Atoms and Molecules:
A New Look at Basic Concepts

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Simple questions

- **Why some elements vigorously react, while others don't?**
- **Why some compounds are stable, while others are not?**
- **Why some parageneses exist, while others do not?**
- **Why high-pressure chemistry is so different?**

  -everything eventually becomes metallic.

  -strange structures of the elements (host-guest Na, K, Rb, Ca,…).

  -emergence of «strange» compounds Na_3Cl, ThH_{10}, etc.

  -«strange» CaS_5, Na_2S_5 exist already at normal conditions.

  -inert gases become more reactive.

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- **Why some molecules are easily formed and other are not? ("Can anyone explain P_4O_{18}?").**
- **Why is symmetry so prevalent among non-biological molecules?**

Simple questions

Why some elements vigorously react, while others don't?

Potassium reacts vigorously with water

Mg + Fe – no reaction!

Simple questions

Why some compounds are stable, while others are not?

<u>Stable in a wide range of conditions:</u>

NaCl
MgO
Al_2O_3
CO_2
SiO_2
Fe_2O_3
PbS
Mg_2SiO_4
…

<u>Stable at specific conditions:</u>

Na_2S, CaC_2 – hydrolize in water
P_2H_4 – ignites in air

<u>Unstable:</u>

NI_3

Simple questions

- **While some parageneses exist, while others don't?**

$2Au_2O_3 + 3Si \rightarrow \mathbf{4Au + 3SiO_2}$

$2HgO + SiS_2 \rightarrow \mathbf{2HgS + SiO_2}$

Simple questions

- **While some parageneses exist, while others don't?**

~~$2Au_2O_3 + 3Si$~~ $\rightarrow$ **$4Au + 3SiO_2$**

~~$2HgO + SiS_2$~~ $\rightarrow$ **$2HgS + SiO_2$**

Simple questions

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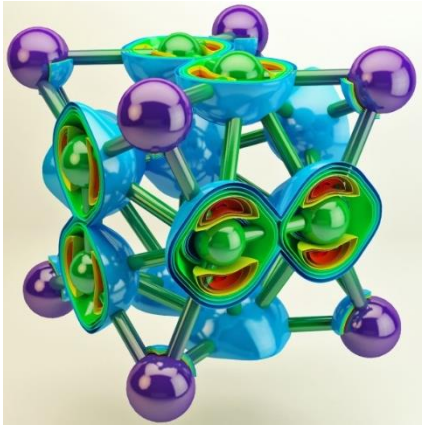
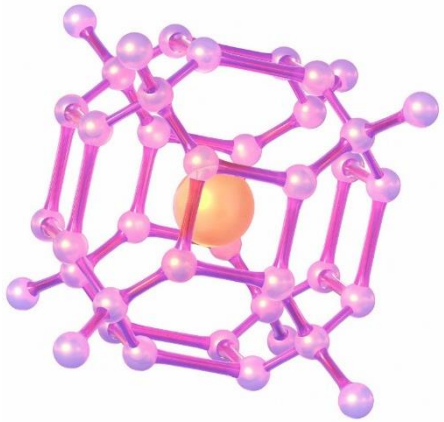
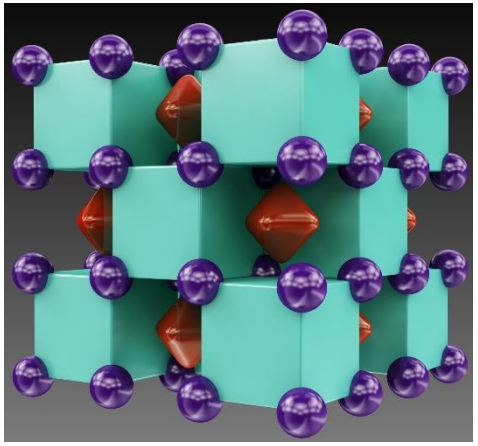


$NaCl_3$ (*Science* 2013)



ThH_{10} (*Mat. Today* 2020)



Na_2He (*Nature Chemistry* 2017)

I. (Not so) simple answers

Thermochemical electronegativity
(from energies of chemical bonds)

Elements are divided into electropositive and electronegative

Humphry Davy (1778-1829)

H. Davy and J.J. Berzelius introduce the notion of «electropositive» (EP) and «electronegative» (EN) elements.

EP+EN – form compounds.

EP+EP and EN+EN – often may not form compounds.

Jons Jacob Berzelius (1779-1848)

Electronegativity is a number characterizing an element (Pauling, 1932)

Linus Pauling (1901-1994)

- Energy of A-B bond is greater than half-sum of A-A and B-B energies. This extra energy is the ionic contribution:

$$D_{AB} = D_{AB}^{cov} + \Delta X_{AB}^2$$

- $D_{cov} = (D_{AA}+D_{BB})/2$.
- $D_{ionic} = \Delta X^2$.
- Degree of ionicity depends on ΔX^2:

$$f(\Delta X) = 1 - e^{-k\cdot\Delta X^2} \qquad (k = 1/4)$$

- Dimensionality: $eV^{1/2}$.
- Most widely used scale, «golden standard».

Pauling's electronegativity scale

Electronegativity increases

Period																		
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.6
6	Cs 0.79	Ba 0.89	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 2.33	Bi 2.02	Po 2.0	At 2.2	Rn
7	Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo
Lanthanides	*	La 1.1	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27		
Actinides	**	Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.3		

$$D_{AB} = D_{AB}^{cov} + \Delta X_{AB}^{2}$$

$K + H_2O = KOH + H_2$

Maximally ionic compound is formed

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Lanthanides	*	La 1.1	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27		
Actinides	**	Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.3		

$$D_{AB} = D_{AB}^{cov} + \Delta X_{AB}^{2}$$

B_2O_3 + 3Mg = 2B + 3MgO

Maximally ionic compound is formed

Pauling's electronegativity scale

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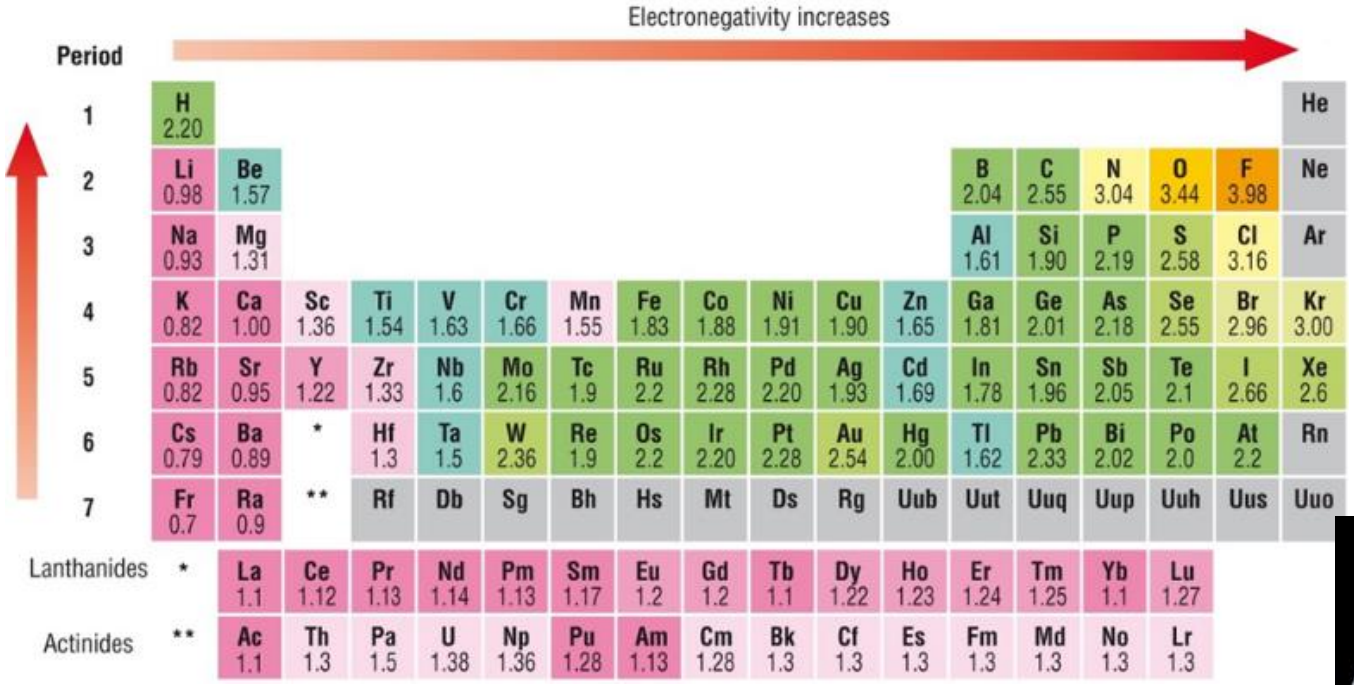
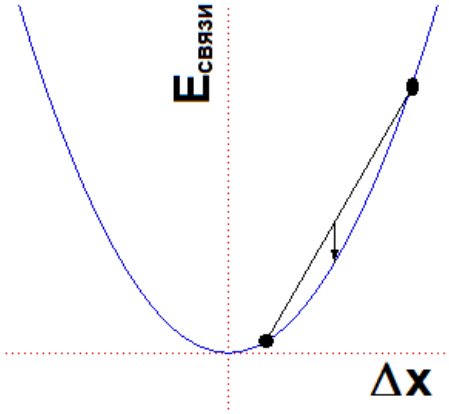
$$D_{AB} = D_{AB}^{cov} + \Delta X_{AB}^{2}$$

