Title: The Chemical Imagination at Work in VERY Tight Places

Date: Mar 28, 2018 02:00 PM

URL: http://pirsa.org/18030070

Abstract: <p>Diamond anvil cells and shock techniques now permit the study of matter under multimegabar (i.e. several hundred GPa) pressures. The properties of matter in this pressure regime differ drastically from those known at 1 atm. Just how different physics and chemistry are at high pressure and the role that a chemical intuition for bonding and structure can have in understanding matter at high pressures will be explored in this lecture. I will discuss in detail an overlapping hierarchy of responses to increased density, consisting of (a) squeezing out van der Waals space (for molecular crystals); (b) increasing coordination; (c) decreasing the bond length of covalent bonds and the size of anions; and (d) an extreme regime of electrons moving off atoms and new modes of correlation. Examples of the startling chemistry and physics that emerge under such extreme conditions will alternate in this account with qualitative chemical ideas about the bonding involved.</p>


GRRRRRR!
TCHRAAC!

The Chemical Imagination at Work in Very Tight Places

Roald Hoffmann

working together with

Neil W. Ashcroft

NSF, DOE (EFree)

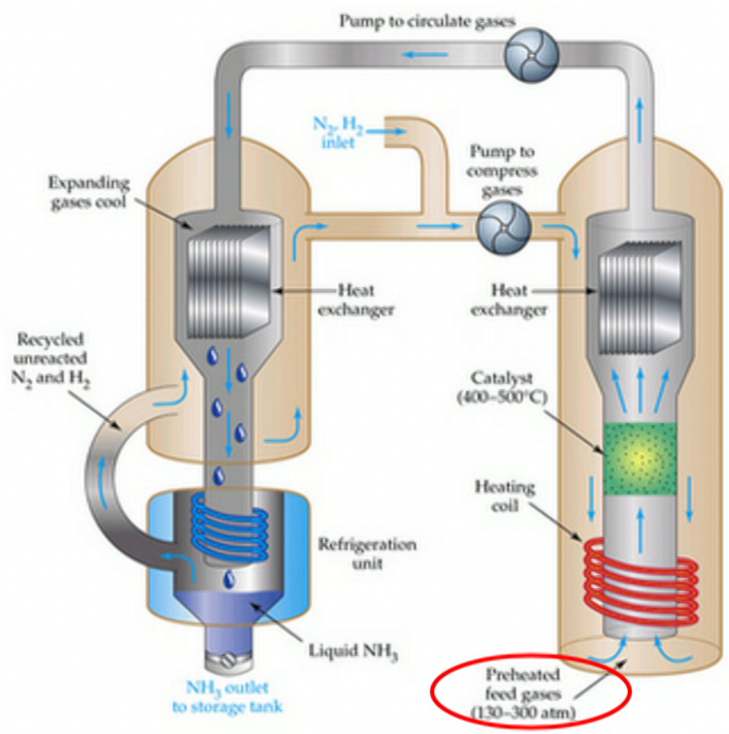
10,000 bar = 9,869 atm = 145,038 lbs/sq.in. = 1 GPa

Pressure at center of earth ~3.5 million atmospheres ~350 Gigapascals

10,000 bar = 9,869 atm = 145,038 lbs/sq.in. = 1 GPa

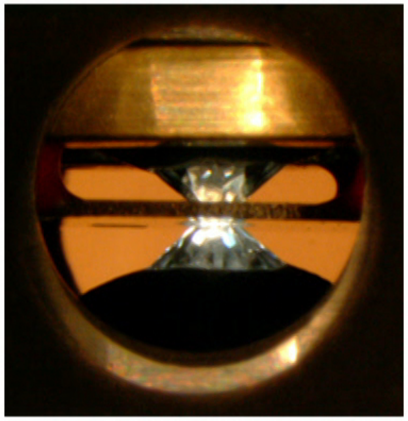
Pressure at center of earth ~3.5 million atmospheres ~350 Gigapascals

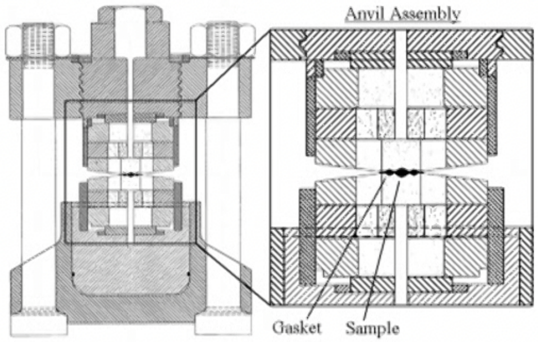
On going from 1 atm to 350 Gpa, the volume of solid Li or methane or benzene decreases by a factor of ~5, NaCl or H_2O ~3, Fe, Au ~1.7

