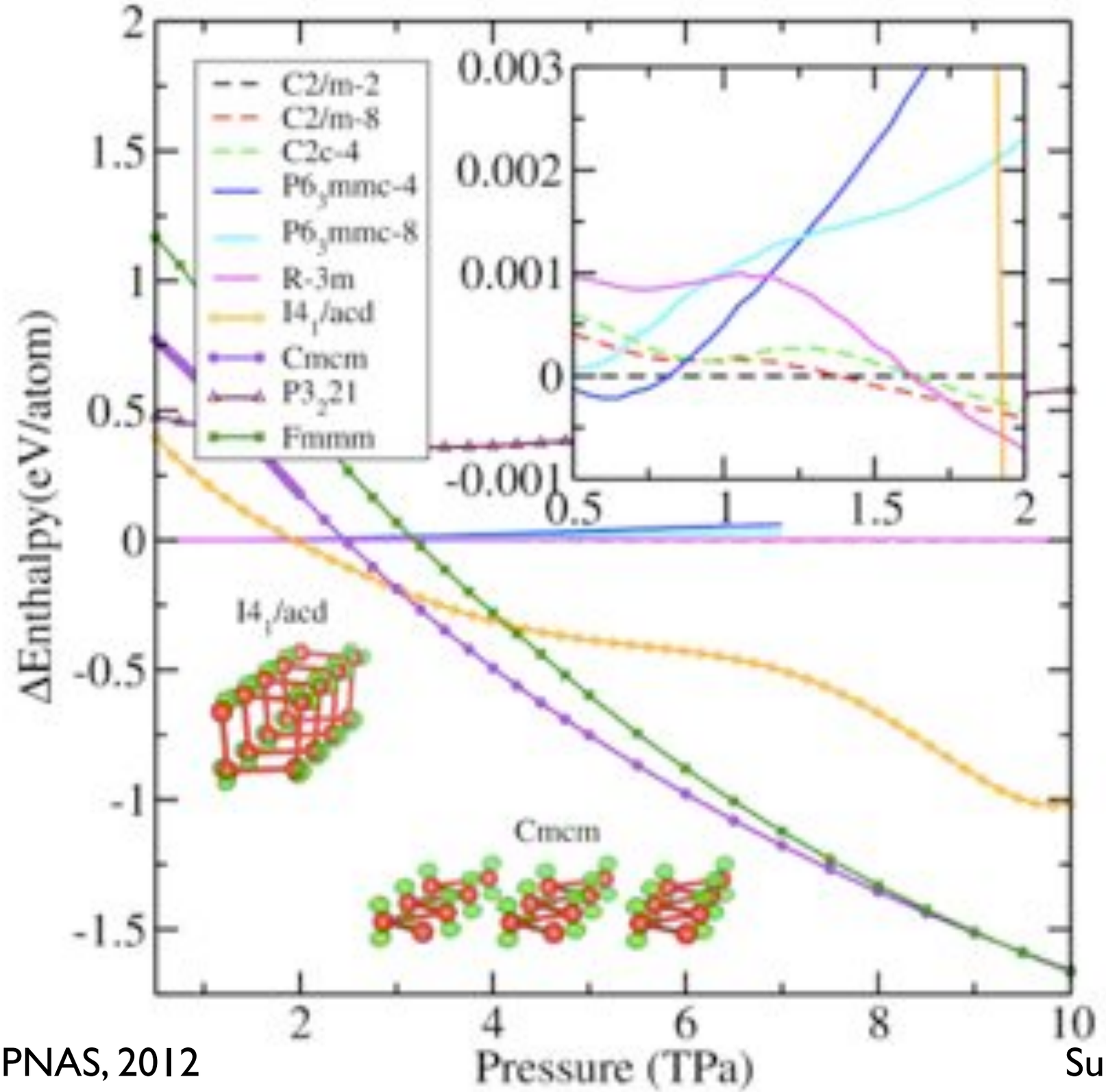






Sun *et al*, condmat, 2012

Oxygen:defeating O_2



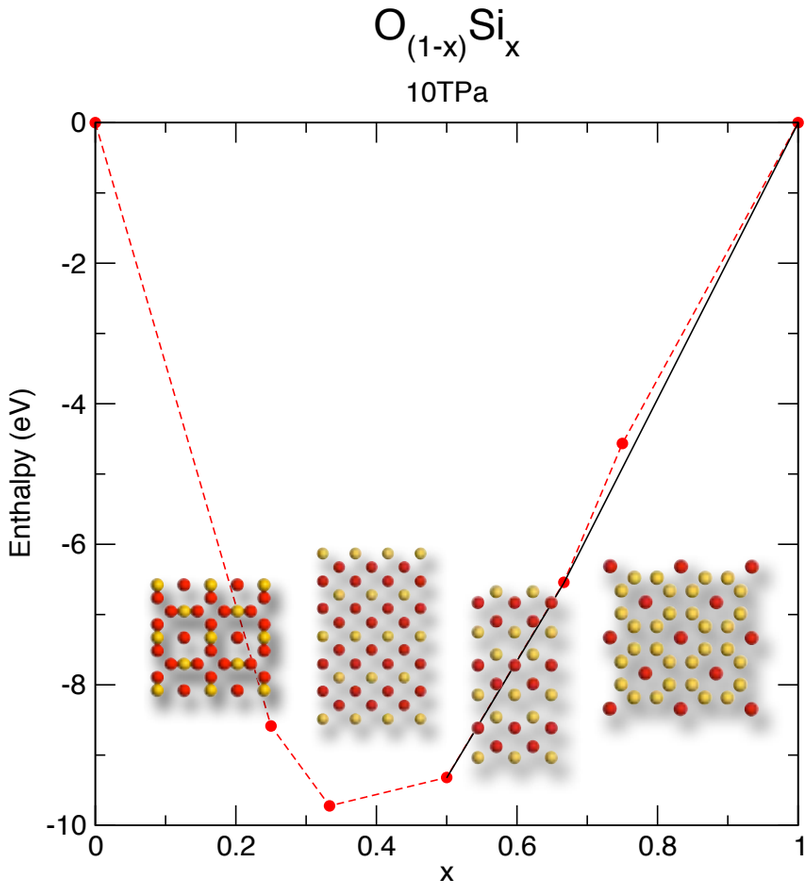
Zhu *et al*, PNAS, 2012

Sun *et al*, PRL, 2012

Dense rock

O, Mg, Al, Si, Ca, Fe

and squeeze (theoretically) to 10TPa



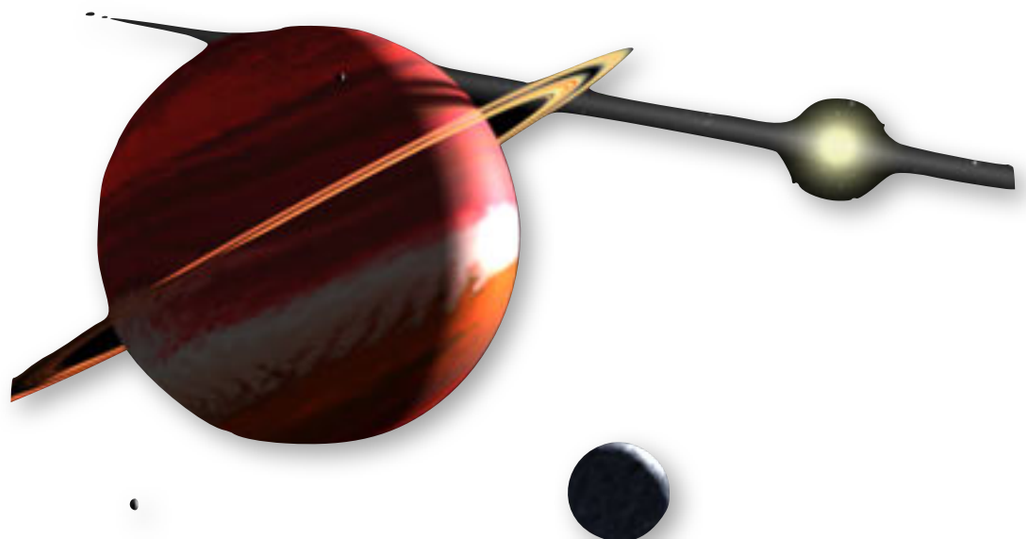
2 x Fe + **50** x O +19 x Si + 17 x Mg + 1 x Al + 2 x Ca