$CH_4 + 2O_2 = CO_2 + 2H_2O + Q$.
Q = 8.3 eV (exp.), 8.8 eV (from electronegativities).
Maximally ionic compound is formed

Pauling's electronegativity scale





$$D_{AB} = D_{AB}^{cov} + \Delta X_{AB}^{2}$$

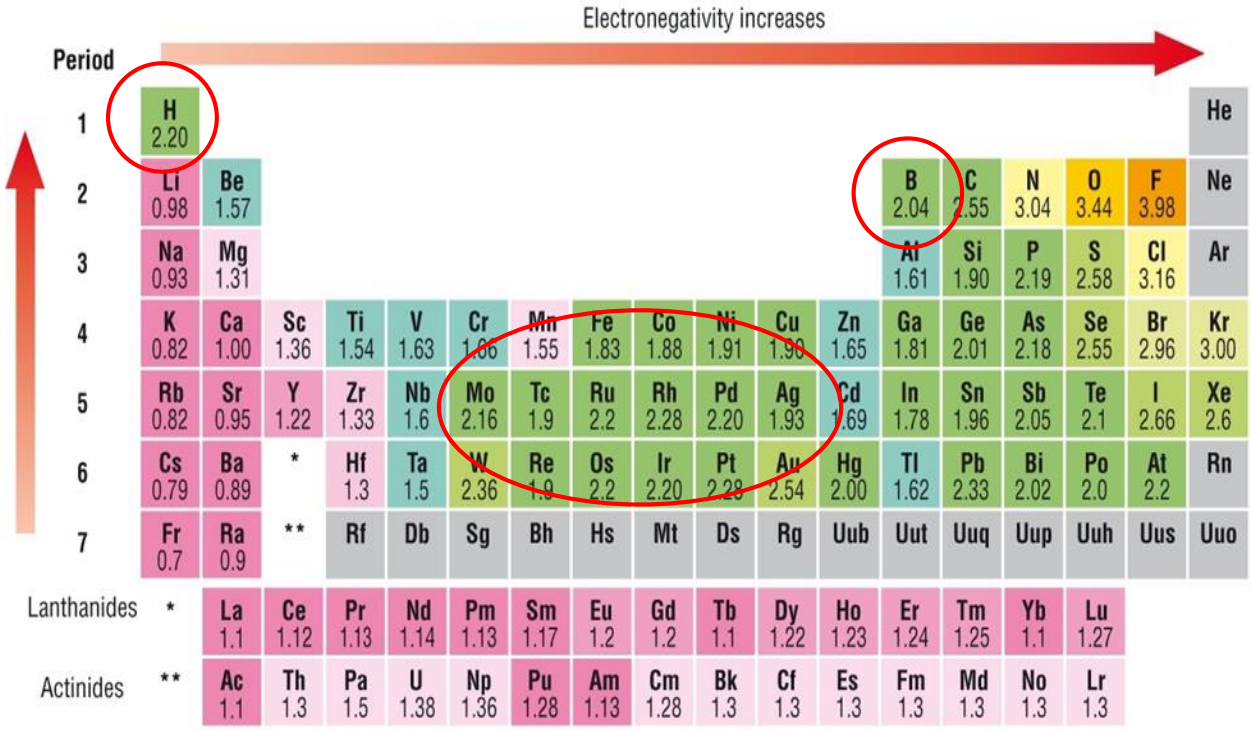
Coexistence of maximally and minimally ionic compounds – $HgS+SiO_2$, not $HgO+SiS_2$.

«Natural selection of minerals» (Urusov, 1998): only few compounds can survive in multicomponent systems.

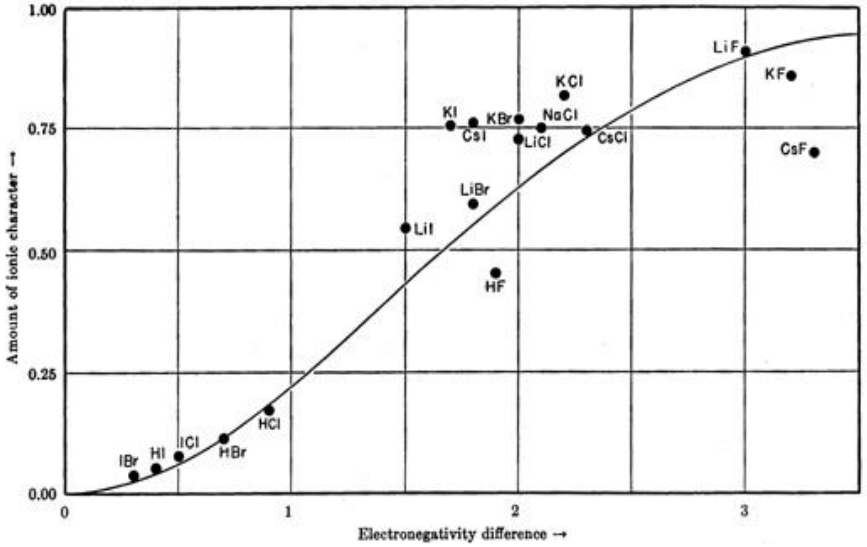
Problems of Pauling's scale

- Strange: borides and hydrides of W, Mo, Ru, Rh, Pd, Os, Ir, Pt, Au should have negative charge on the metal and positive – on B (H).
- Strange dimensionality - $eV^{1/2}$.
- Very often wrong predictions of direction of reactions:

$2NaF + CaCl_2 = 2NaCl + CaF_2$. Q = +0.23 eV (prediction), -0.92 eV (exp.)



Electronegativity determines many properties



Ionicity degree as a function of electronegativity difference
(L.Pauling, "The nature of the chemical bond")

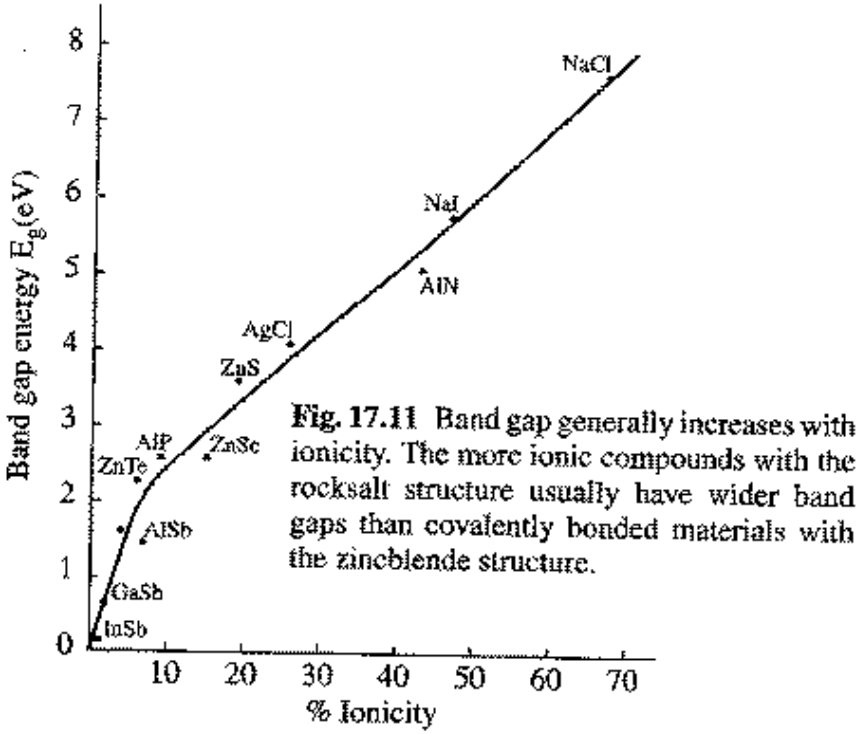


Fig. 17.11 Band gap generally increases with ionicity. The more ionic compounds with the rocksalt structure usually have wider band gaps than covalently bonded materials with the zincblende structure.