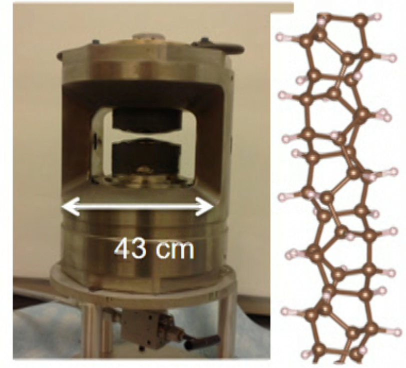


Haber-Bosch process

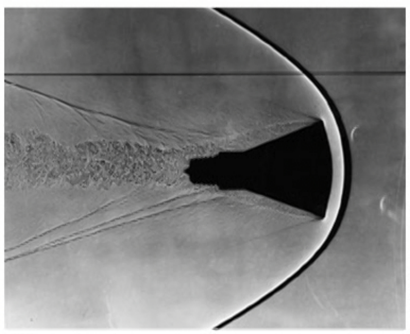
$$N_2 + 3H_2 \leftrightarrows 2NH_3$$

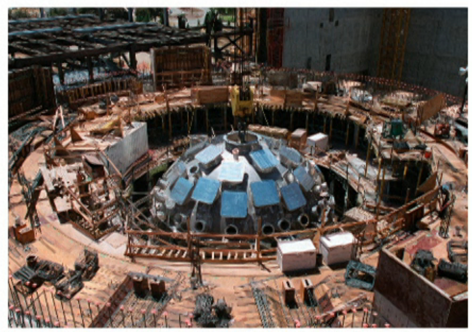


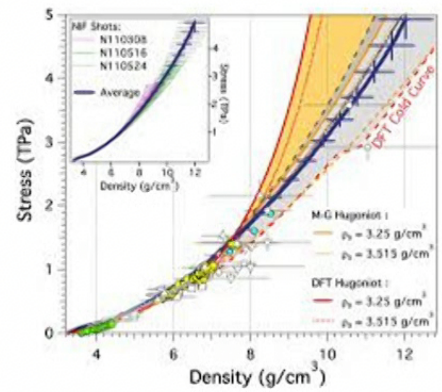


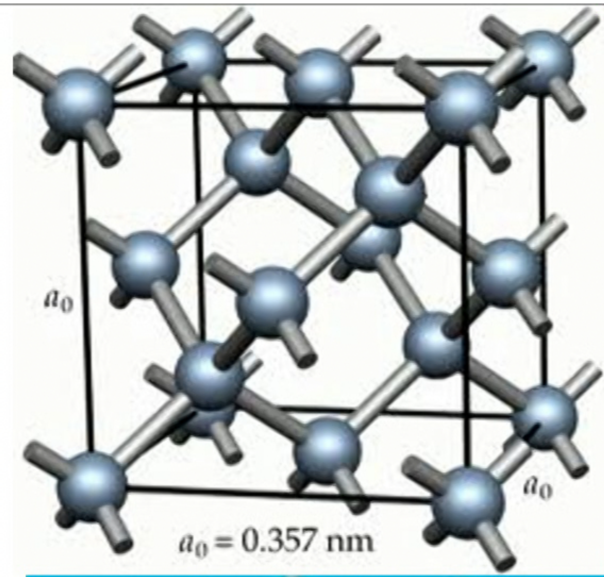


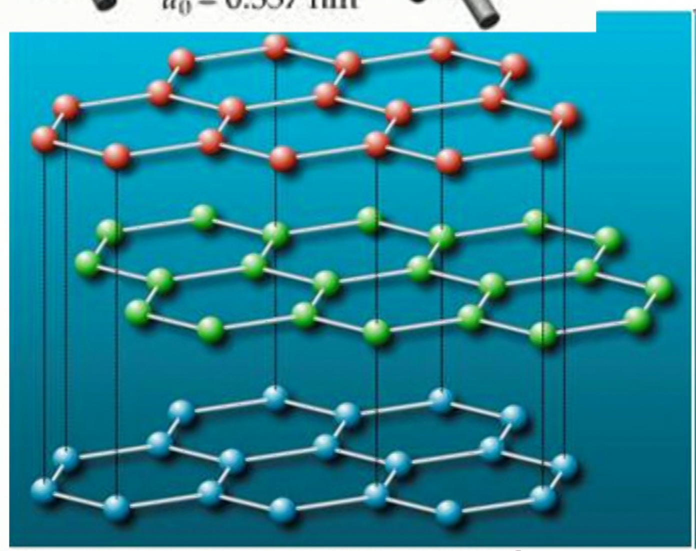
Paris-Edinburgh cell at ORNL



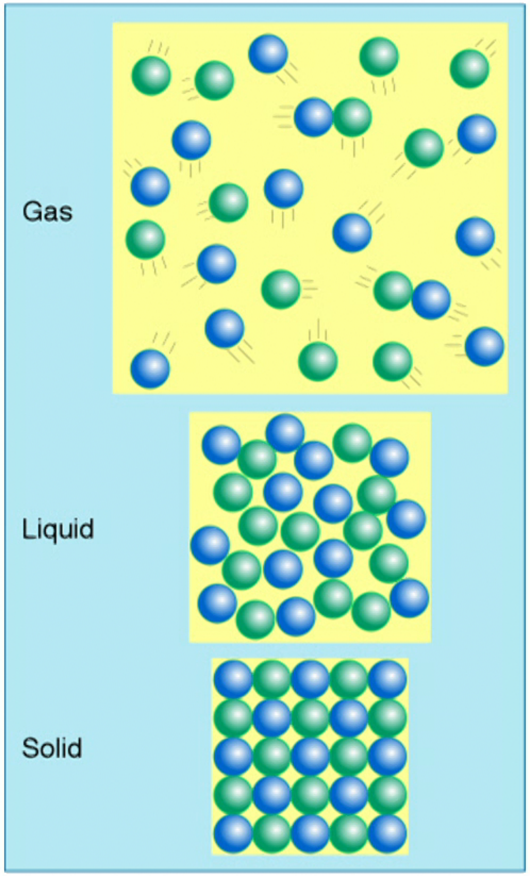


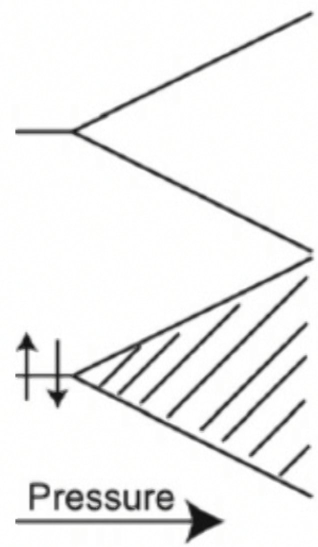






densities of graphite 2.27, diamond 3.51 g/cm^3

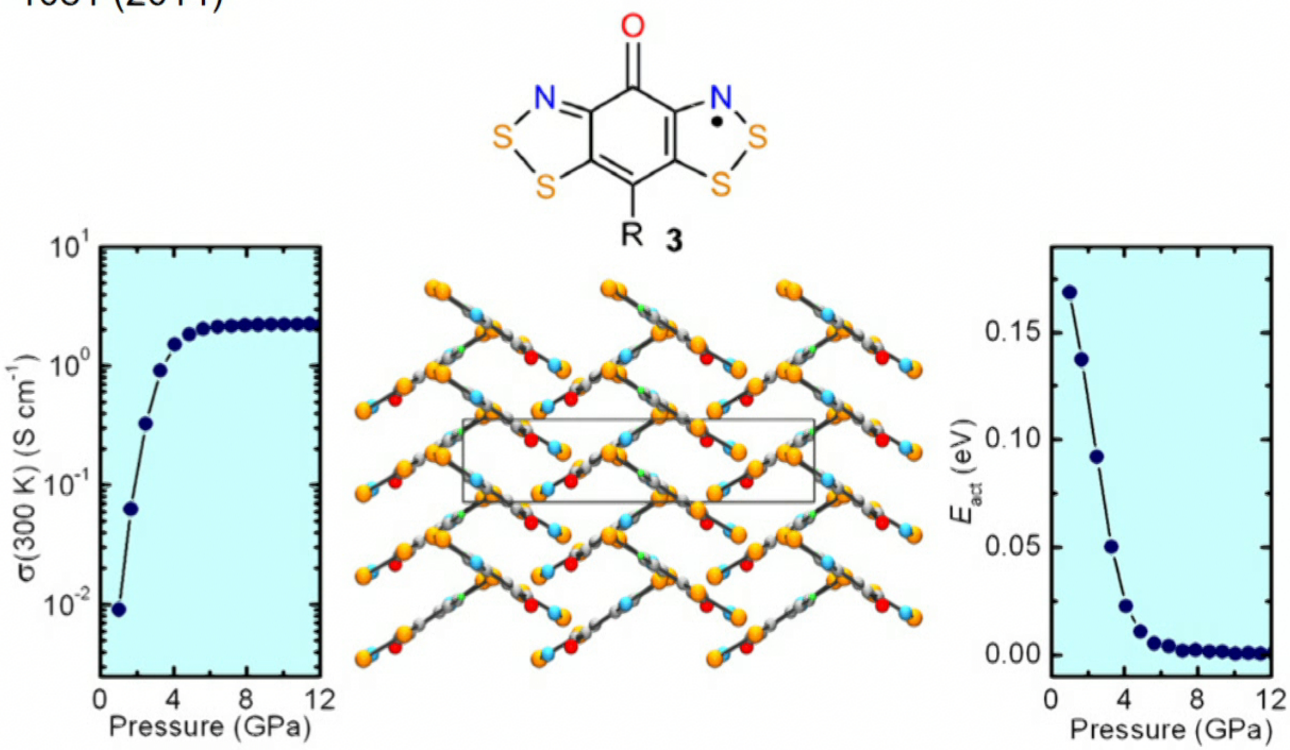

Gas
Liquid
Solid



Virtually all materials become metallic under sufficiently high pressure.

(but… some – Li, Na -- that are metallic at low P become insulating before eventually returning to metallicity)

J. W. L. Wong, A. Mailman, K. Lekin, S. M. Winter, W. Yong, J. Zhao, S. V. Garimella, J. S. Tse, R. A. Secco, S. Desgreniers, Y. Ohishi, F. Borondics and R. T. Oakley. "Pressure Induced Phase Transitions and Metallization of a Neutral Radical Conductor." *J. Am. Chem. Soc.* **136**, 1070-1081 (2014)

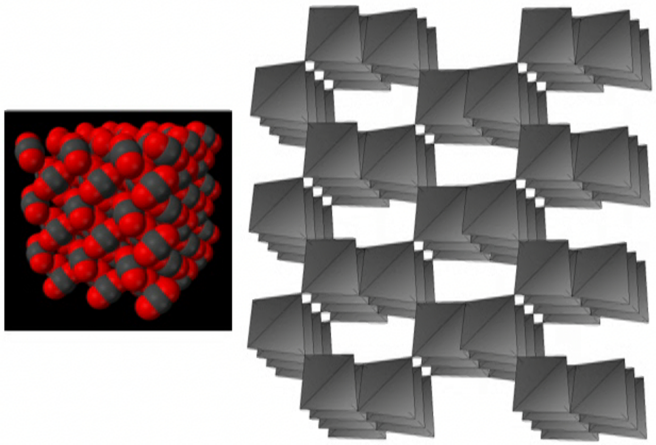


The extreme landscape of high pressure

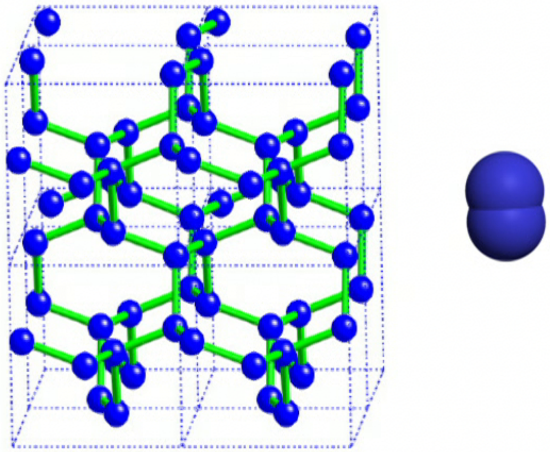
Xe and I_2 can be metallized *[Goettel et al, Ruoff et al]*, as can CsI and BaTe *[Eremets et al, Grzybowski et al]*

The extreme landscape of high pressure

Xe and I_2 can be metallized *[Goettel et al, Ruoff et al]*, as can CsI and BaTe *[Eremets et al, Grzybowski et al]*

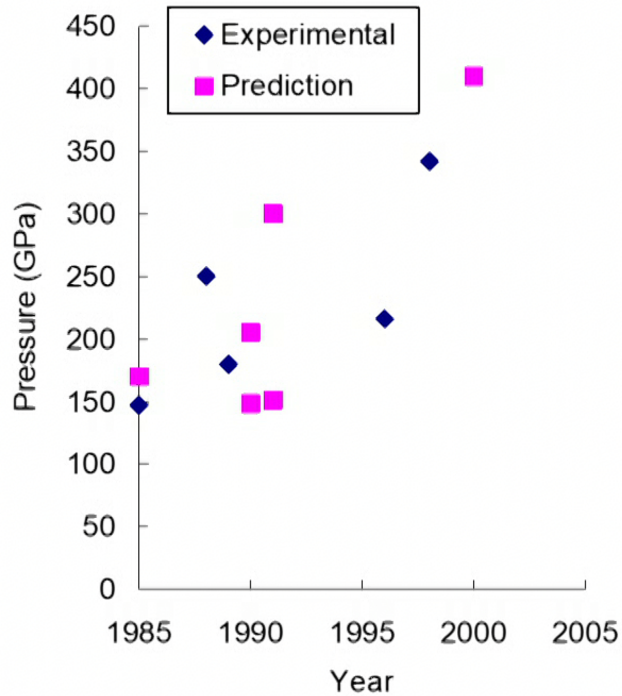


CO_2 (V) 50 GPa



"N_2" >110 GPa and 2000 K *[Eremets et al]*

Metallic hydrogen



100 GPa = 1 Mbar

M. I. Eremets & I. A. Troyan
MPI Chemie, Mainz
Nature Materials, 10, 927–931 (2011)

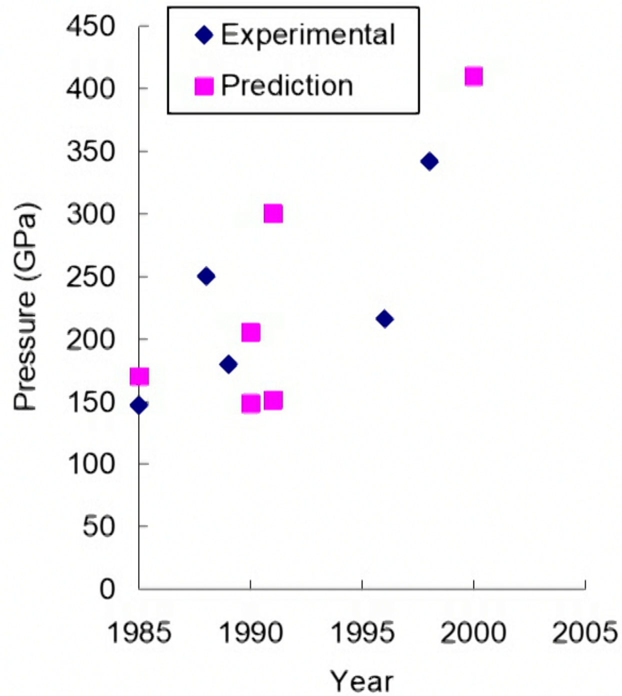
W.J. Nellis, Arthur L. Ruoff, Isaac F. Silvera
Has Metallic Hydrogen Been Made in a Diamond Anvil Cell?
arXiv:1201.0407, 2012

Dias, R.; Silvera, I. F. *(2016). "Observation of the Wigner-Huntington Transition to Solid Metallic Hydrogen". Science 255, 715 (2017)*

W. J. Nellis
"Dynamic Compression of Materials: Metallization of Fluid Hydrogen at High Pressures", Rep. Prog. Phys. 69, 1479-1580 (2006).

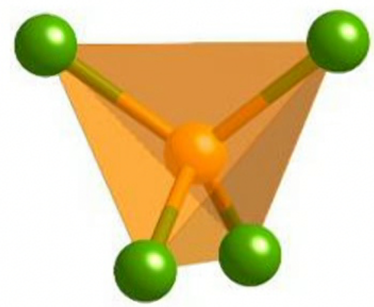
Chemical precompression

Metallic hydrogen



100 GPa = 1 Mbar

Neil Ashcroft



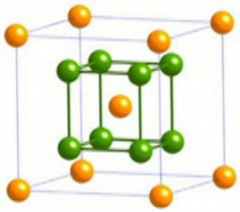
CH_4, SiH_4, GeH_4, …
$LiBH_4$, $NaAlH_4$, …
K_2ReH_9, $(NH_4)_2ReH_9$

SiH_4 m.p. -185 C, b.p. -112 C
Autoignites 21 C

Structures and Potential Superconductivity in SiH_4 at High Pressure - *En Route* to "Metallic Hydrogen"

Ji Feng, Wojciech Grochala, Tomasz Jaroń, Roald Hoffmann, Aitor Bergara and N. W. Ashcroft

Physical Review Letters, **96**, 017006, (2006).