0.5 x Al_2O_3 + 17 x MgO + 12.5 x SiO_2 + 6.5 x SiO_3 + 2 x FeCa

2 x Fe + **25** x O +19 x Si + 17 x Mg + 1 x Al + 2 x Ca

1 x AlO +17 x MgO + 7 x Si_2O + 5 x Si + 2 x FeCa

Calculate binary convex hulls using AIRSS

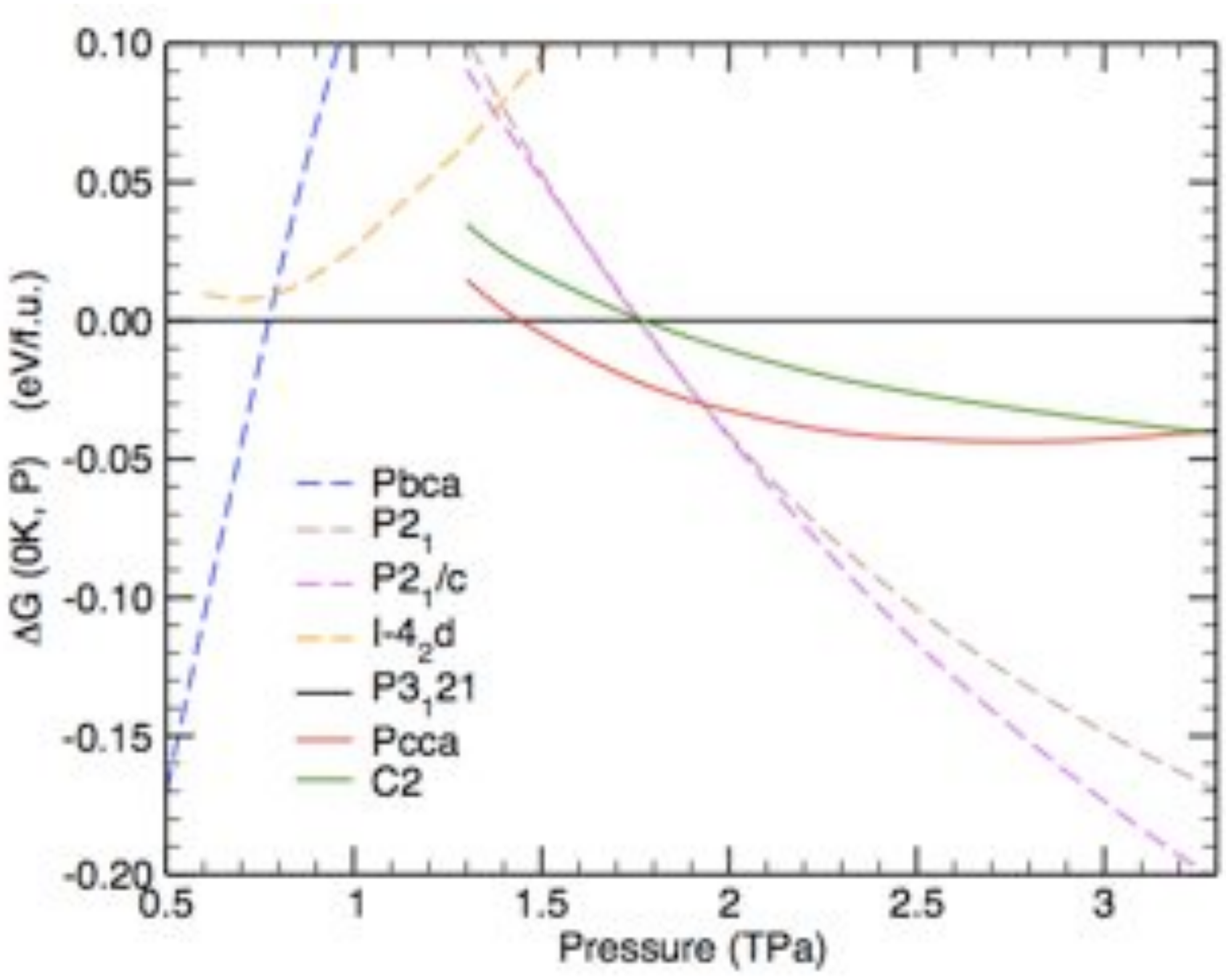


H_2O at TPa

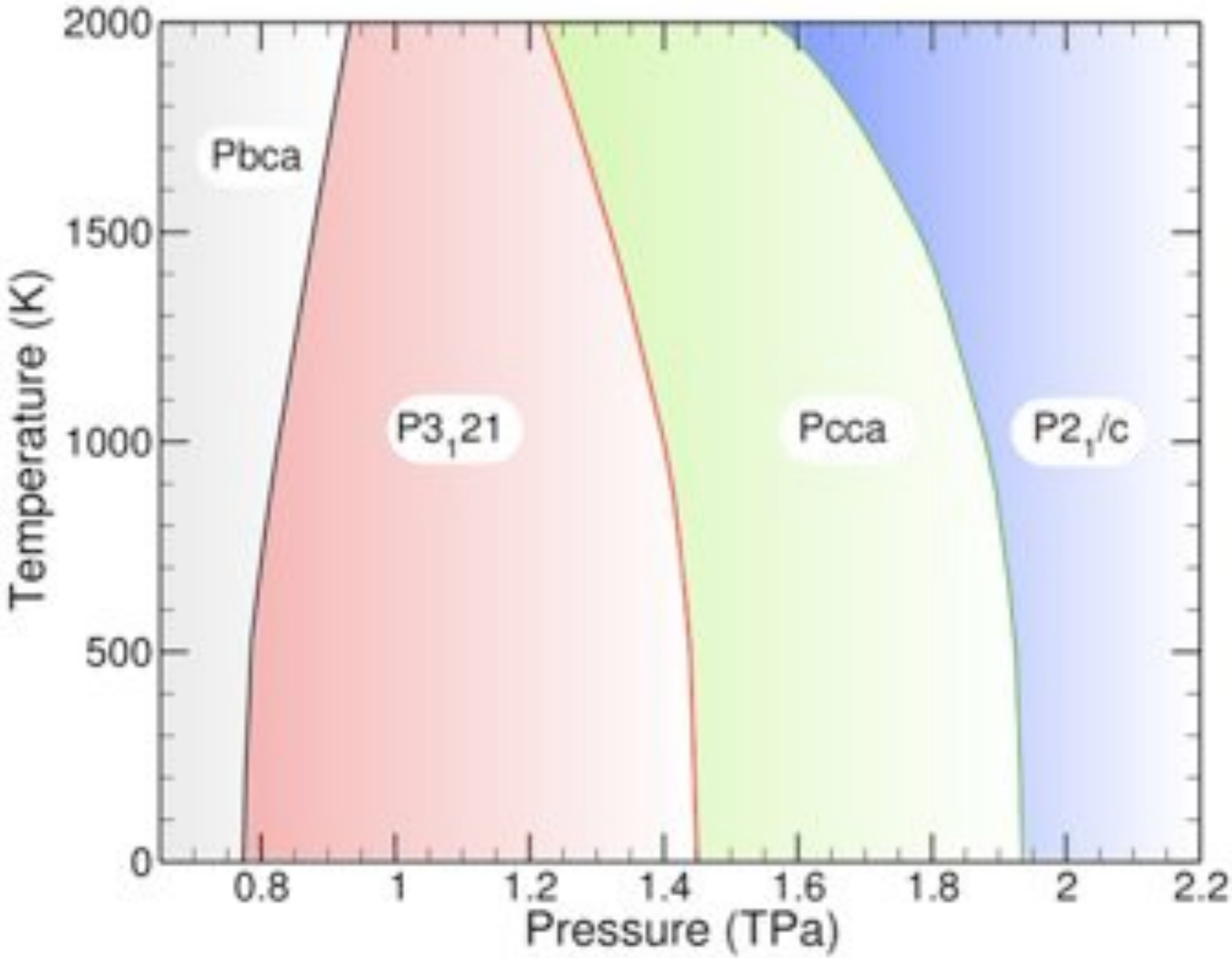
Space group	Stability range (TPa)	No. fu	Source
Ice X	–0.30	2	Ref. [12]
Pbcm	0.30–0.71	4	Ref. [13]
Pbca	0.71–0.78	8	Ref. [14]
$P3_121$	0.78–2.01	12	This work
Pcca	2.01–2.24	12	This work
*C*2	2.24–2.36	12	This work
$P2_1$	2.36–2.75	4	Ref. [15–17]
$P2_1/c$	2.75–6.06	8	Ref. [16]
$C2/m$	6.06–	2	Ref. [15]