Band gap as a function of ionicity degree.
(R. Newnham, "Properties of materials")

Hardness of materials

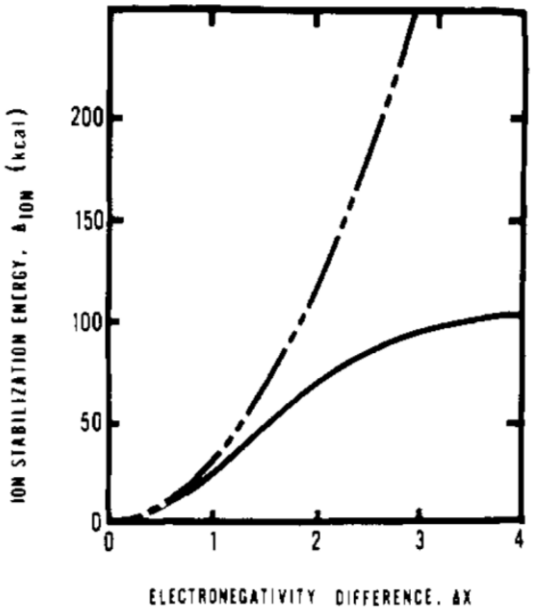
[Li et al., Phys. Rev. Lett. 2009; Lyakhov & Oganov, PRB 2011]:

$$H_k(\mathrm{GPa}) = 423.8 N_v X_{ab} e^{-2.7 f_i} - 3.4$$

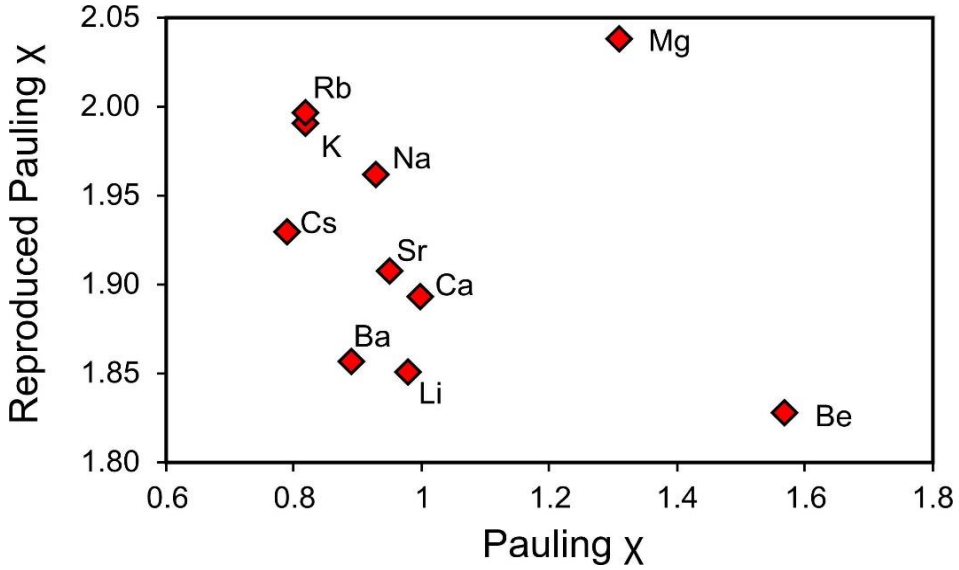
Nv - bond density
V - volume
Nab - number of bonds of type ab
Xab - "bond electronegativity"
fi - bond ionicity

Problems of Pauling's scale

Works poorly for strongly ionic bonds.
Overestimation of ionic energy (Matcha, 1983).



Calibrating on fluorides, one gets absurd results: X(Cs)>X(Li)>X(Be).



New scale of electronegativities

[Tantardini, Oganov, *Nature Communications*, 2021]

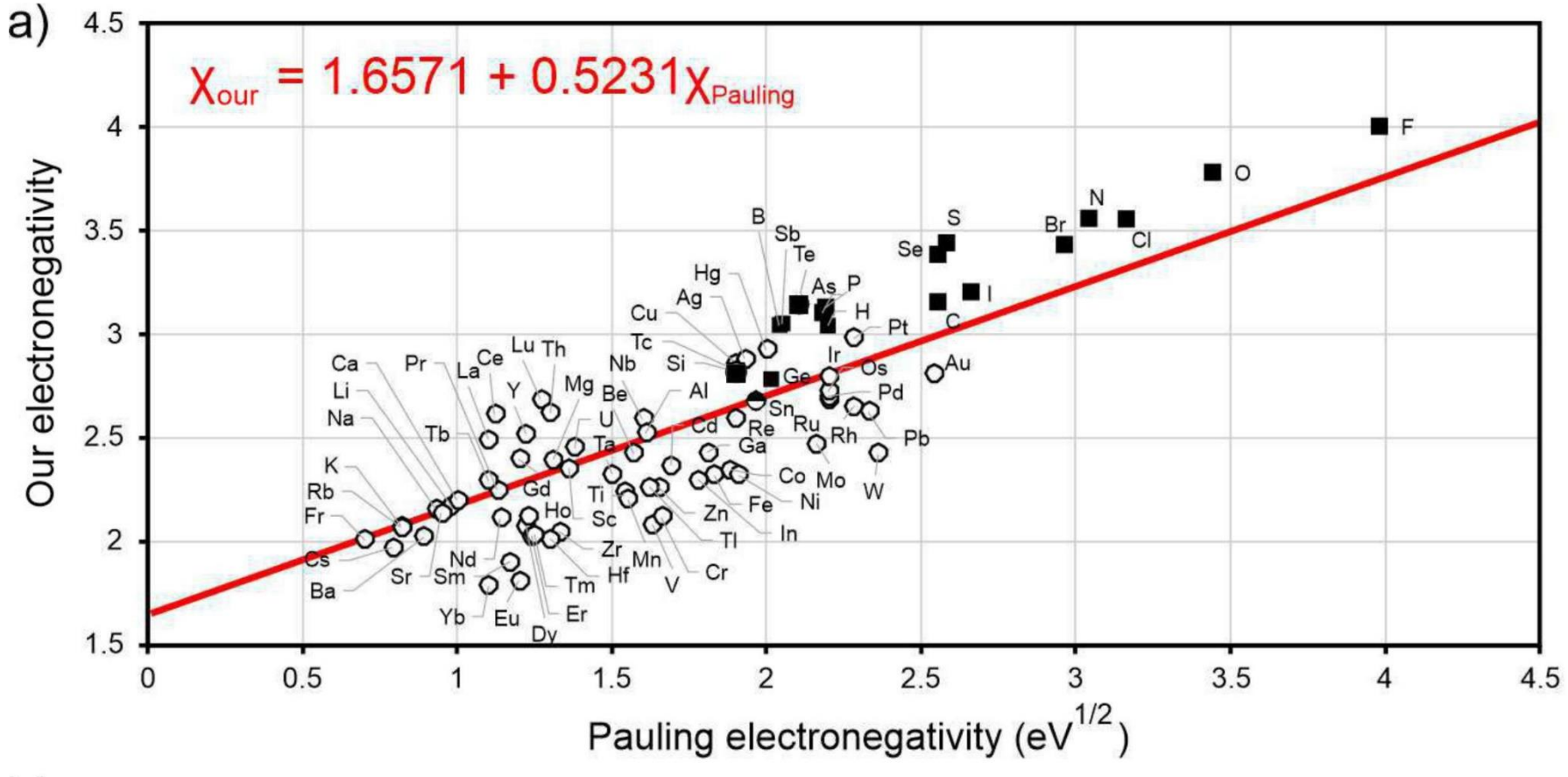
$$D_{AB} = D_{AB}^{cov} \cdot (1 + \Delta X_{AB}^2)$$

- $D_{ionic}/D_{cov} = \Delta X^2$.
- $D_{cov} = (D_{AA}+D_{BB})/2$.
- Electronegativity is dimensionless.