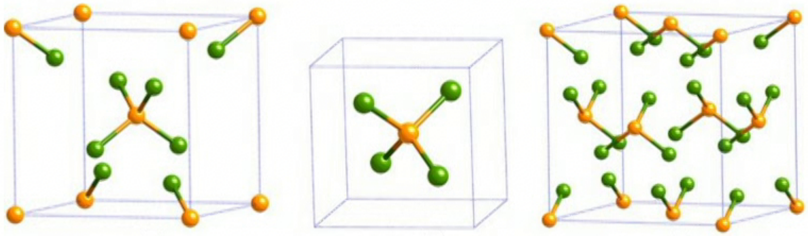


M1. $Im\bar{3}m$

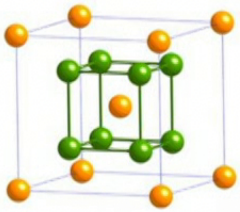
Structures and Potential Superconductivity in SiH_4 at High Pressure - *En Route* to "Metallic Hydrogen"

Ji Feng, Wojciech Grochala, Tomasz Jaroń, Roald Hoffmann, Aitor Bergara and N. W. Ashcroft

Physical Review Letters, ***96***, *017006, (2006).*



T1. $I\bar{4}3m$ **T2**. $P\bar{4}3m$ **T3**. $I\bar{4}2m$

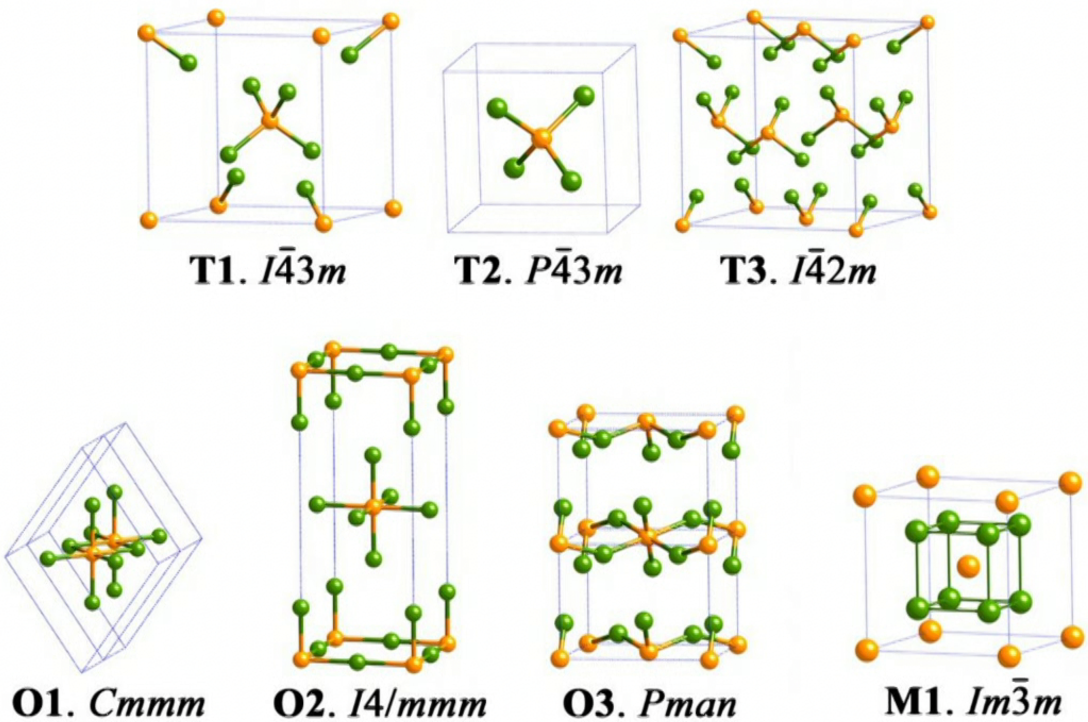


M1. $Im\bar{3}m$

Structures and Potential Superconductivity in SiH_4 at High Pressure - *En Route* to “Metallic Hydrogen”

Ji Feng, Wojciech Grochala, Tomasz Jaroń, Roald Hoffmann, Aitor Bergara and N. W. Ashcroft

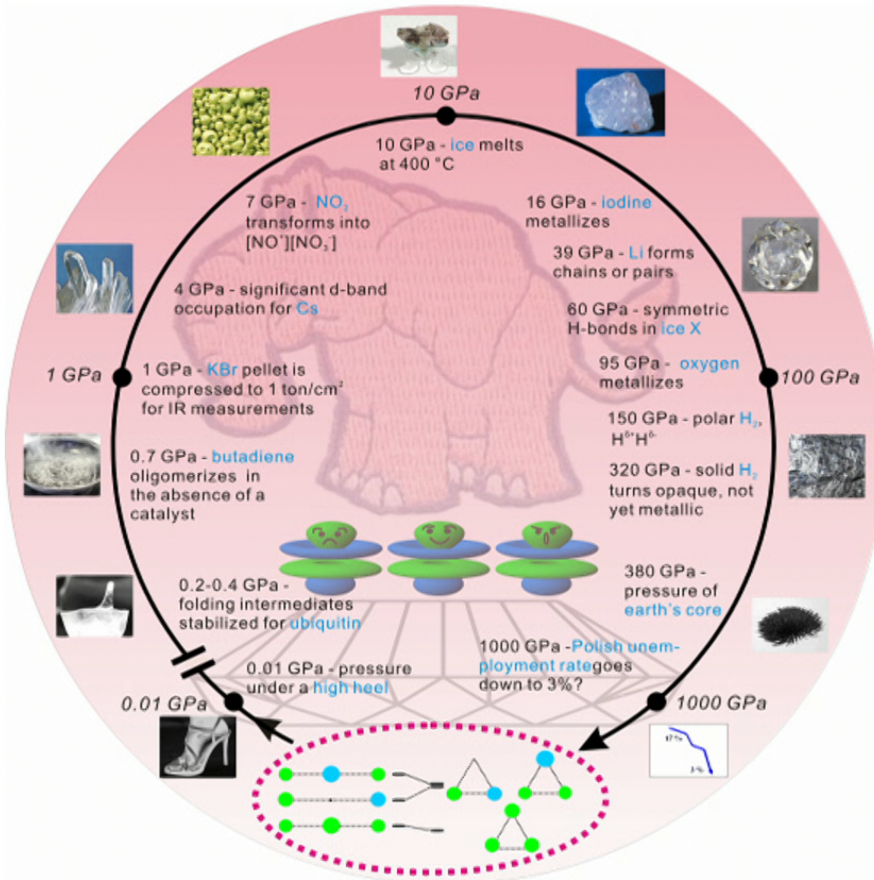
Physical Review Letters, **96**, 017006, (2006).



The Chemical Imagination at Work in *Very* Tight Places

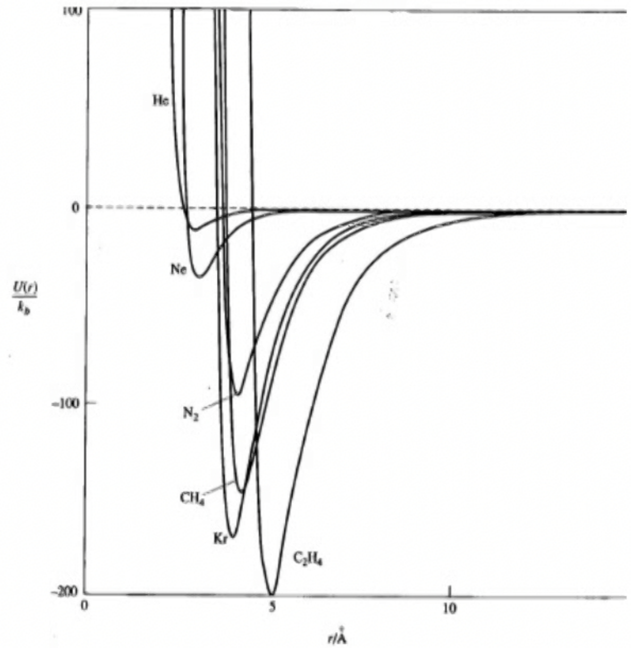
Wojciech Grochala, Roald Hoffmann, Ji Feng, and Neil W. Ashcroft

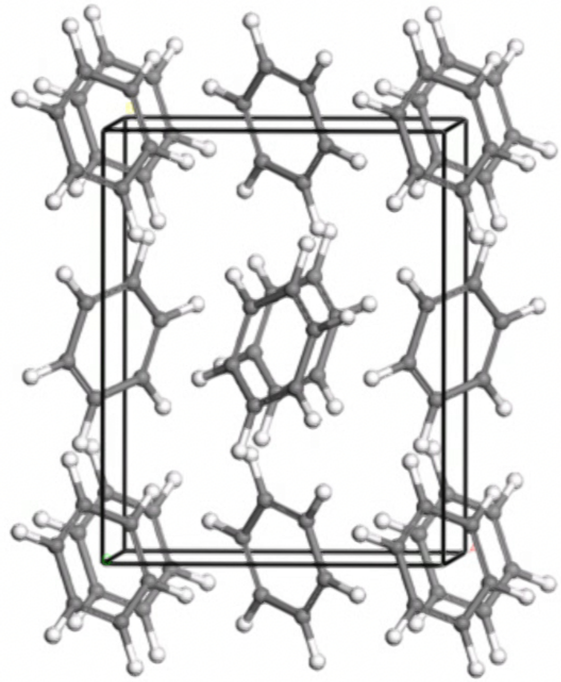
Angewandte Chemie, **46**(20), 3620-3642 (2007).