P (TPa)	Phase	density (g/cm^3)
0	ordered-Ih	0.917 (expt)
0.1	X	3.18
0.5	*Pbcm*	4.87
0.8	*Pbca*	5.70
1.0	$P3_121$	6.29
2.0	*Pcca*	8.16
2.25	*C*2	8.55
2.5	$P2_1$	8.94
3.25	$P2_1/c$	9.93
6.0	$C2/m$	12.84

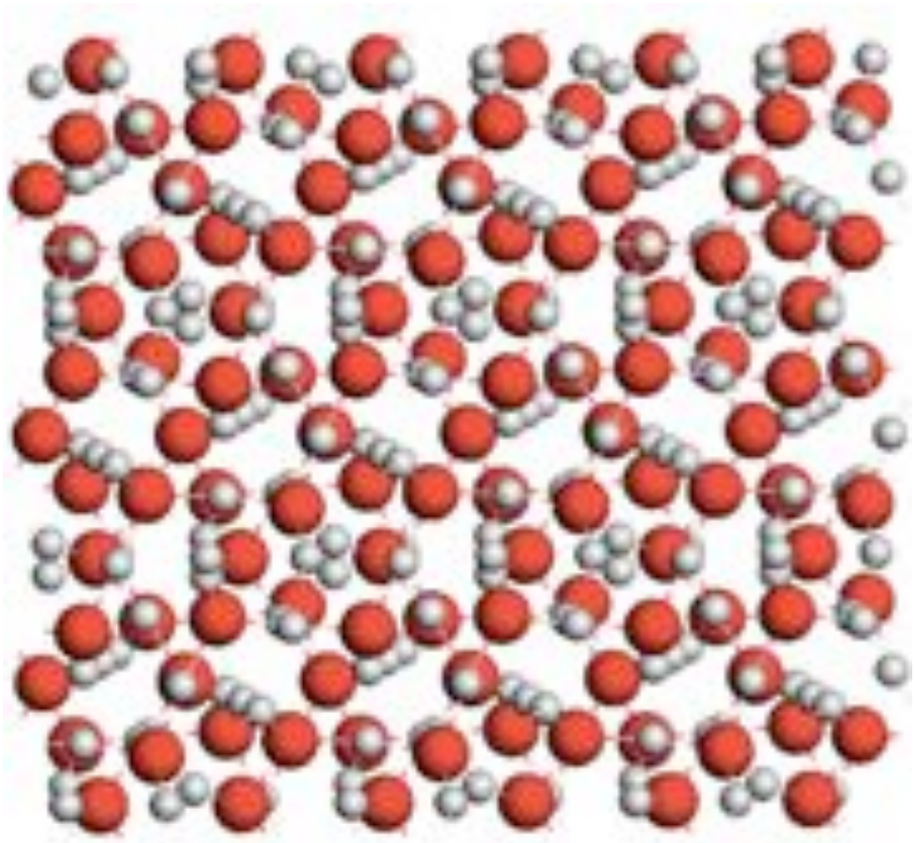
Enthalpies

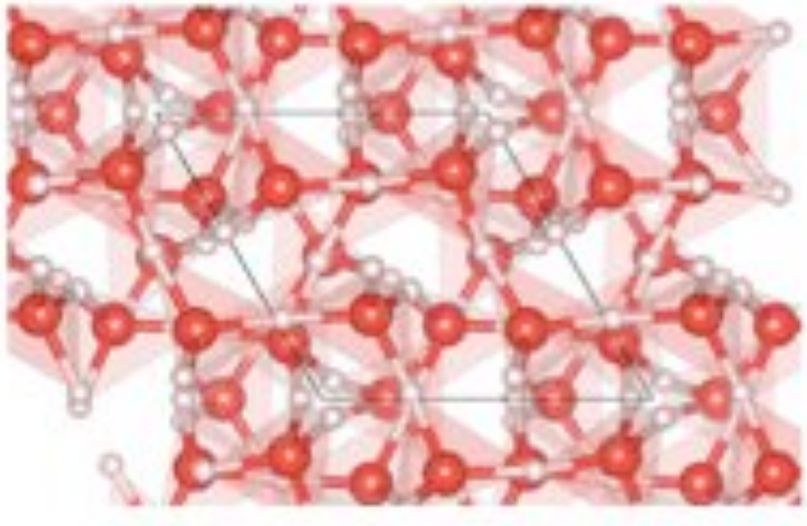

0.10
0.05
0.00
-0.05
-0.10
-0.15
-0.20
0.5
1
1.5
2
2.5
3
ΔG (0K, P) (eV/f.u.)
Pressure (TPa)
Pbca
P2$_1$
P2$_1$/c
I-4$_2$d
P3$_1$21
Pcca
C2