1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1 H 3.04																	2 He 4.42
3 Li 2.17	4 Be 2.42											5 B 3.04	6 C 3.15	7 N 3.56	8 O 3.78	9 F 4.00	10 Ne 4.44
11 Na 2.15	12 Mg 2.39											13 Al 2.52	14 Si 2.82	15 P 3.16	16 S 3.44	17 Cl 3.56	18 Ar 3.57
19 K 2.07	20 Ca 2.20	21 Sc 2.35	22 Ti 2.23	23 V 2.08	24 Cr 2.12	25 Mn 2.20	26 Fe 2.32	27 Co 2.34	28 Ni 2.32	29 Cu 2.86	30 Zn 2.26	31 Ga 2.43	32 Ge 2.79	33 As 3.15	34 Se 3.37	35 Br 3.45	36 Kr 3.37
37 Rb 2.07	38 Sr 2.13	39 Y 2.52	40 Zr 2.05	41 Nb 2.59	42 Mo 2.47	43 Tc 2.82	44 Ru 2.68	45 Rh 2.65	46 Pd 2.70	47 Ag 2.88	48 Cd 2.36	49 In 2.29	50 Sn 2.68	51 Sb 3.05	52 Te 3.14	53 I 3.20	54 Xe 3.12
55 Cs 1.97	56 Ba 2.02		72 Hf 2.01	73 Ta 2.32	74 W 2.42	75 Re 2.59	76 Os 2.72	77 Ir 2.79	78 Pt 2.98	79 Au 2.81	80 Hg 2.92	81 Tl 2.26	82 Pb 2.62	83 Bi 2.69	84 Po 2.85	85 At 3.04	86 Rn 3.04
87 Fr 2.01	88 Ra 2.15		104 Rf 2.27	105 Db 2.38	106 Sg 2.51	107 Bh 2.48	108 Hs 2.52	109 Mt 2.66	110 Ds 2.73	111 Rg 2.83	112 Cn 3.03	113 Nh 2.49	114 Fl 2.57	115 Mc 2.21	116 Lv 2.42	117 Ts 2.61	118 Og 2.59

57 La 2.49	58 Ce 2.61	59 Pr 2.24	60 Nd 2.11	61 Pm 2.24	62 Sm 1.90	63 Eu 1.81	64 Gd 2.40	65 Tb 2.29	66 Dy 2.07	67 Ho 2.12	68 Er 2.02	69 Tm 2.03	70 Yb 1.78	71 Lu 2.68
89 Ac 2.22	90 Th 2.62	91 Pa 2.33	92 U 2.45	93 Np 2.35	94 Pu 2.22	95 Am 2.28	96 Cm 2.31	97 Bk 2.08	98 Cf 2.18	99 Es 2.29	100 Fm 2.38	101 Md 2.47	102 No 2.06	103 Lr 2.10

Good correlation and good separation into metals and non-metals



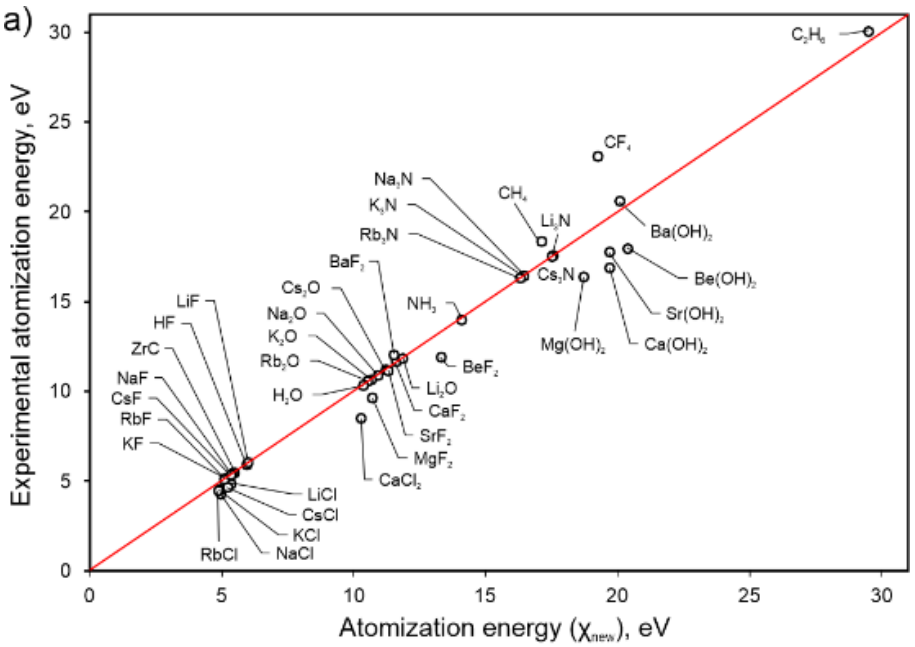
Correlates with Pauling's scale.

Empty symbols – metals, filled – non-metals.

New scale gives atomization energies of molecules within 5% of experiment

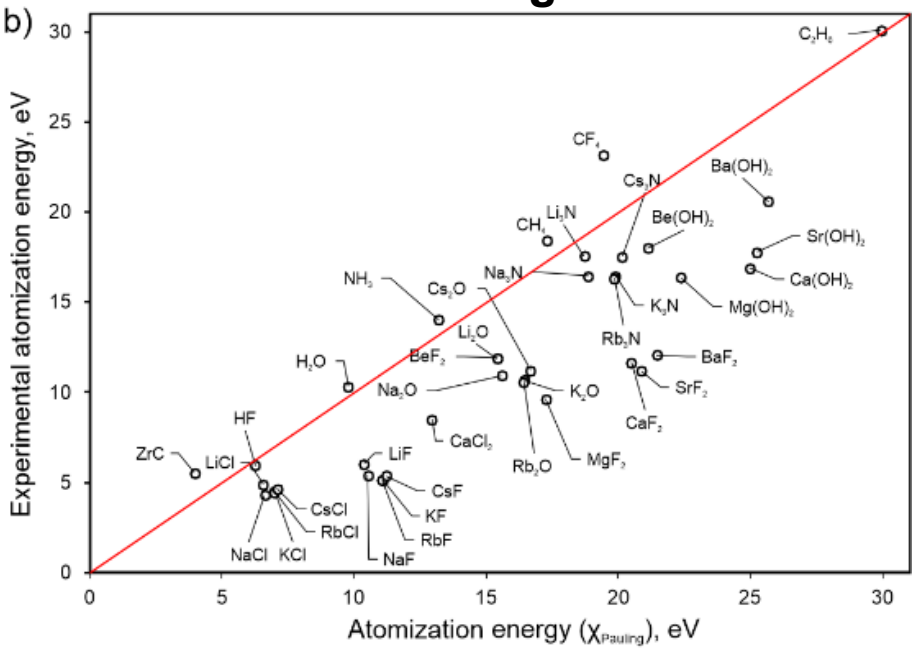
[Tantardini, Oganov, *Nature Communications*, 2021]

From our scale:



Relative error 5%

From Pauling's scale:

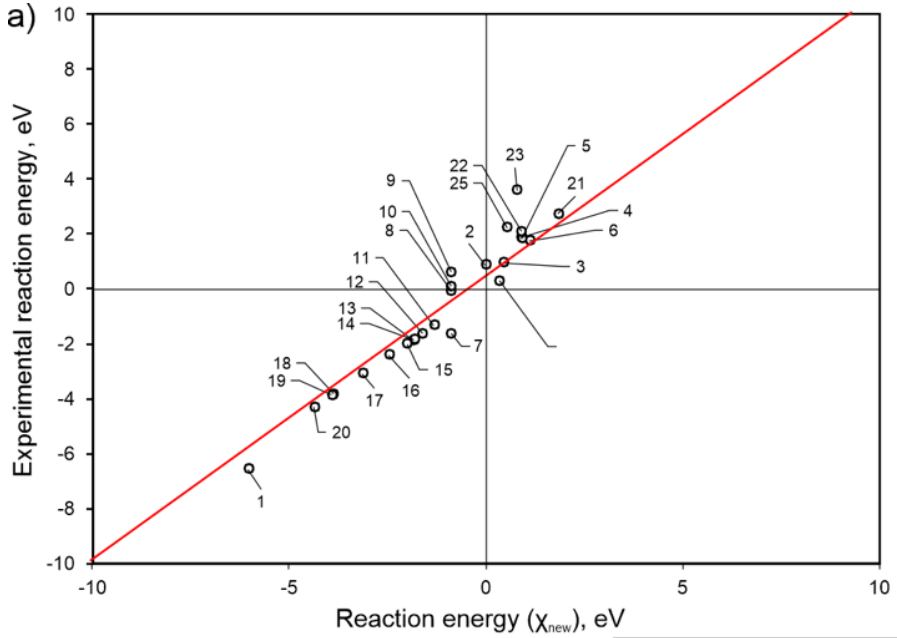


Relative error 40%

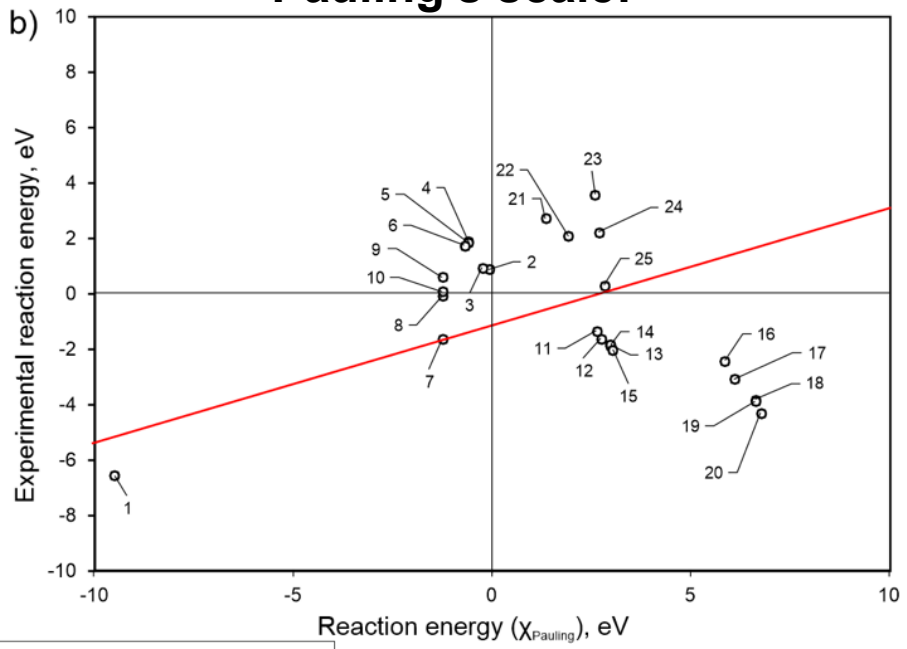
New scale correctly predicts directions of chemical reactions

[Tantardini, Oganov, *Nature Communications*, 2021]

Our scale:



Pauling's scale:



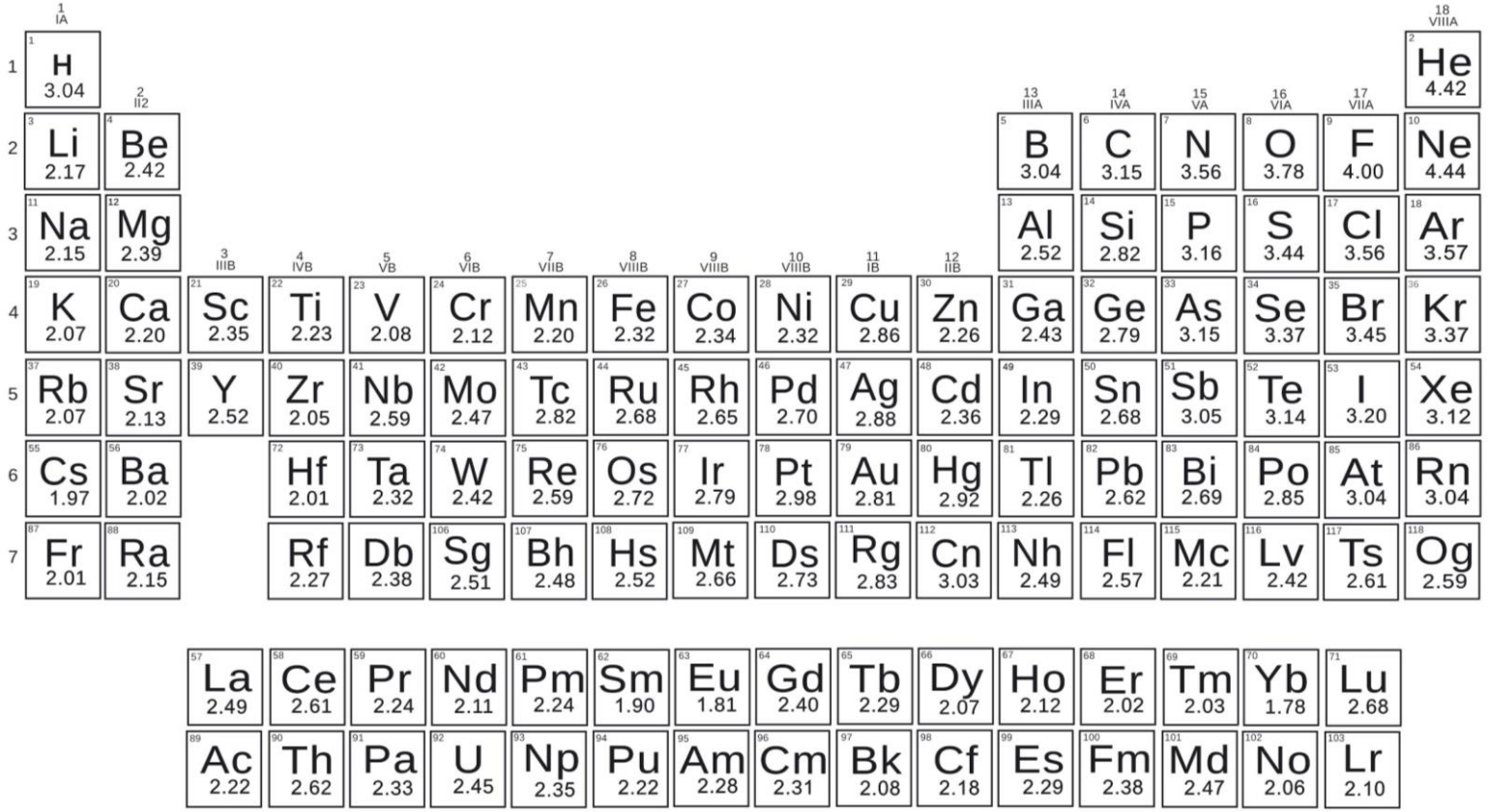
1 - $C_2H_6+Zr_2 \rightarrow 2ZrC+3H_2$
2 - $2LiF+CaCl_2 \rightarrow 2LiCl+CaF_2$
3 - $2NaF+CaCl_2 \rightarrow 2NaCl+CaF_2$
4 - $2KF+CaCl_2 \rightarrow 2KCl+CaF_2$
5 - $2RbF+CaCl_2 \rightarrow 2RbCl+CaF_2$
6 - $2CsF+CaCl_2 \rightarrow 2CsCl+CaF_2$
7 - $CH_4+HF \rightarrow CH_3F+H_2$
8 - $CH_3F+HF \rightarrow CH_2F_2+H_2$
9 - $CH_2F_2+HF \rightarrow CHF_3+H_2$
10 - $CHF_3+HF \rightarrow CF_4+H_2$
11 - $Li_2O+2HF \rightarrow 2LiF+H_2O$
12 - $Na_2O+2HF \rightarrow 2NaF+H_2O$
13 - $K_2O+2HF \rightarrow 2KF+H_2O$
14 - $Rbi_2O+2HF \rightarrow 2RbF+H_2O$
15 - $Cs_2O+2HF \rightarrow 2CsF+H_2O$
16 - $2Li_3N+H_2O \rightarrow 3Li_2O+2NH_3$
17 - $2Na_3N+H_2O \rightarrow 3Na_2O+2NH_3$
18 - $2K_3N+H_2O \rightarrow 3K_2O+2NH_3$
19 - $2Rb_3N+H_2O \rightarrow 3Rb_2O+2NH_3$
20 - $2Cs_3N+H_2O \rightarrow 3Cs_2O+2NH_3$
21 - $Be(OH)_2+2HF \rightarrow BeF_2+2H_2O$
22 - $Mg(OH)_2+2HF \rightarrow MgF_2+2H_2O$
23 - $Ca(OH)_2+2HF \rightarrow CaF_2+2H_2O$
24 - $Sr(OH)_2+2HF \rightarrow SrF_2+2H_2O$
25 - $Ba(OH)_2+2HF \rightarrow BaF_2+2H_2O$

New scale of electronegativities

[Tantardini, Oganov, *Nature Communications*, 2021]

Oxidation of glucose: $C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O$.
Energy release: 30 eV (exp.), 33 eV (prediction).

Combustion of methane: $CH_4 + 2O_2 = CO_2 + 2H_2O$.
Energy release: 8.3 eV (exp.), 12.0 eV (prediction).
Combustion in fluorine: 19.7 eV (exp.), 19.2 eV (prediction).