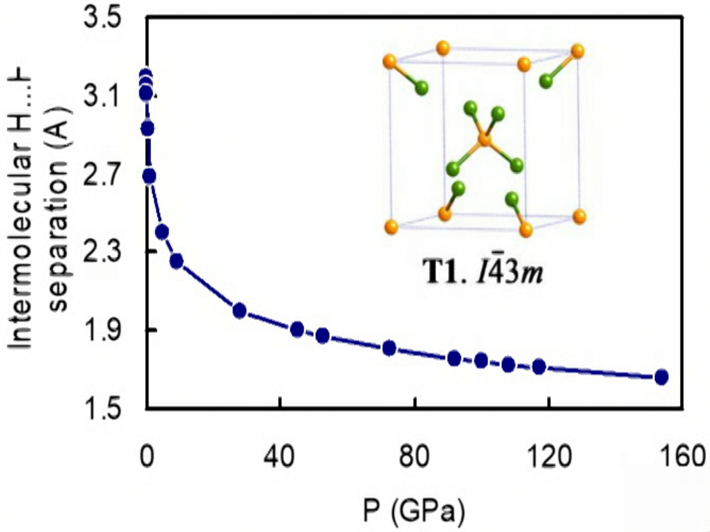
A Hierarchy of Responses to Pressure in Crystals

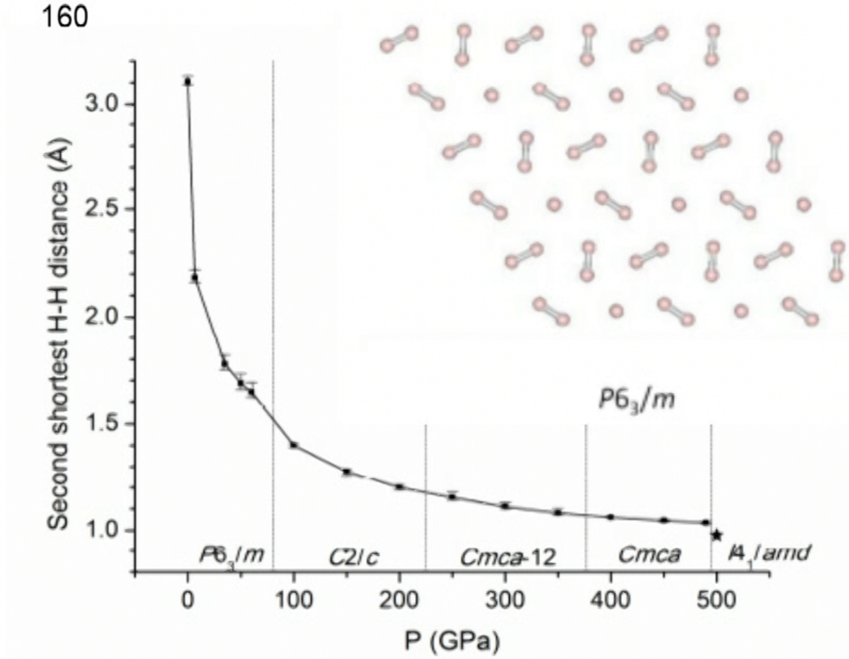
- Penetrating the repulsive region of intermolecular potentials
- Increasing coordination at main group and transition metal elements
- Decreasing the bond length of covalent bonds, and the size of anions
- A new world of electrons moving off their atoms, new modes of correlation





dispersion (= van der Waals) forces -- weak forces between molecules and atoms, attractive at long distance ($1/r^6$, due to induced-dipole, induced-dipole interactions), repulsive at short separations

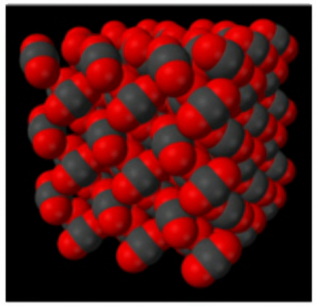




van der Waals space is most easily compressed.

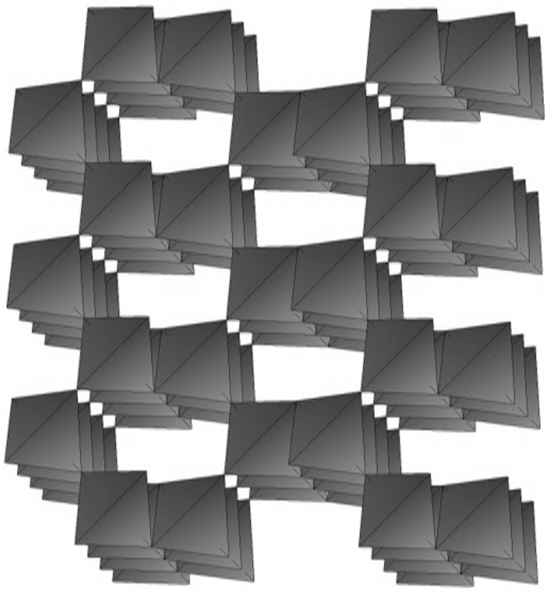
A Hierarchy of responses to Pressure in Crystals

- Penetrating the repulsive region of intermolecular potentials
- Increasing coordination at main group and transition metal elements
- Decreasing the bond length of covalent bonds, and the size of anions
- A new world of electrons moving off their atoms, new modes of correlation

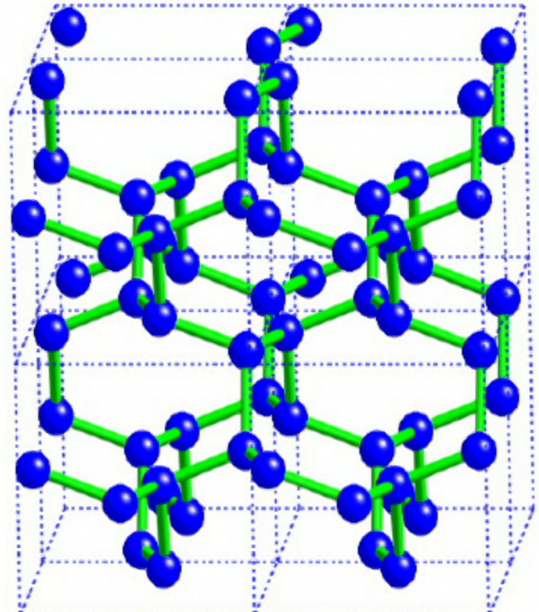


Coordination Alchemy

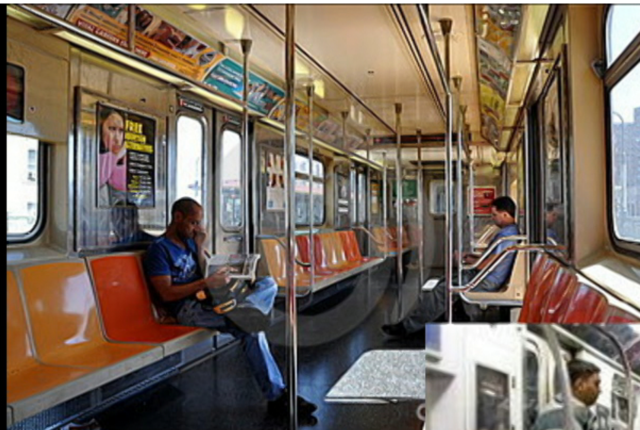
$$\Delta H = \Delta E + P\Delta V$$



CO_2 (V) 50 GPa, 1800 K



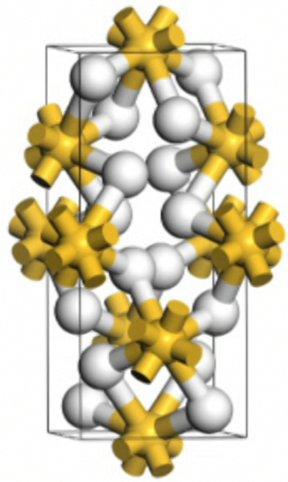
"N_2" >110 GPa, 2000 K




1697

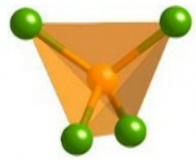
A Hierarchy of Responses to Pressure in Crystals

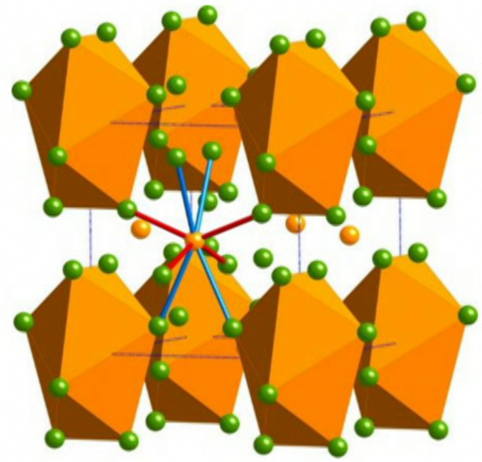
- Penetrating the repulsive region of intermolecular potentials
- Increasing coordination at main group and transition metal elements



$I4_1/a$

C.J. Pickard, R.J. Needs

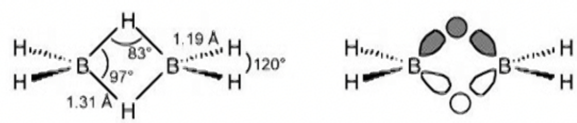




Feng et al

each Si atom has 8 nearest neighbor hydrogens, two each bridging to a neighboring Si. The stoichiometry is $SiH_{8/2.}$ Each Si-H_2-Si unit uses 4 electrons (one each from each Si and each H) to bond together in diborane fashion the four centers.

each Si has around it 8 electron deficient bent Si-H-Si three-center bonds

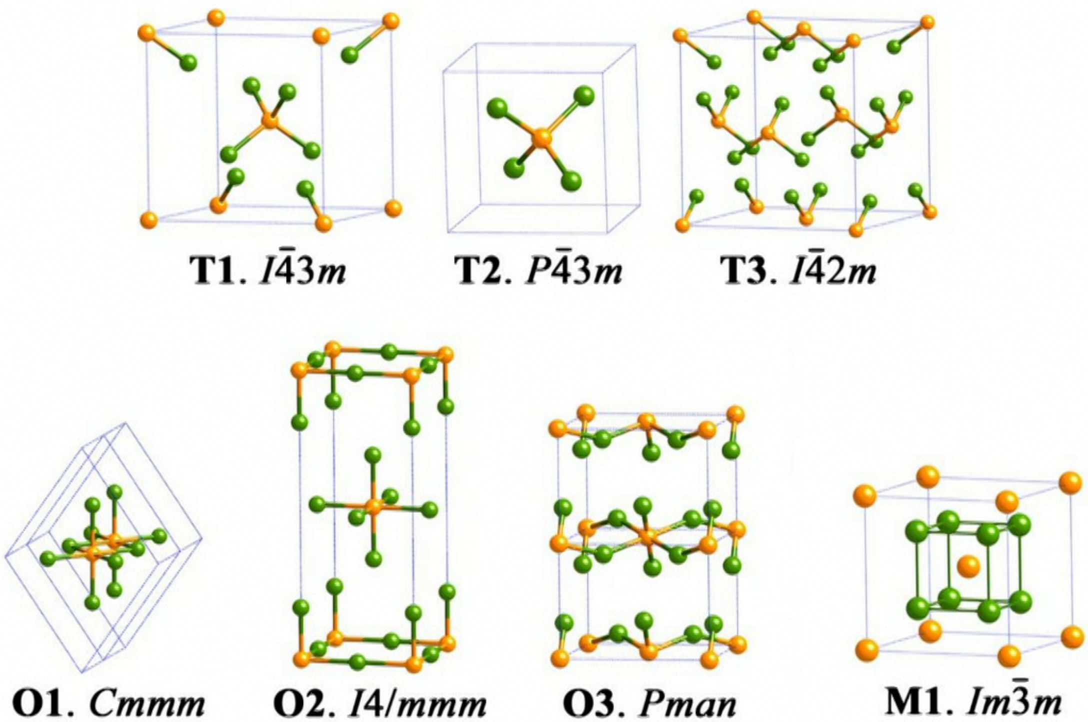


(a) (b)

Structures and Potential Superconductivity in SiH_4 at High Pressure - *En Route* to "Metallic Hydrogen"

Ji Feng, Wojciech Grochala, Tomasz Jaroń, Roald Hoffmann, Aitor Bergara and N. W. Ashcroft

Physical Review Letters, **96**, 017006, (2006).