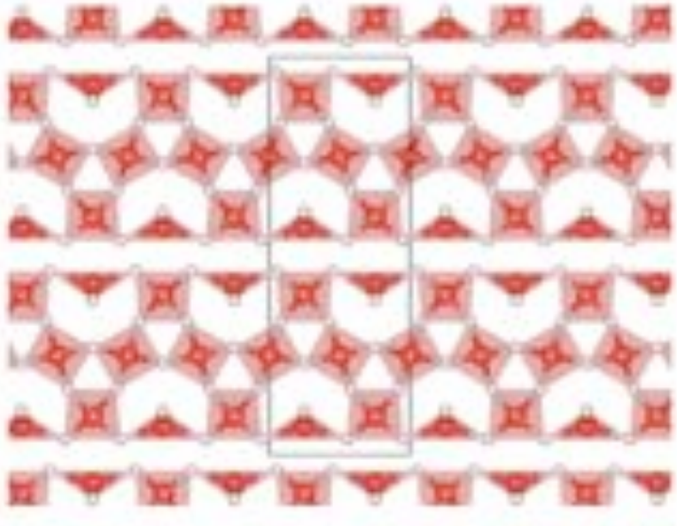
Phase Diagram

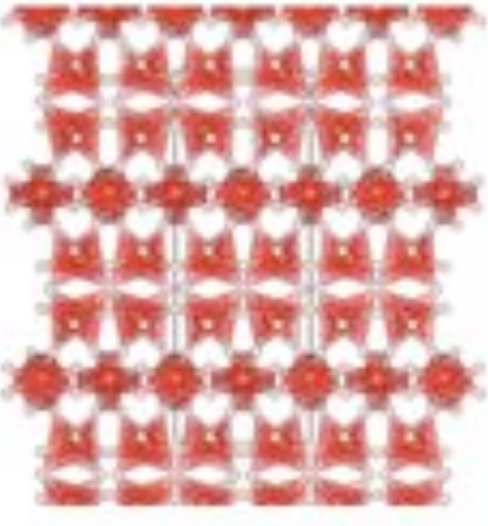


Structures

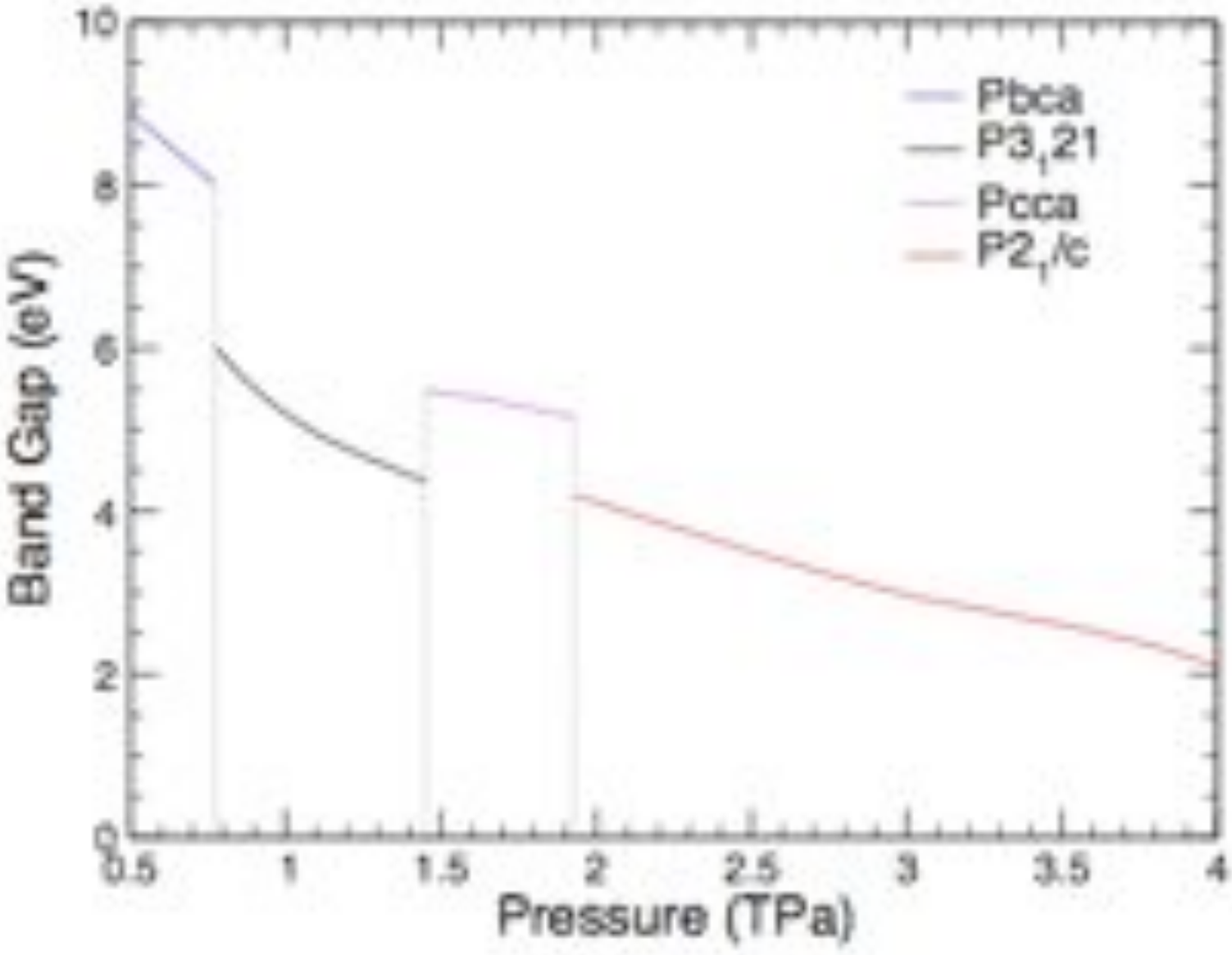