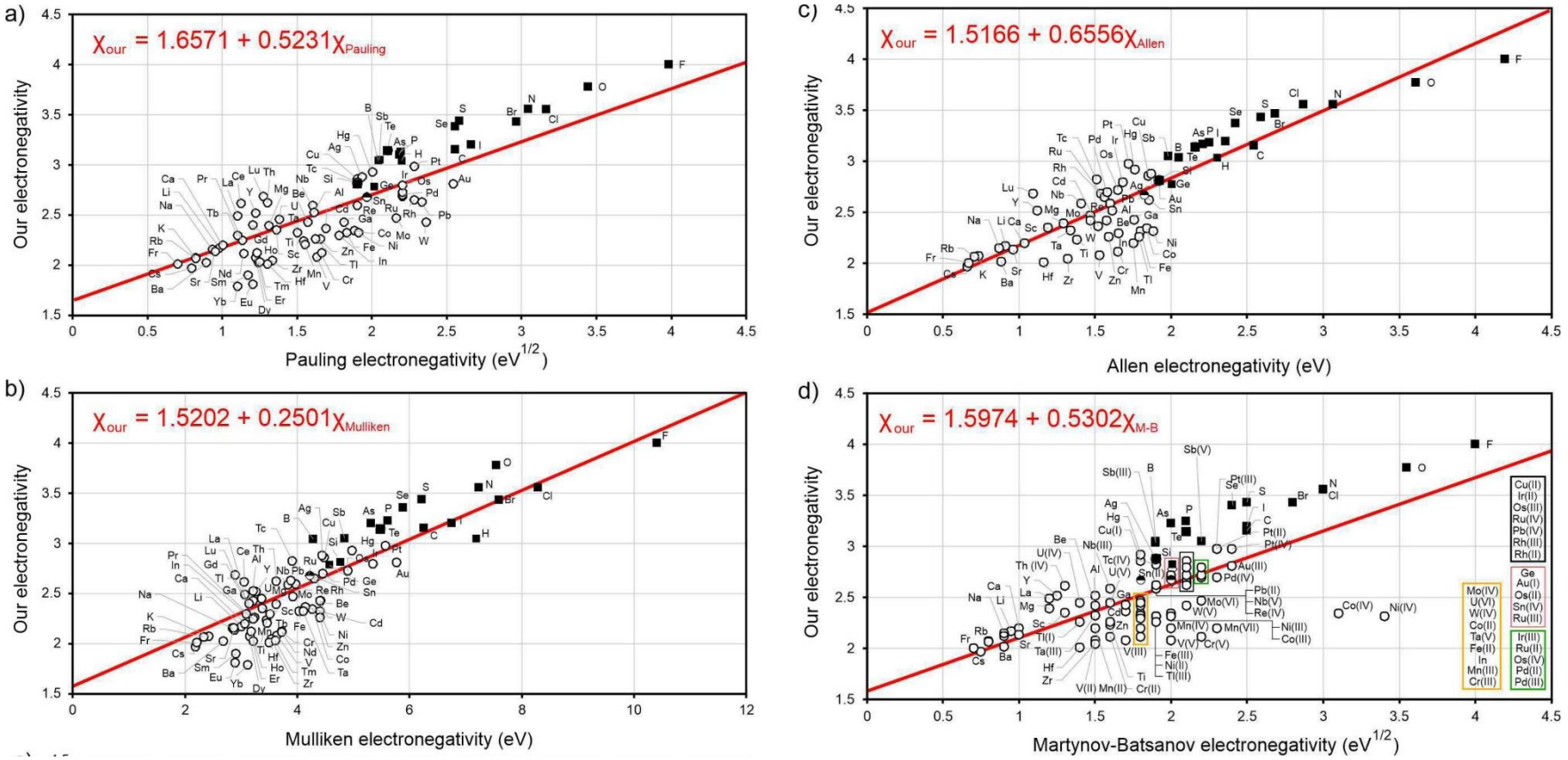


New scale correlates well with other scale and separates metals from non-metals

Correlations with scales:

(a) Pauling, (b) Mulliken, (c) Allen, (d) Martynov-Batsanov.

Empty symbols – metals, filles – non-metals.



New scale better identifies acid-forming elements ($X_H < X_X < X_O$)

Pauling

H 2.20

13	14	15	16	17
B 2.04	C 2.55	N 3.04	O 3.44	F 3.98
Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16
Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96
In 1.78	Sn 1.96	Sb 2.05	Te 2.10	I 2.66

Mulliken

H 7.18

13	14	15	16	17
B 4.29	C 6.26	N 7.23	O 7.54	F 10.41
Al 3.21	Si 4.77	P 5.62	S 6.22	Cl 8.29
Ga 3.15	Ge 4.55	As 5.31	Se 5.89	Br 7.59
In 3.04	Sn 4.27	Sb 4.89	Te 5.49	I 6.76

Allen

H 2.300

13	14	15	16	17
B 2.051	C 2.544	N 3.066	O 3.610	F 4.193
Al 1.613	Si 1.916	P 2.253	S 2.589	Cl 2.869
Ga 1.756	Ge 1.994	As 2.211	Se 2.424	Br 2.685
In 1.656	Sn 1.824	Sb 1.984	Te 2.158	I 2.359

Tantardini-Oganov

H 3.04

13	14	15	16	17
B 3.04	C 3.15	N 3.56	O 3.78	F 4.00
Al 2.52	Si 2.82	P 3.16	S 3.44	Cl 3.50
Ga 2.43	Ge 2.79	As 3.15	Se 3.37	Br 3.45
In 2.29	Sn 2.68	Sb 3.05	Te 3.14	I 3.20

Thanks to M. Syroeshkin (IOC RAS) for the idea and slide.

Simple questions

Why some elements vigorously react, while others don't?

Potassium reacts vigorously with water

Mg + Fe – no reaction!

Simple questions

Why some compounds are stable, while others are not?

<u>Stable in a wide range of conditions:</u>

NaCl
MgO
Al_2O_3
CO_2
SiO_2
Fe_2O_3
PbS
Mg_2SiO_4
…

<u>Stable at specific conditions:</u>

Na_2S, CaC_2 – hydrolize in water
P_2H_4 – ignites in air

<u>Unstable:</u>

NI_3

Simple questions

- **While some parageneses exist, while others don't?**

$2Au_2O_3 + 3Si \rightarrow \mathbf{4Au + 3SiO_2}$

$2HgO + SiS_2 \rightarrow \mathbf{2HgS + SiO_2}$

Simple questions

- **While some parageneses exist, while others don't?**

~~$2Au_2O_3 + 3Si$~~ $\rightarrow$ **$4Au + 3SiO_2$**

~~$2HgO + SiS_2$~~ $\rightarrow$ **$2HgS + SiO_2$**

II. (Not so) simple answers

Another definition of electronegativity (from properties of isolated atoms)

Electronegativity is the ability of an atom to shift electron density to itself

Robert Mulliken (1896-1986)

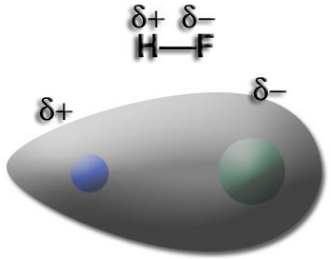
1934: X = (I+A)/2,
where I is ionization potential, A – electron affinity.

X = -(dE/dN) = -chemical potential of the electron in an atom!

Ralph Pearson (1919-)

1983 (with R. Parr): Chemical hardness $\eta = (I-A)/2$
$\eta = d^2E/dN^2$ – measure of stability of electron configuration.

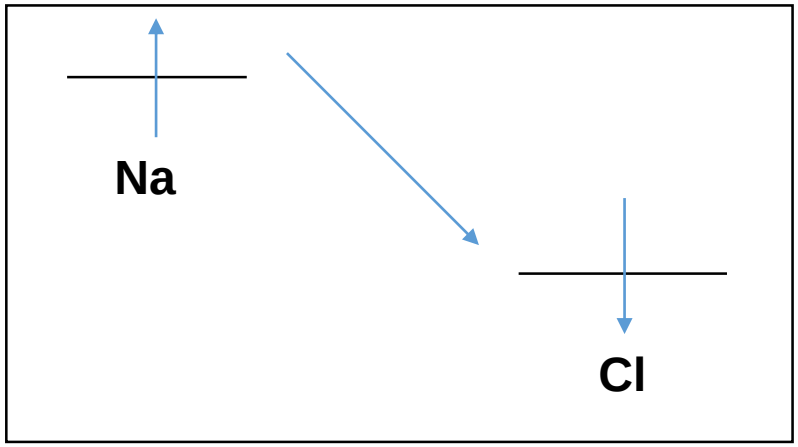
Определение: Electronegativity is the power of a bonded atom to attract electrons (or charge density) to itself.