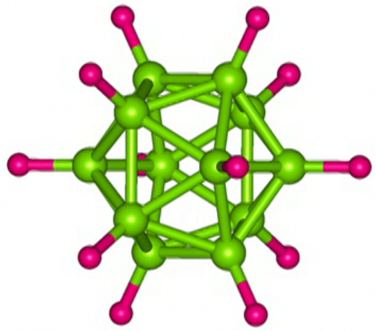


Increased density with increasing pressure

→ higher coordination

→ more bonds, full or partial, with same number of electrons

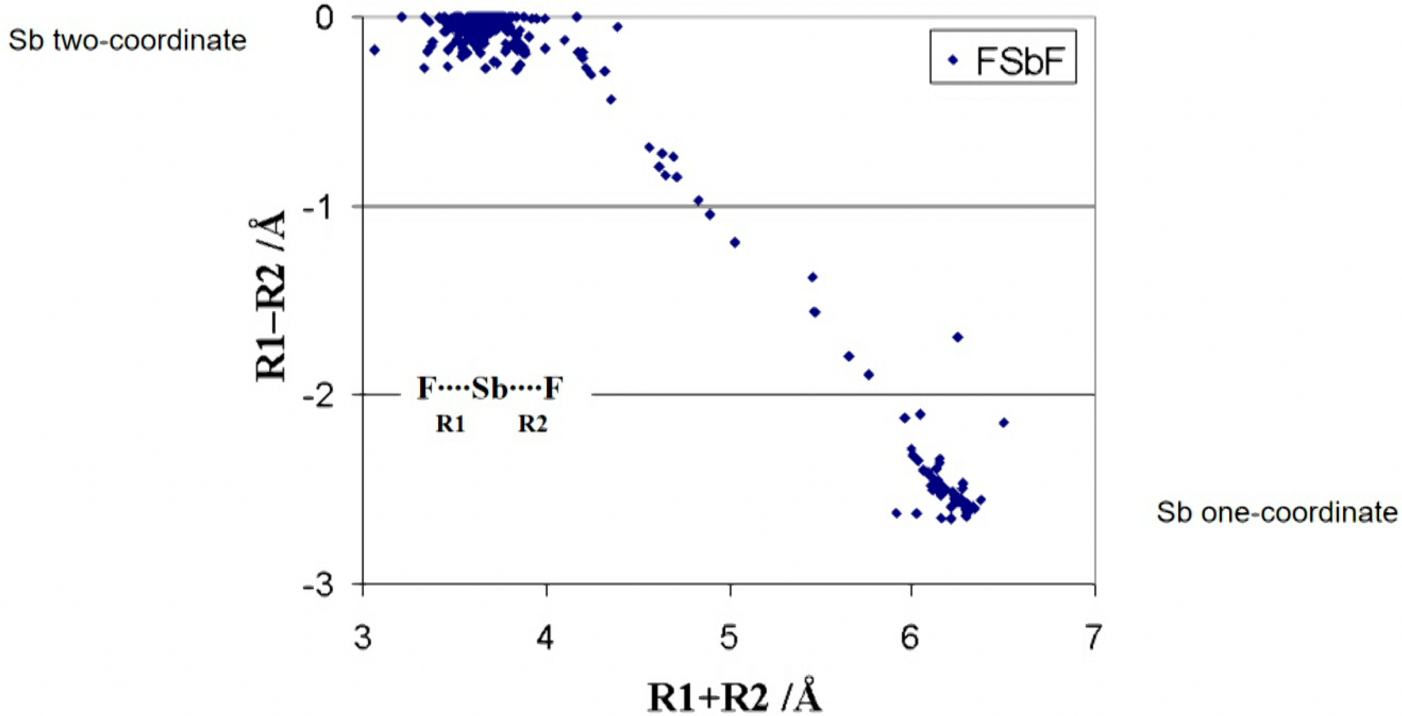
→ multicenter bonding, electron-rich or electron-poor



$B_{12}H_{12}^{2-}$

PF_5

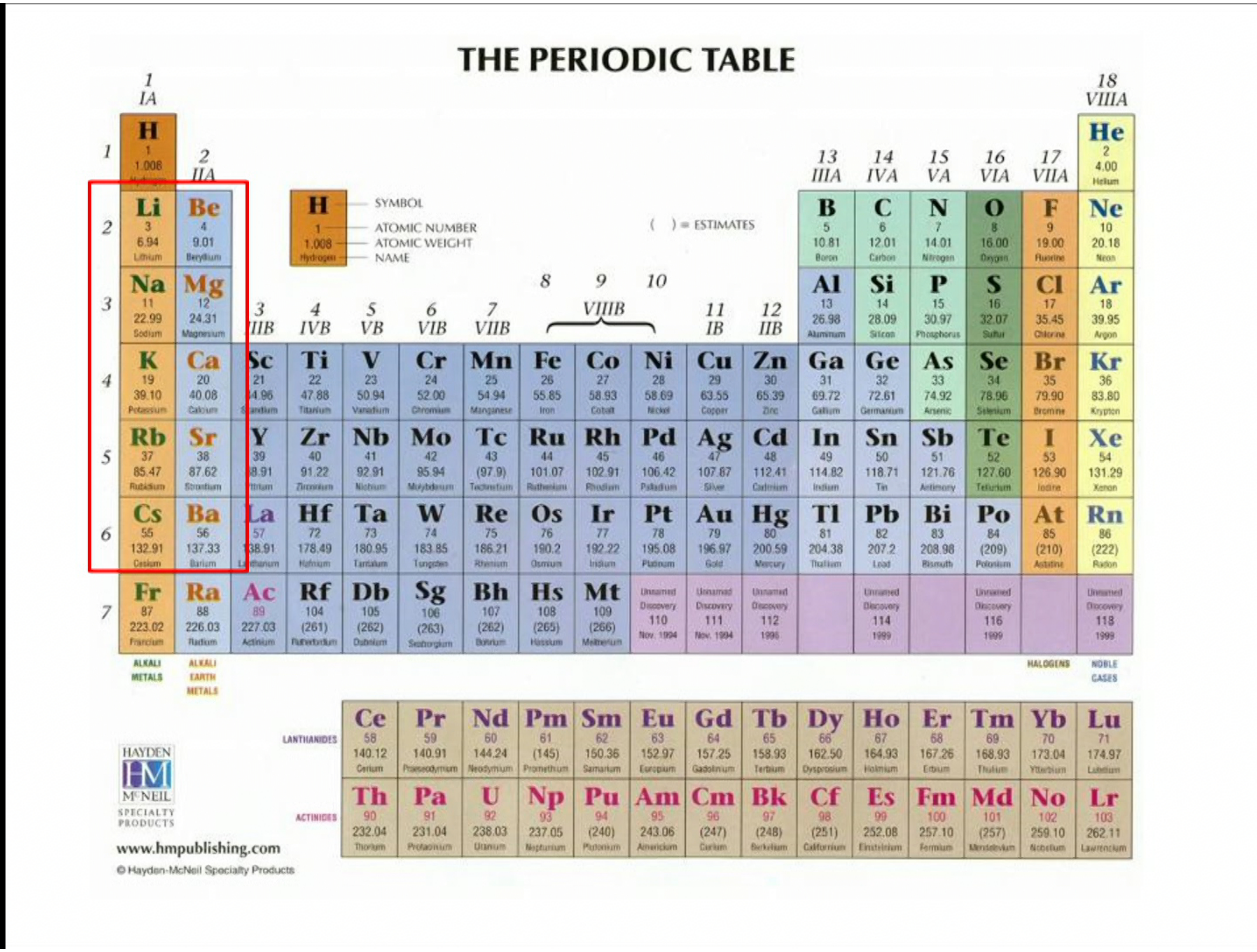
How to use P=1 atm data to understand what will happen at higher pressures



Cambridge Structural Database

A Hierarchy of Responses to Pressure in Crystals

- Penetrating the repulsive region of intermolecular potentials
- Increasing coordination at main group and transition metal elements
- Decreasing the bond length of covalent bonds, and the size of anions
- A new world of electrons moving off their atoms, new modes of correlation