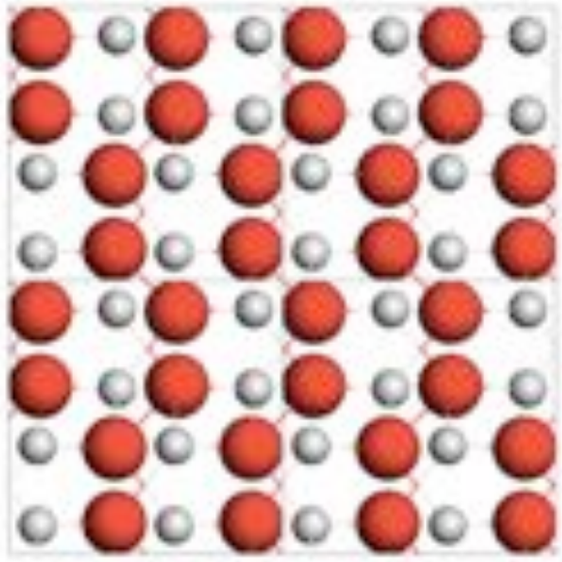


Electronic properties



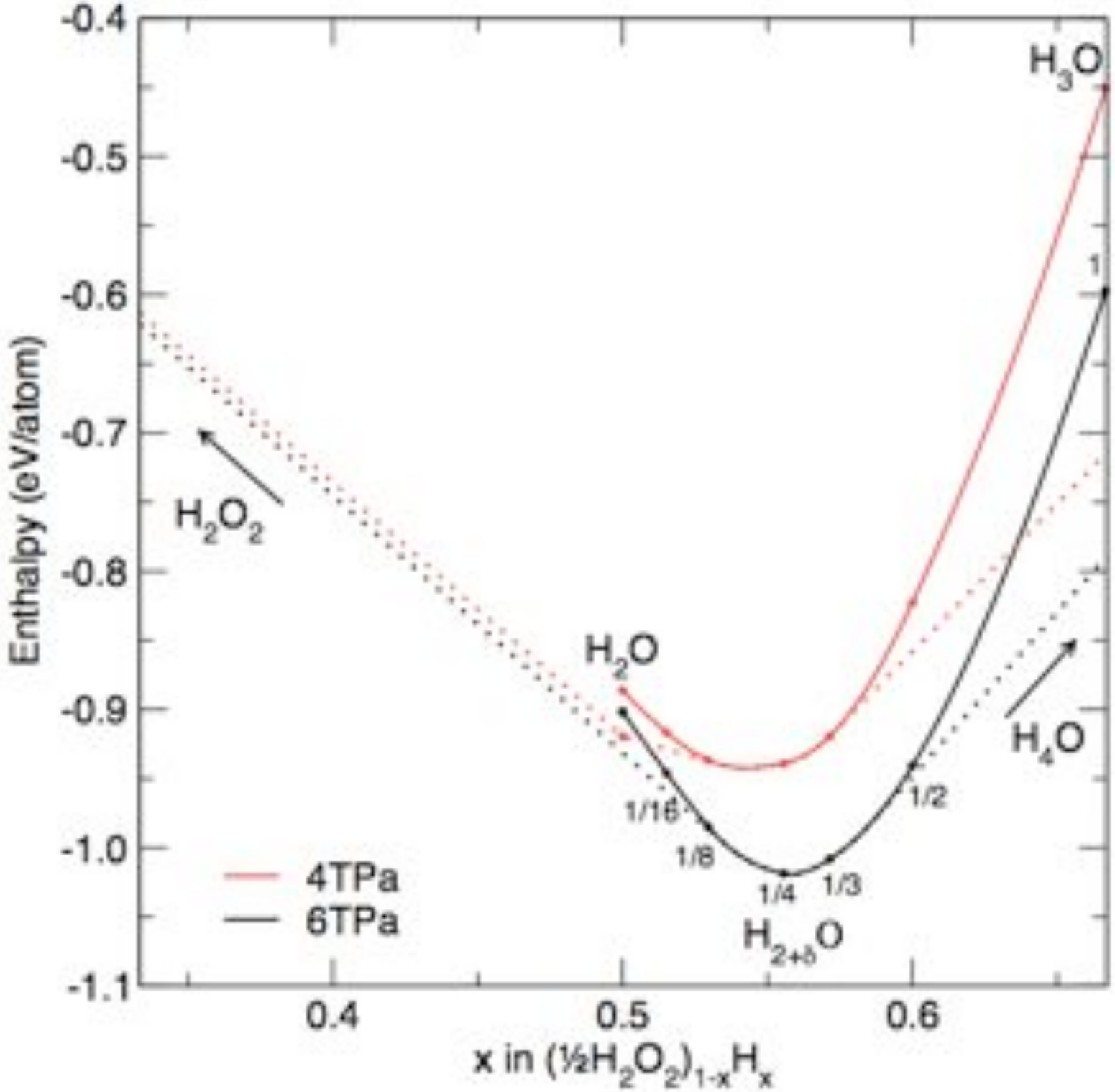
Does H_2O exist?