Green Book, 2nd ed., p. 20 PAC, 1994, 66, 1077 (Glossary of terms used in physical chemistry (IUPAC Recommendations 1994)), page 1111

ЭElectronegativity is the ability of an atom to shift electron density to itself

Electronegativity X = -(dE/dN) = -chemical potential of the electron in an atom!

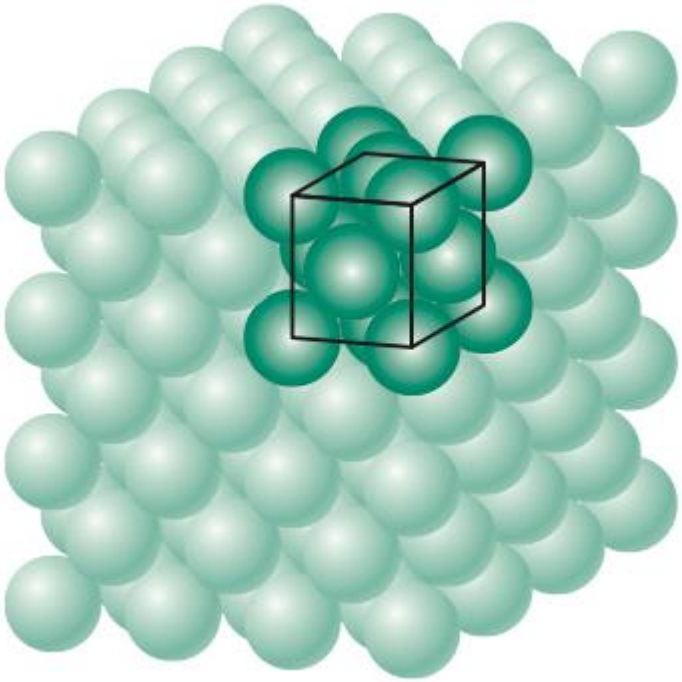


Explains charge transfer and energy release.

- Electronegativity $X = (I+A)/2$ ~ position of the Fermi level.
- Chemical hardness $\eta = (I-A)/2$ = half of HOMO-LUMO gap ~ half of band gap.
- Electronegativity depends on the number of electrons: $X(N) = X_0 - \eta N$
- At normal conditions A is small, hence $\eta \approx X$ and is not very interesting. Is it so under pressure?

Helium matrix method

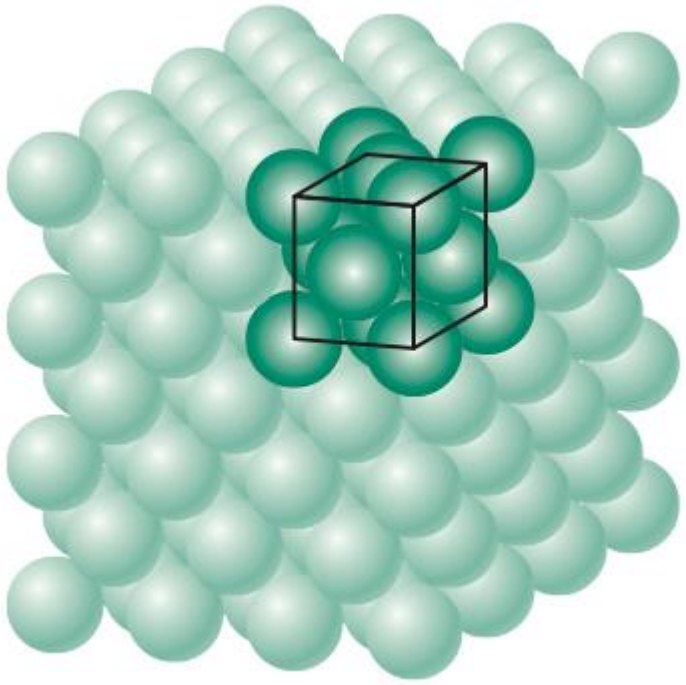
- Pressure is created by other atoms (in vacuum P=0).
- Large, isotropic and maximally inert matrix. We chose He with fcc-structure and large 3x3x3 supercell, where one He is replaced by atom of interest.
- Compress the system to pressure of interest and calculate the properties.

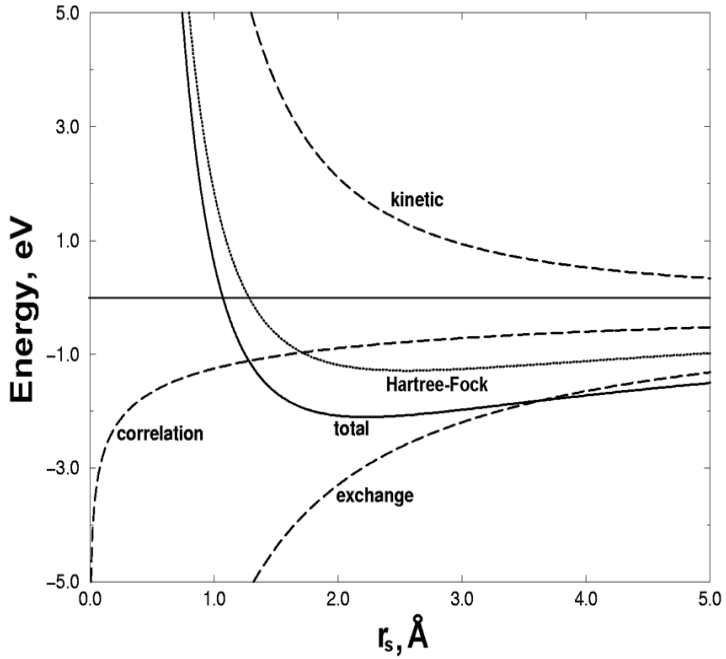


Paradox of electronegativity under pressure

X = (I+A)/2, but:

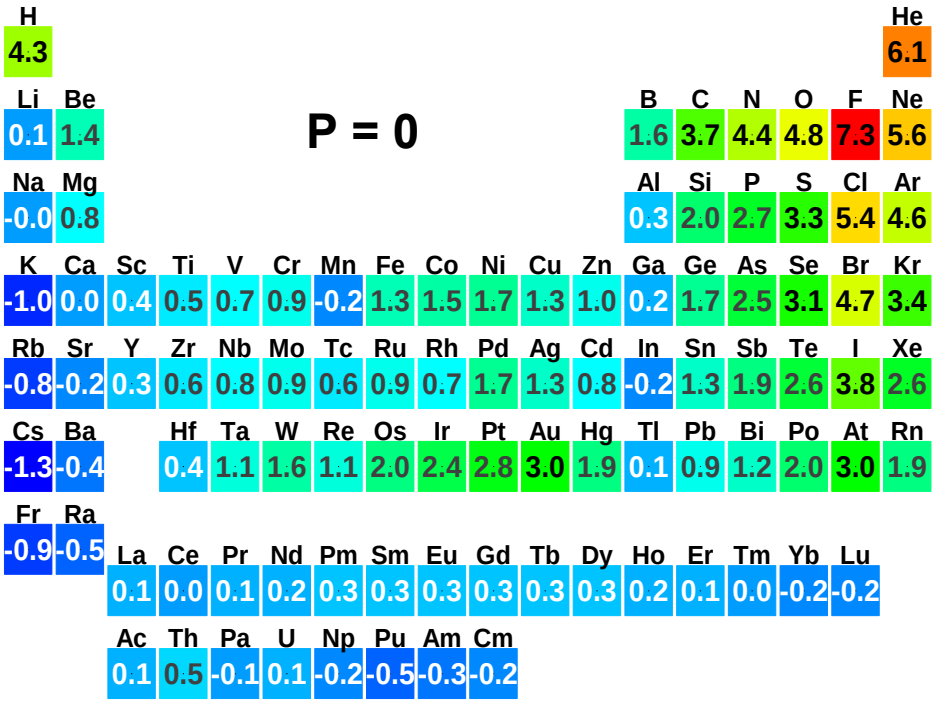
- I and A are not energies, but enthalpies.
- Reservois of electrons – not vacuum, but electron gas under pressure P.
- Our electronegativity = -chemical potential of electrons in the atom relative to electron gas at the same pressure.
- For metals electronegativity is close to zero!