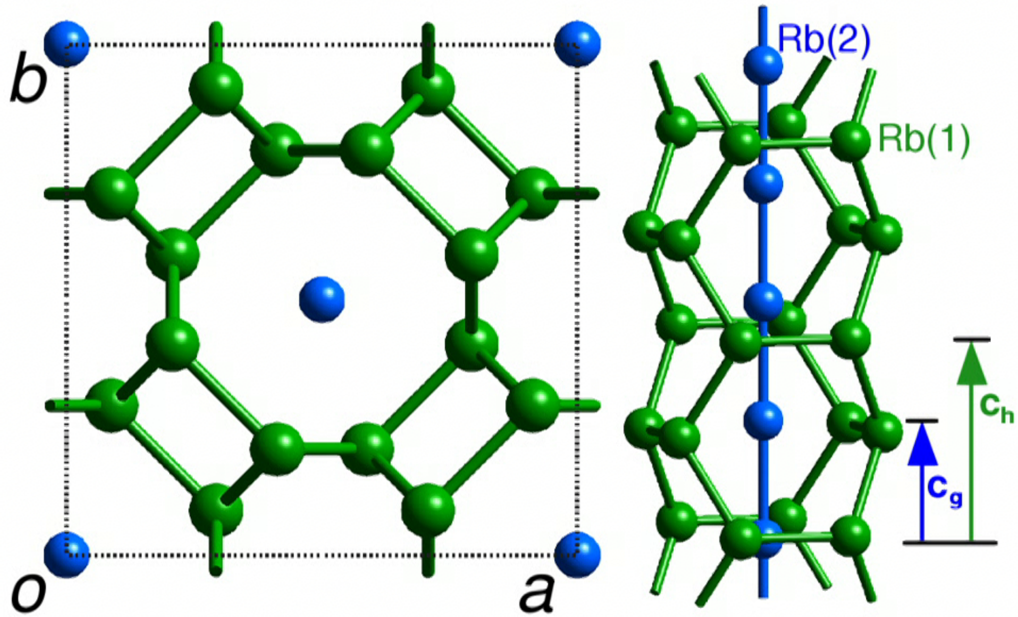

THE PERIODIC TABLE
1 IA
2 IIA
13 IIIA
14 IVA
15 VA
16 VIA
17 VIIA
18 VIIIA
3 IIIB
4 IVB
5 VB
6 VIB
7 VIIB
8 9 10 VIIIB
11 IB
12 IIB
SYMBOL
ATOMIC NUMBER
ATOMIC WEIGHT
NAME
( ) = ESTIMATES
H 1 1.008 Hydrogen
He 2 4.00 Helium
Li 3 6.94 Lithium
Be 4 9.01 Beryllium
B 5 10.81 Boron
C 6 12.01 Carbon
N 7 14.01 Nitrogen
O 8 16.00 Oxygen
F 9 19.00 Fluorine
Ne 10 20.18 Neon
Na 11 22.99 Sodium
Mg 12 24.31 Magnesium
Al 13 26.98 Aluminum
Si 14 28.09 Silicon
P 15 30.97 Phosphorus
S 16 32.07 Sulfur
Cl 17 35.45 Chlorine
Ar 18 39.95 Argon
K 19 39.10 Potassium
Ca 20 40.08 Calcium
Sc 21 44.96 Scandium
Ti 22 47.88 Titanium
V 23 50.94 Vanadium
Cr 24 52.00 Chromium
Mn 25 54.94 Manganese
Fe 26 55.85 Iron
Co 27 58.93 Cobalt
Ni 28 58.69 Nickel
Cu 29 63.55 Copper
Zn 30 65.39 Zinc
Ga 31 69.72 Gallium
Ge 32 72.61 Germanium
As 33 74.92 Arsenic
Se 34 78.96 Selenium
Br 35 79.90 Bromine
Kr 36 83.80 Krypton
Rb 37 85.47 Rubidium
Sr 38 87.62 Strontium
Y 39 88.91 Yttrium
Zr 40 91.22 Zirconium
Nb 41 92.91 Niobium
Mo 42 95.94 Molybdenum
Tc 43 (97.9) Technetium
Ru 44 101.07 Ruthenium
Rh 45 102.91 Rhodium
Pd 46 106.42 Palladium
Ag 47 107.87 Silver
Cd 48 112.41 Cadmium
In 49 114.82 Indium
Sn 50 118.71 Tin
Sb 51 121.76 Antimony
Te 52 127.60 Tellurium
I 53 126.90 Iodine
Xe 54 131.29 Xenon
Cs 55 132.91 Cesium
Ba 56 137.33 Barium
La 57 138.91 Lanthanum
Hf 72 178.49 Hafnium
Ta 73 180.95 Tantalum
W 74 183.85 Tungsten
Re 75 186.21 Rhenium
Os 76 190.2 Osmium
Ir 77 192.22 Iridium
Pt 78 195.08 Platinum
Au 79 196.97 Gold
Hg 80 200.59 Mercury
Tl 81 204.38 Thallium
Pb 82 207.2 Lead
Bi 83 208.98 Bismuth
Po 84 (209) Polonium
At 85 (210) Astatine
Rn 86 (222) Radon
Fr 87 223.02 Francium
Ra 88 226.03 Radium
Ac 89 227.03 Actinium
Rf 104 (261) Rutherfordium
Db 105 (262) Dubnium
Sg 106 (263) Seaborgium
Bh 107 (262) Bohrium
Hs 108 (265) Hassium
Mt 109 (266) Meitnerium
Unnamed Discovery 110 Nov. 1994
Unnamed Discovery 111 Nov. 1994
Unnamed Discovery 112 1996
Unnamed Discovery 114 1999
Unnamed Discovery 116 1999
Unnamed Discovery 118 1999
ALKALI METALS
ALKALI EARTH METALS
HALOGENS
NOBLE GASES
LANTHANIDES
Ce 58 140.12 Cerium
Pr 59 140.91 Praseodymium
Nd 60 144.24 Neodymium
Pm 61 (145) Promethium
Sm 62 150.36 Samarium
Eu 63 152.97 Europium
Gd 64 157.25 Gadolinium
Tb 65 158.93 Terbium
Dy 66 162.50 Dysprosium
Ho 67 164.93 Holmium
Er 68 167.26 Erbium
Tm 69 168.93 Thulium
Yb 70 173.04 Ytterbium
Lu 71 174.97 Lutetium
ACTINIDES
Th 90 232.04 Thorium
Pa 91 231.04 Protactinium
U 92 238.03 Uranium
Np 93 237.05 Neptunium
Pu 94 (240) Plutonium
Am 95 243.06 Americium
Cm 96 (247) Curium
Bk 97 (248) Berkelium
Cf 98 (251) Californium
Es 99 252.08 Einsteinium
Fm 100 257.10 Fermium
Md 101 (257) Mendelevium
No 102 259.10 Nobelium
Lr 103 262.11 Lawrencium
HAYDEN McNEIL SPECIALTY PRODUCTS
www.hmpublishing.com
© Hayden-McNeil Specialty Products

A Hierarchy of Responses to Pressure in Crystals

- Penetrating the repulsive region of intermolecular potentials
- Increasing coordination at main group and transition metal elements
- Decreasing the bond length of covalent bonds, and the size of anions
- A new world of electrons moving off their atoms, new modes of correlation

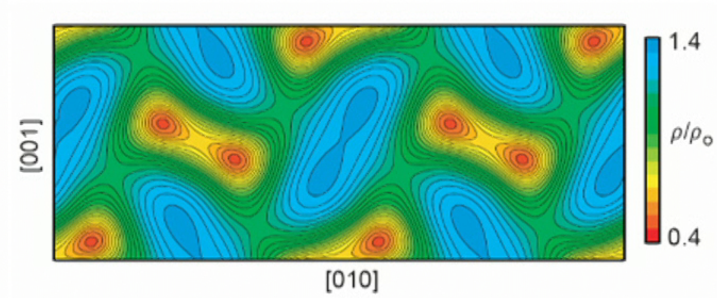
At 1 atm **Ba** is bcc. At 5.5 GPa **Ba-II** is fcc. At 25GPa **Ba-IV** goes into a structure with 288 atoms in a commensurate unit cell

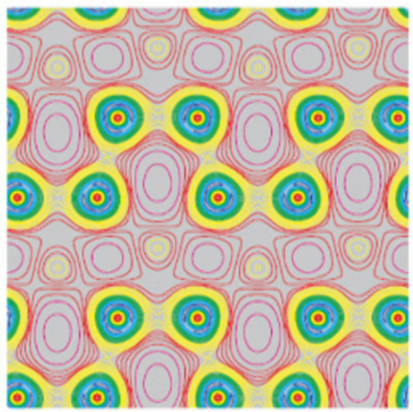
R.J. Nelmes, Edinburgh



Rb-IV at 17.2 GPa

Elemental Li



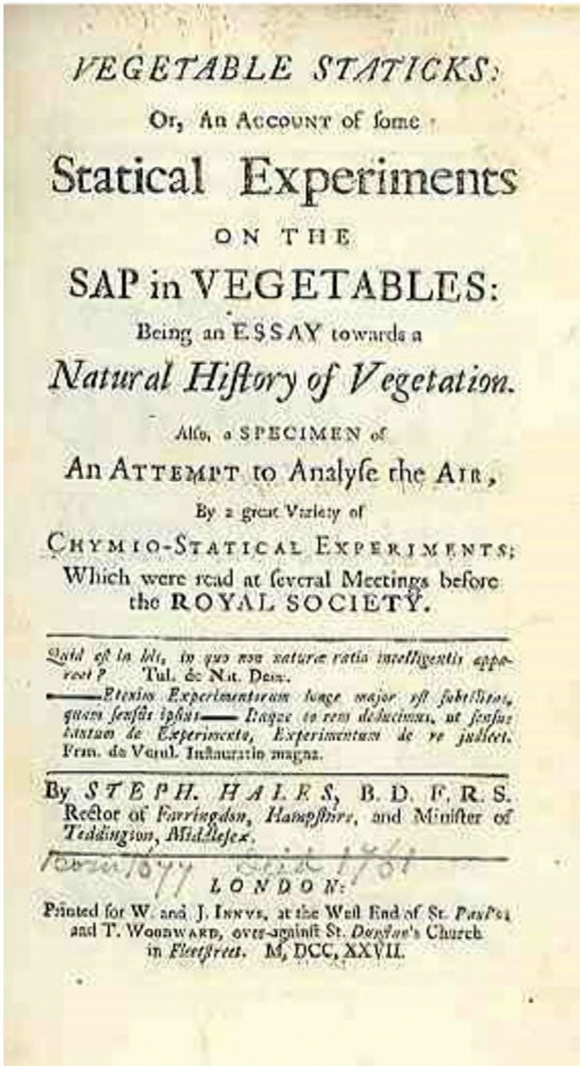


top: Ashcroft group 1999

botttom: Nelmes group 2003

close packing is not close enough

The packing of identical spheres maximizes at ~74% ($\pi/\sqrt{18}$)



VEGETABLE STATICKS:

Or, An ACCOUNT of ſome

Statical Experiments

ON THE

SAP in VEGETABLES:

Being an ESSAY towards a

Natural Hiſtory of Vegetation.

Alſo, a SPECIMEN of

An ATTEMPT to Analyſe the AIR,

By a great Variety of

CHYMIO-STATICAL EXPERIMENTS;

Which were read at ſeveral Meetings before the ROYAL SOCIETY.

Quid eſt in his, in quo non naturæ ratio intelligentis appareat? Tul. de Nat. Deor.

——*Etenim Experimentorum longe major eſt ſubtilitas, quam ſenſûs ipſius*——*Itaque eo rem deducimus, ut ſenſus tantum de Experimento, Experimentum de re judicet.* Fran. de Verul. Inſtauratio magna.

By *STEPH. HALES*, B. D. F. R. S. Rector of *Farringdon*, *Hampſhire*, and Miniſter of *Teddington*, *Middleſex*.

Born 1677 Died 1761

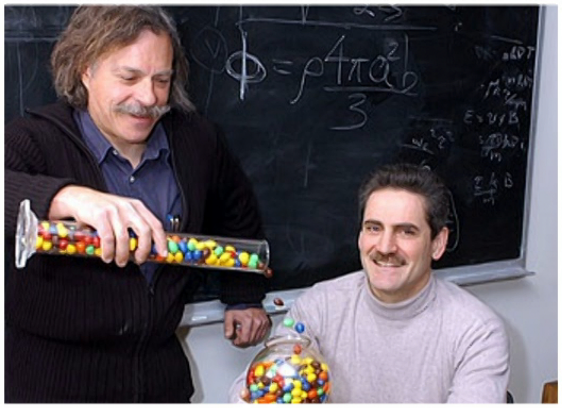
LONDON:

Printed for W. and J. INNYS, at the Weſt End of St. *Paul's*; and T. WOODWARD, over-againſt St. *Dunſtan's* Church in *Fleetſtreet*. M, DCC, XXVII.

"I compressed several fresh parcels of Pease in the same Pot, with a force equal to 1600, 800, and 400 pounds; in which Experiments, tho' the Pease dilated, yet they did not raise the lever, because what they increased in bulk was, by the great incumbent weight, pressed into the interstices of the Pease, which they adequately filled up, being thereby formed into pretty regular Dodecahedrons."

close packing is not close enough

The packing of identical spheres maximizes at ~74% (π/√18). If spheres are deformed, they can pack more efficiently -- *vide* work on ellipsoids and M&M's, and the trivial case of extreme deformation to cubes. Other polyhedra can also pack space fully

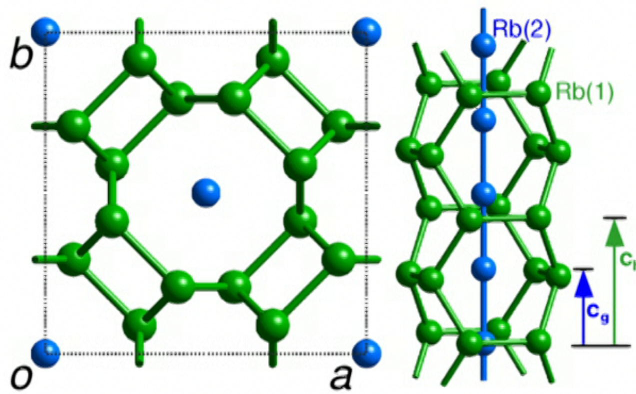


Paul Chaikin NYU

close packing is not close enough

The packing of identical spheres maximizes at ~74% ($\pi/\sqrt{18}$). If spheres are deformed, they can pack more efficiently -- *vide* work on ellipsoids and M&M's, and the trivial case of extreme deformation to cubes. Other polyhedra can also pack space fully.