Maybe not - H_2O_2 is very stable



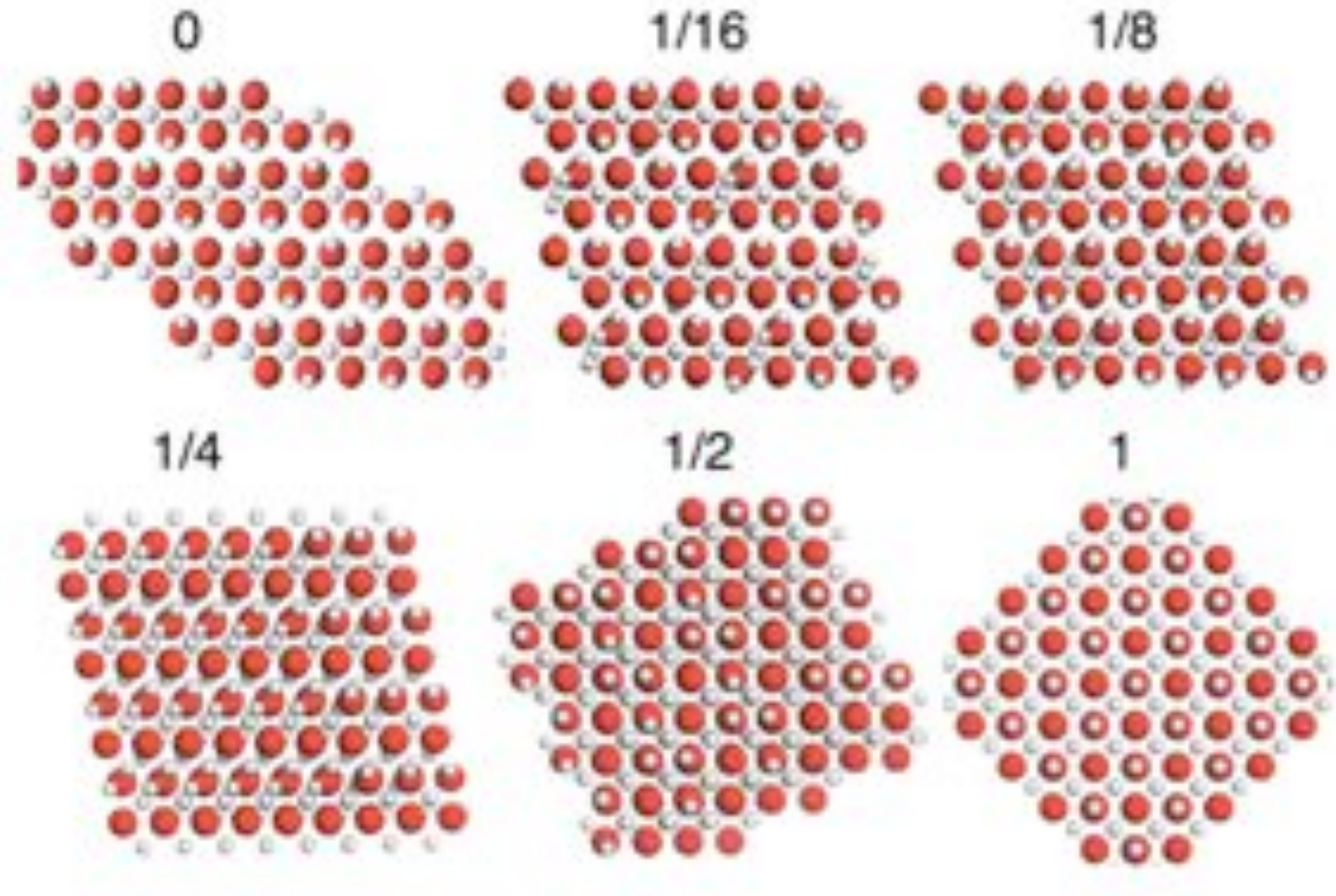
$$\mathrm{H_2O} \rightarrow \frac{\delta}{1+\delta}\frac{1}{2}\,\mathrm{H_2O_2} + \frac{1}{1+\delta}\,\mathrm{H_{2+\delta}O}$$