Spheres of different size may pack more efficiently than spheres of identical size..



Phase Diagram and Structural Diversity of the Densest Binary Sphere Packings

Adam B. Hopkins,[1] Yang Jiao,[2] Frank H. Stillinger,[1] and Salvatore Torquato[1,2,3,4,5]

[1]*Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA*

[2]*Princeton Institute for the Science and Technology of Materials, Princeton University, Princeton, New Jersey 08544, USA*

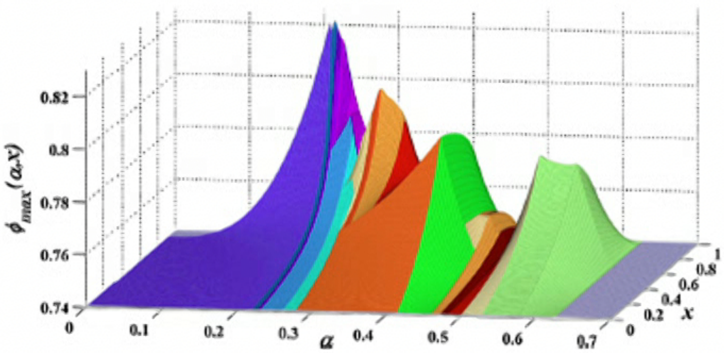
[3]*Department of Physics, Princeton University, Princeton, New Jersey 08544, USA*

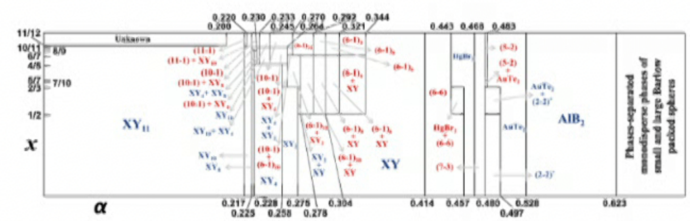
[4]*Princeton Center for Theoretical Science, Princeton University, Princeton, New Jersey 08544, USA*

[5]*Program in Applied and Computational Mathematics, Princeton University, Princeton, New Jersey 08544, USA*

(Received 22 June 2011; published 13 September 2011)

The densest binary sphere packings have historically been very difficult to determine. The only rigorously known packings in the α-x plane of sphere radius ratio α and relative concentration x are at the Kepler limit $\alpha = 1$, where packings are monodisperse. Utilizing an implementation of the Torquato-Jiao sphere-packing algorithm [S. Torquato and Y. Jiao, Phys. Rev. E **82**, 061302 (2010)], we present the most comprehensive determination to date of the phase diagram in (α, x) for the densest binary sphere packings. Unexpectedly, we find many distinct new densest packings.





close packing is not close enough

The packing of identical spheres maximizes at ~74% ($\pi/\sqrt{18}$). If spheres are deformed, they can pack more efficiently -- *vide* work on ellipsoids and M&M's, and the trivial case of extreme deformation to cubes. Other polyhedra can also pack space fully.

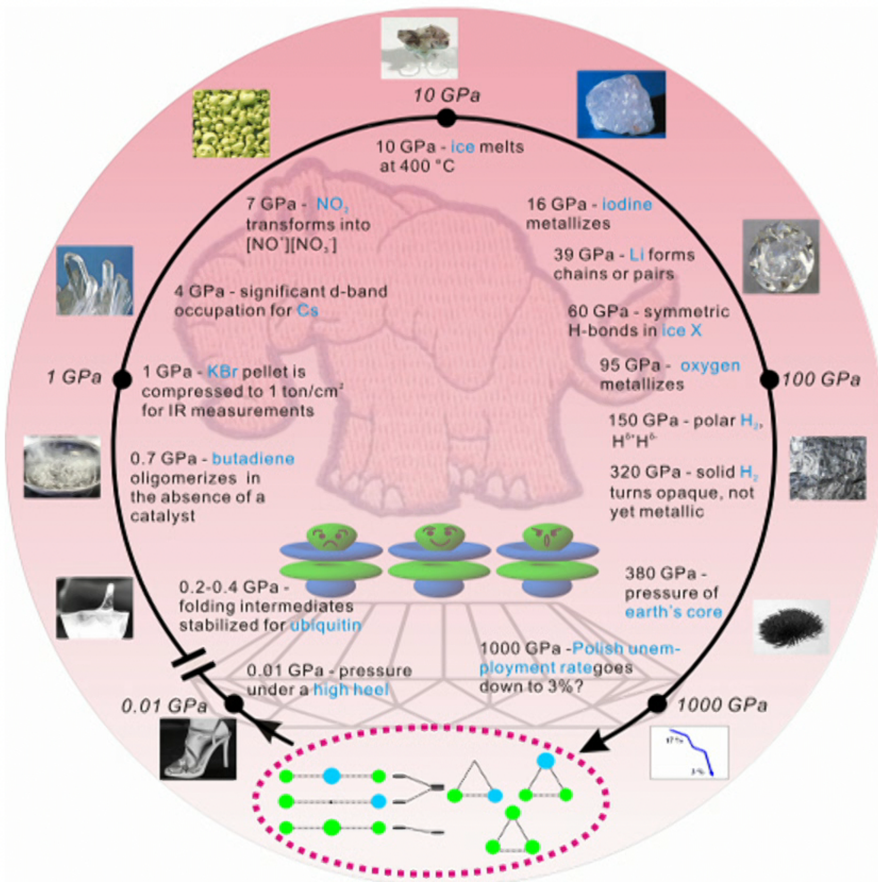
Spheres of different size may pack more efficiently than spheres of identical size. So…. at some pressure there may be a driving force for a lattice of element E to "electronically disproportionate" to $(E^{\delta+})_m(E^{\delta-})_n$ sublattices. Such sublattices could be of any dimensionality; there could be more than two sublattices.

Electron transfer between the sublattices may not be needed to differentiate them. One could imagine a disproportionation to sublattices A, B, C where each is roughly neutral, but characterized by different kinds of bonding – covalent, ionic, or metallic – within each sublattice.

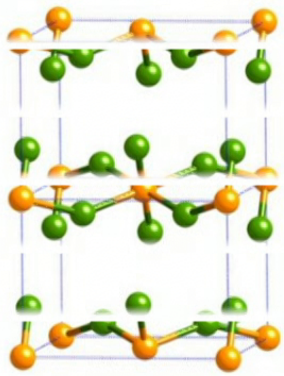
The Chemical Imagination at Work in *Very* Tight Places

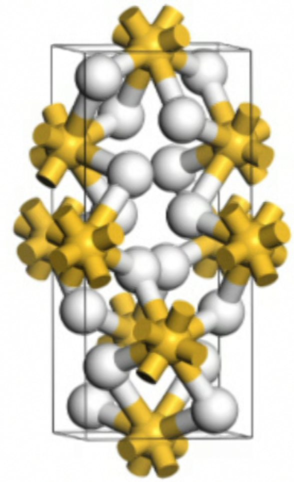
Wojciech Grochala, Roald Hoffmann, Ji Feng, and Neil W. Ashcroft

Angewandte Chemie, **46**(20), 3620-3642 (2007).

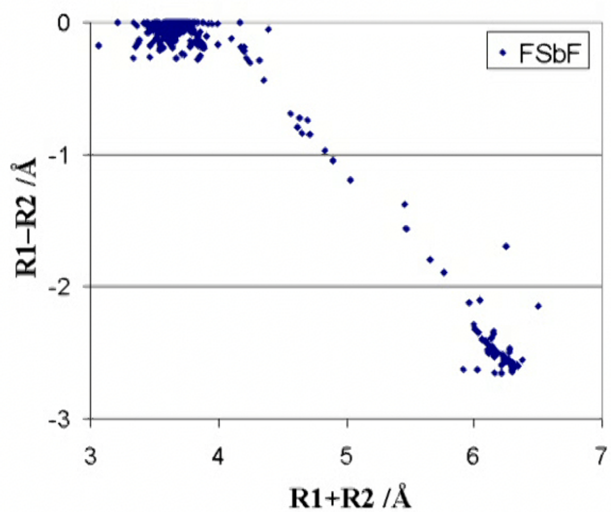


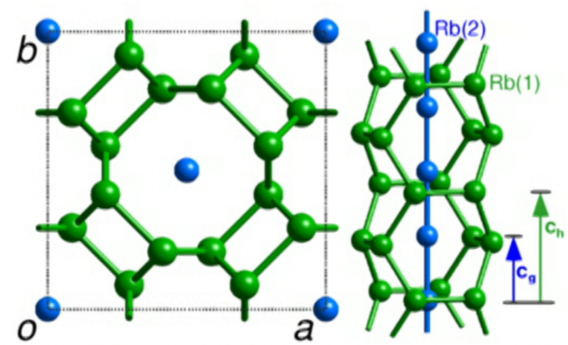
The Chemical Imagination at Work in *Very* Tight Places





$I4_1/a$

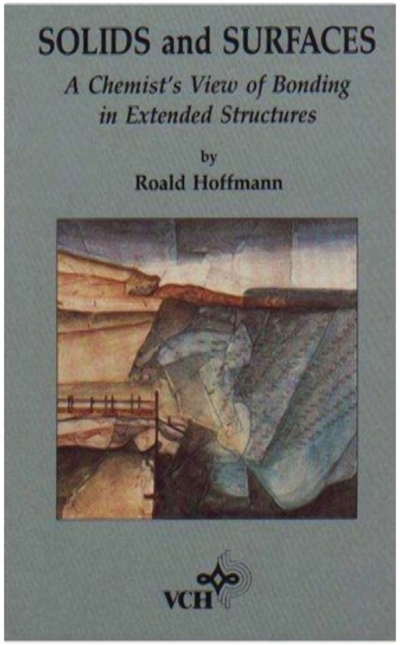


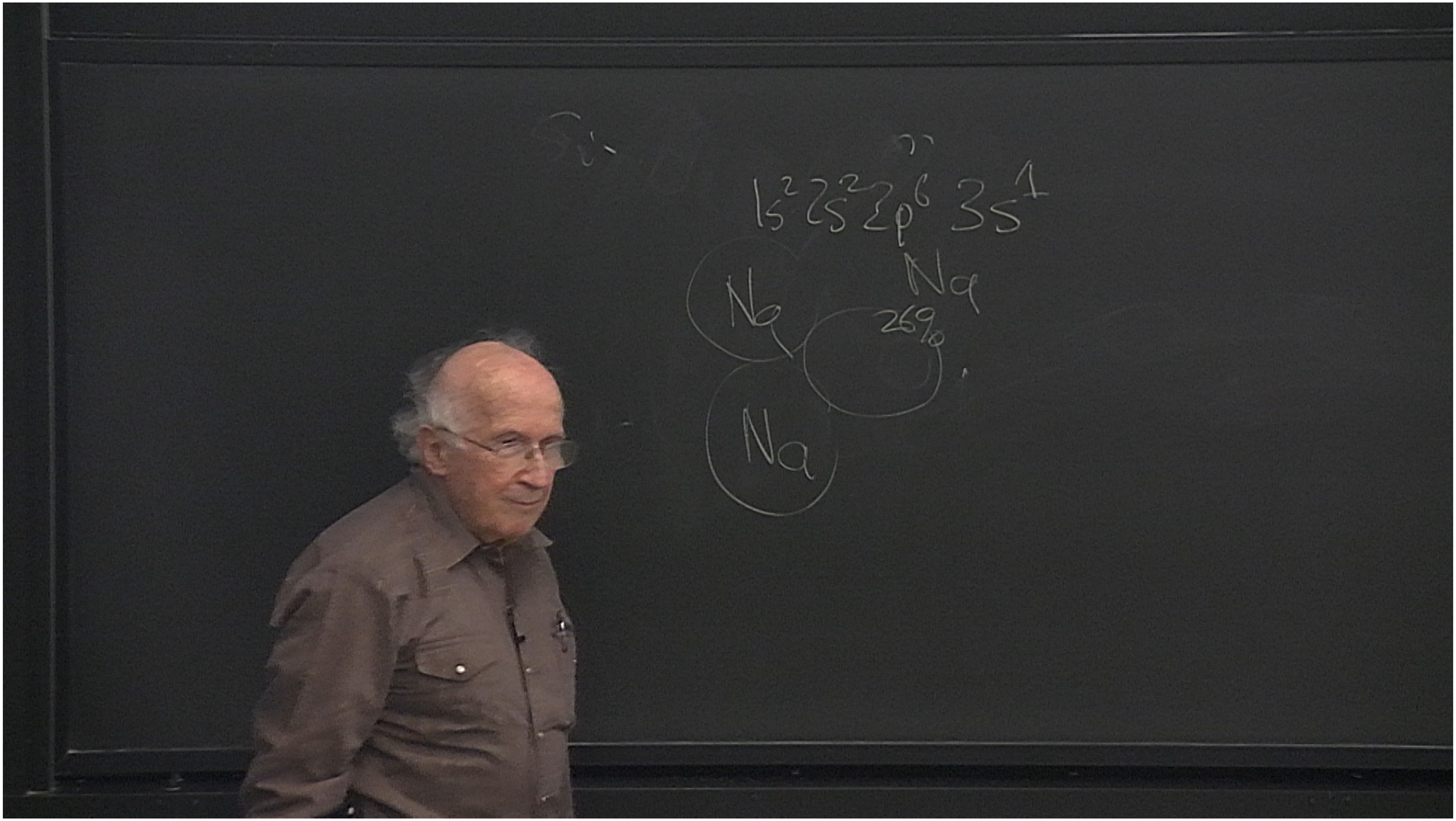


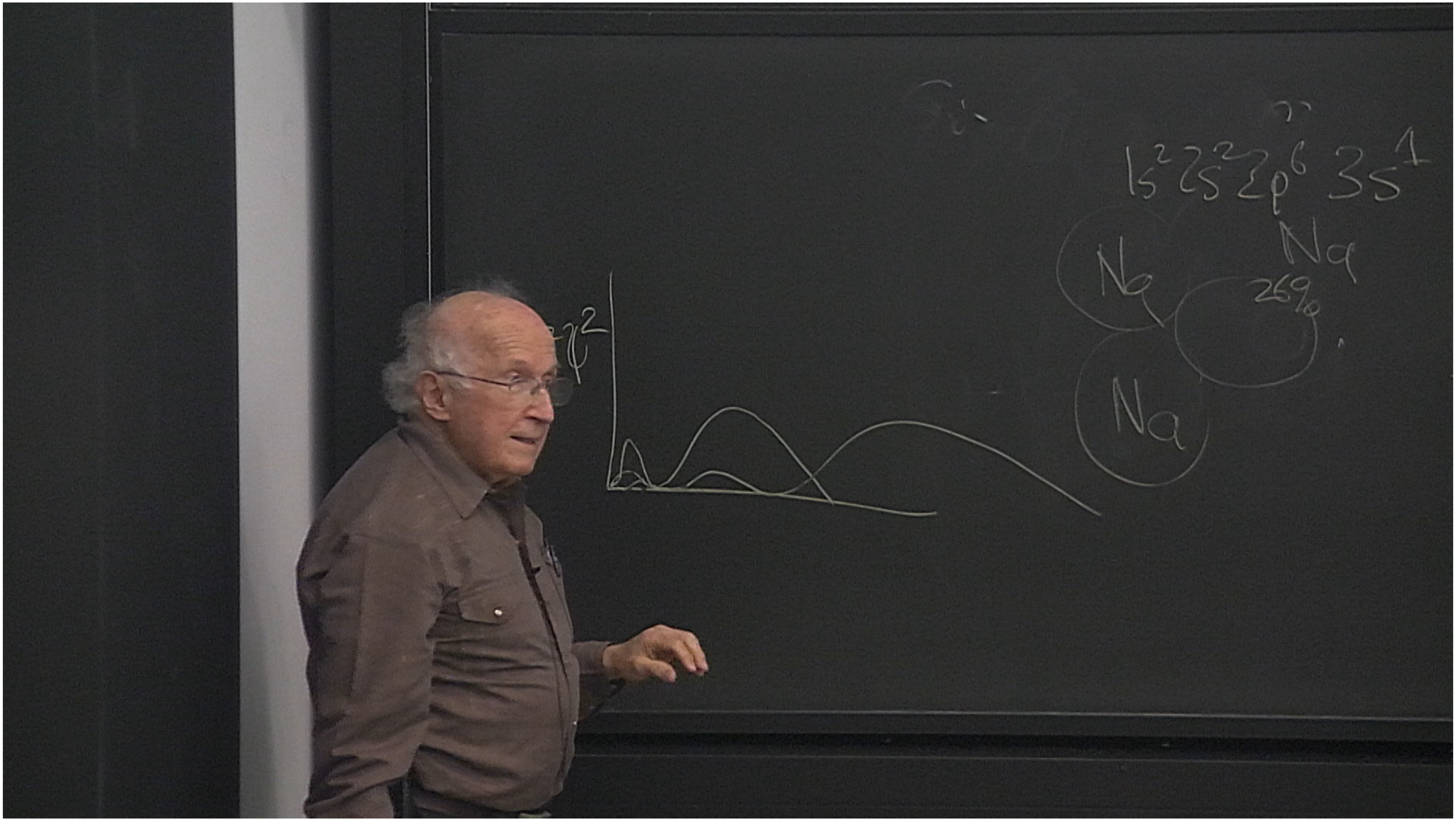
A playground for sure,

but also another reason,

a personal and philosophical one….

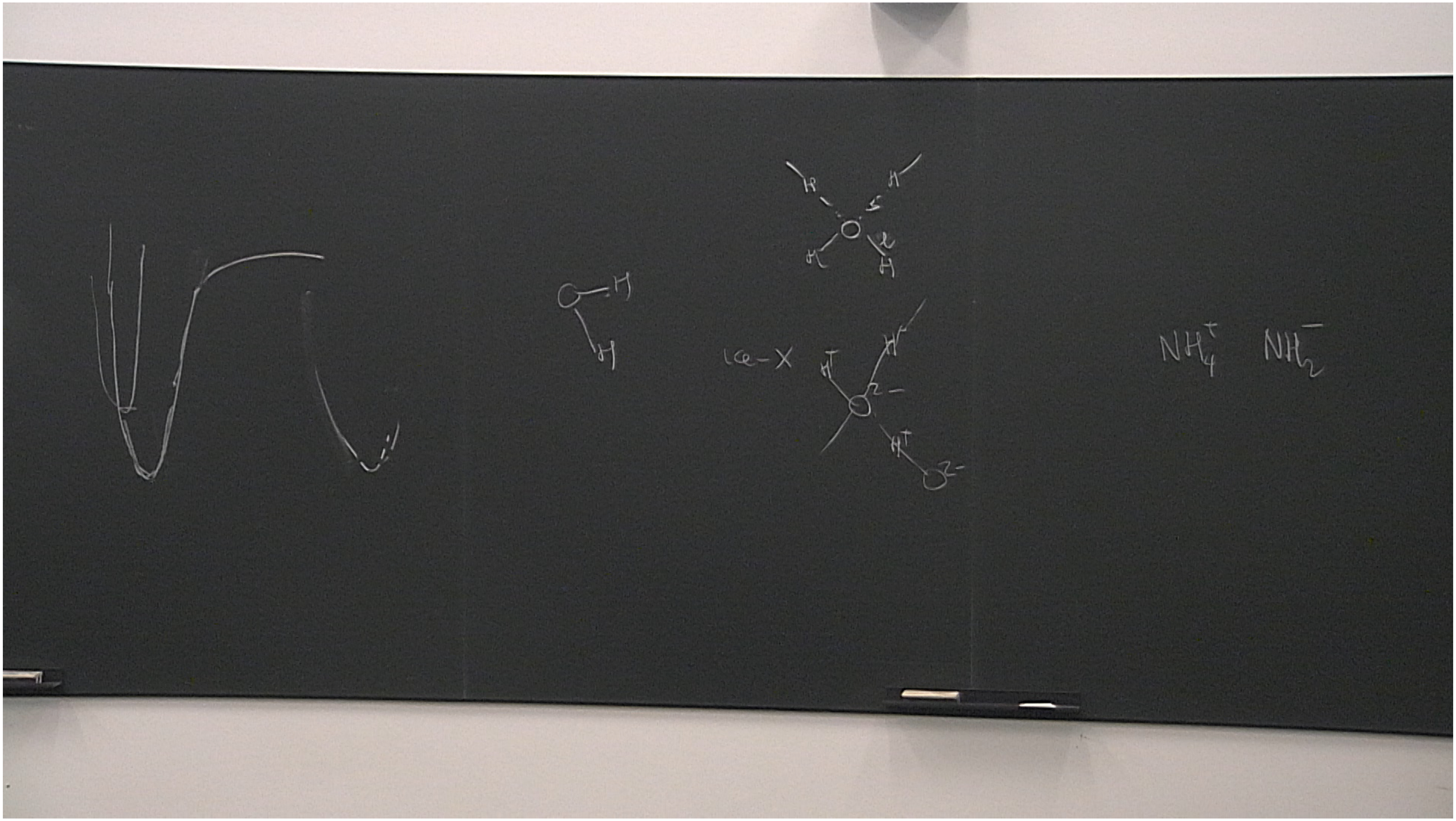



1s²2s²2p⁶ 3s¹
Na
Na
26%
Na



$1s^2 2s^2 2p^6 3s^1$
Na
Na
Na
26%


$r^2\psi^2$
$1s^2 2s^2 2p^6 3s^1$
Na
Na
Na
Na
26%


Ice-X
NH4+ NH2-