Decomposition of H_2O

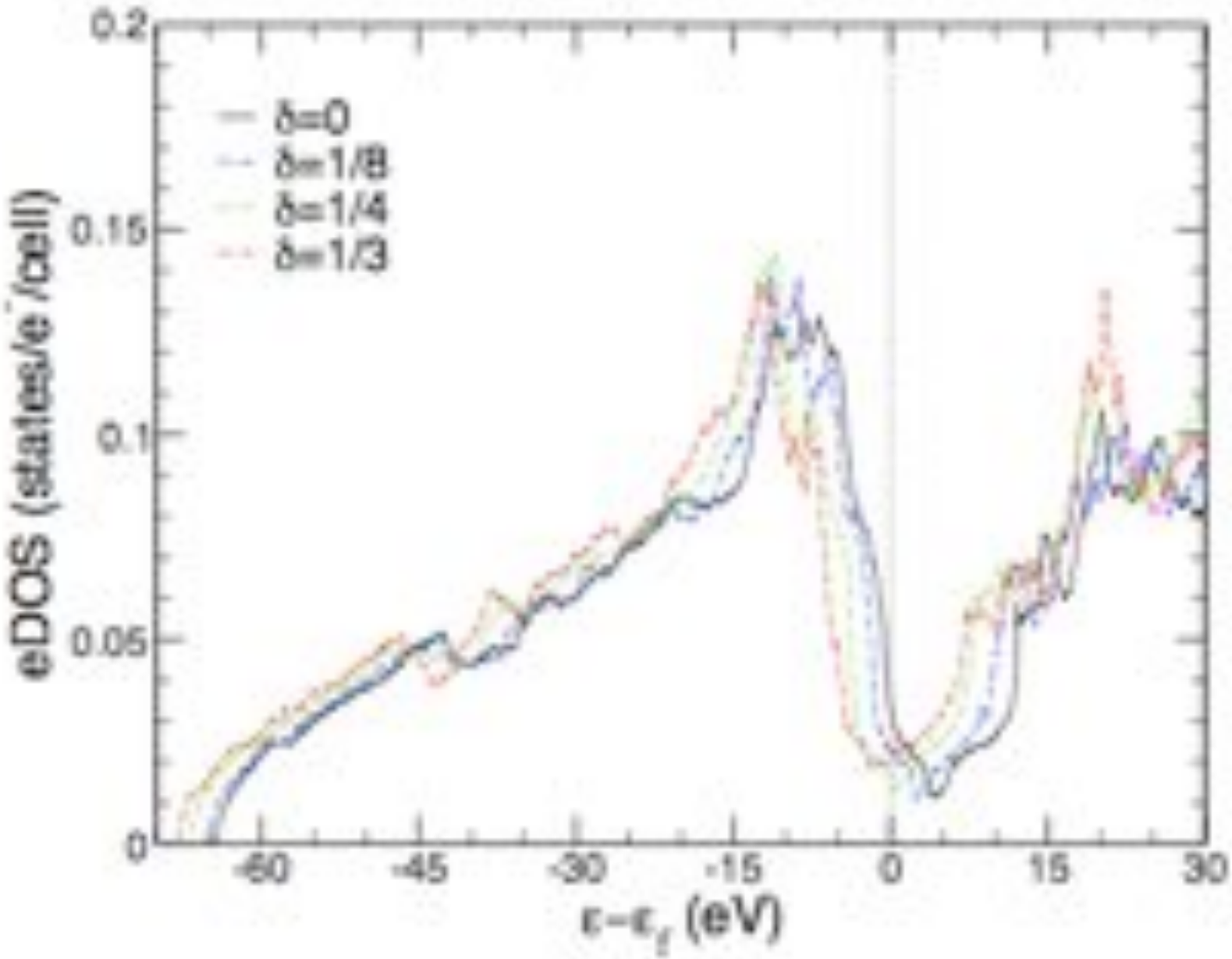


H_2O is not a thermodynamically stable composition above 5TPa

A hydrogen sponge



Fermi surface effects



The doping of C2/m with H moves E_f to a minimum in the eDOS

Perspective

Virtual experimentation

AIRSS - **much** better than you would think

It will be increasingly difficult to distinguish theory, modelling and experiment

Acknowledgements
Richard J Needs

EPSRC
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http://www.castep.org/
The CDG