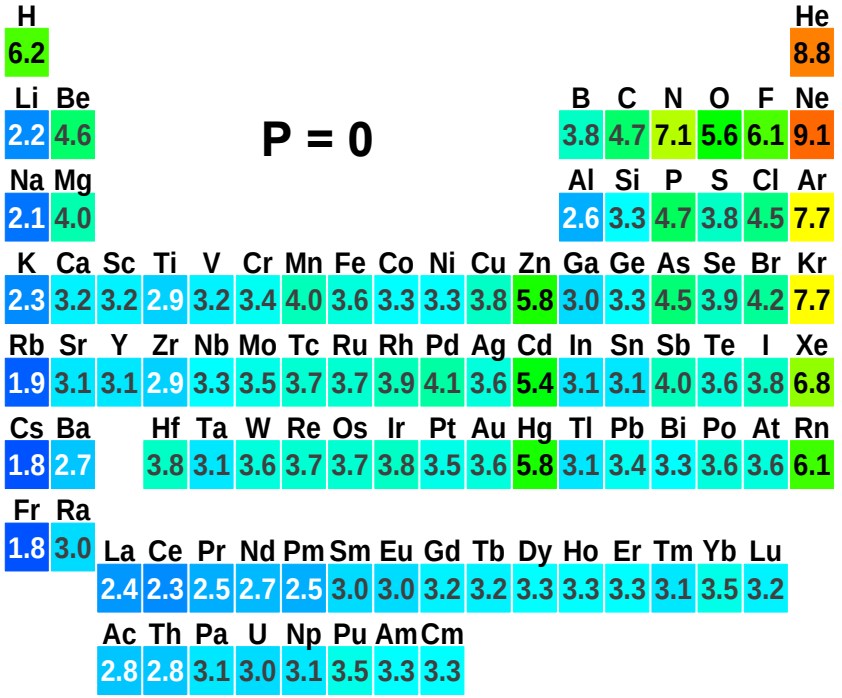


Electronegativity under pressure: key to understanding high-pressure chemistry

[Dong & Oganov, *PNAS* 2022]



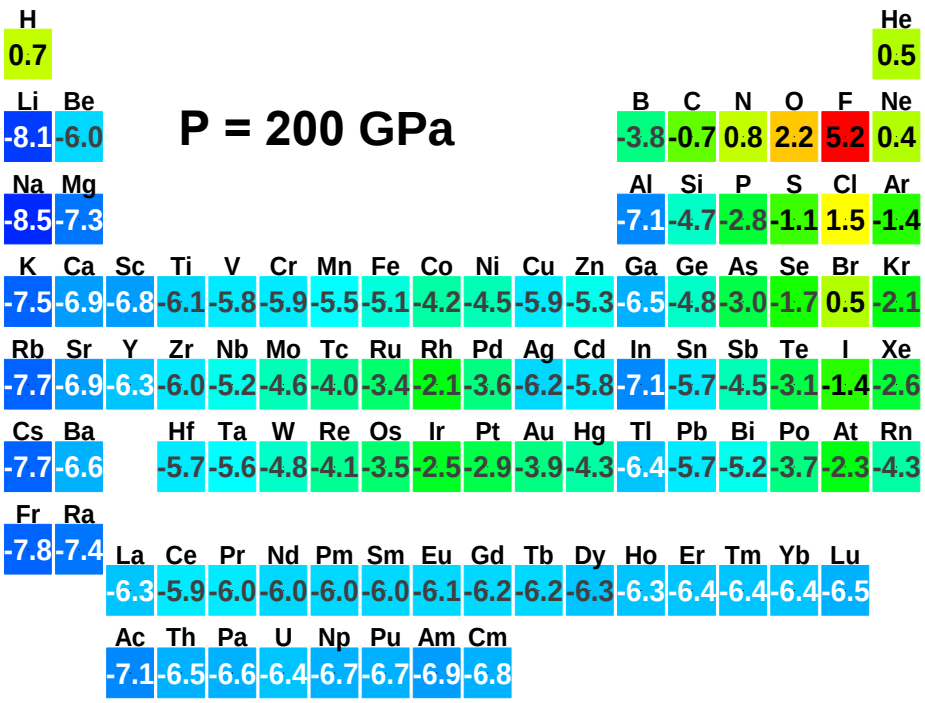
Electronegativity



Chemical hardness

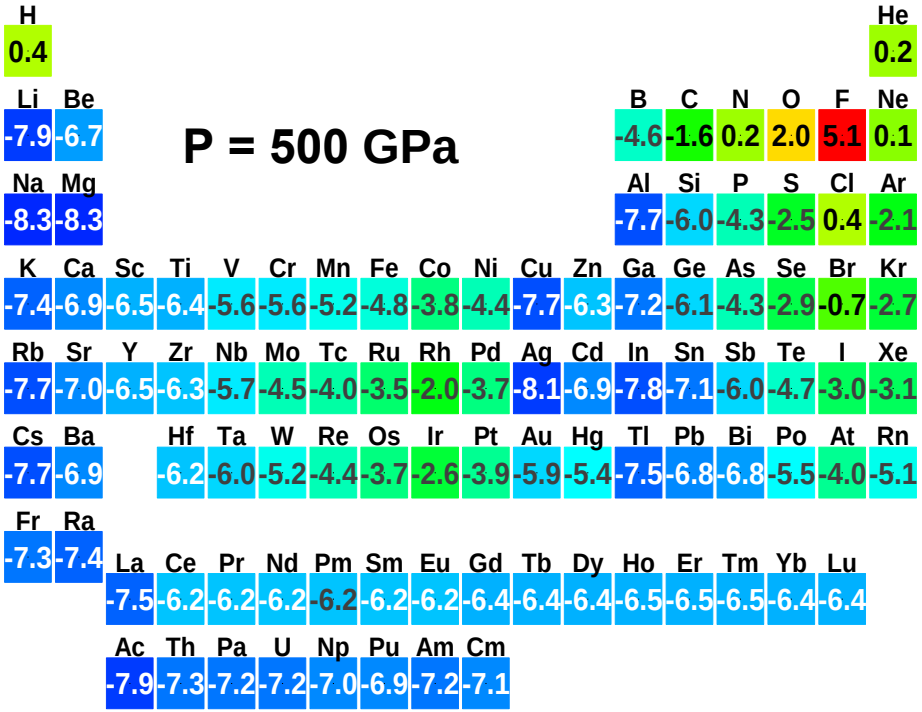
Electronegativity under pressure: key to understanding high-pressure chemistry
[Dong & Oganov, *PNAS* 2022]

Electronegativity and chemical hardness overall decrease with pressure

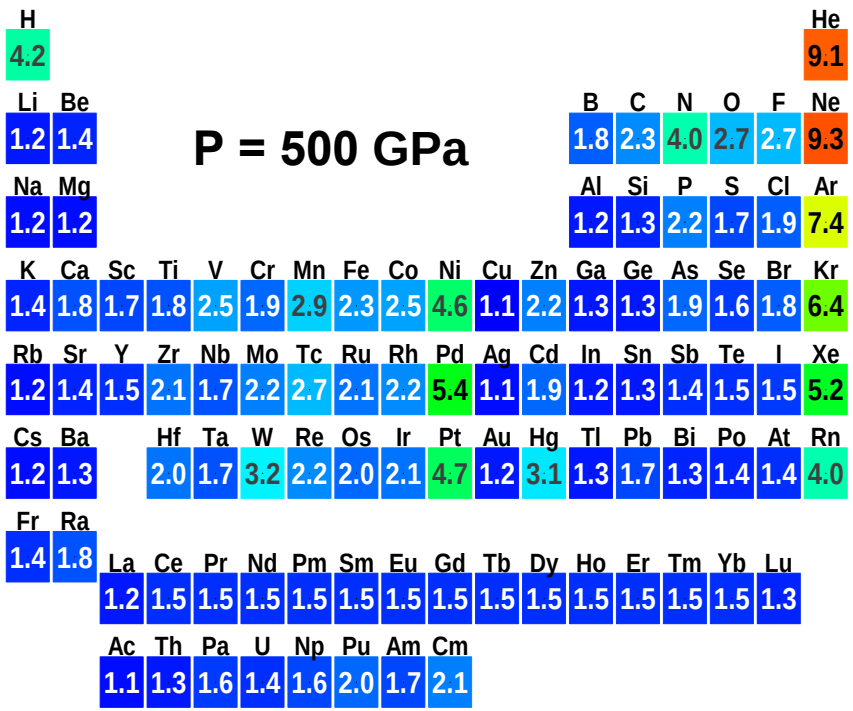


Electronegativity under pressure: key to understanding high-pressure chemistry
[Dong & Oganov, *PNAS* 2022]

Chemical hardnes = ½ HOMO-LUMO gap.
Decreases with pressure, but remains positive.



Electronegativity



Chemical hardness

Our electronegativities and chemical hardnesses explain many phenomena under pressure

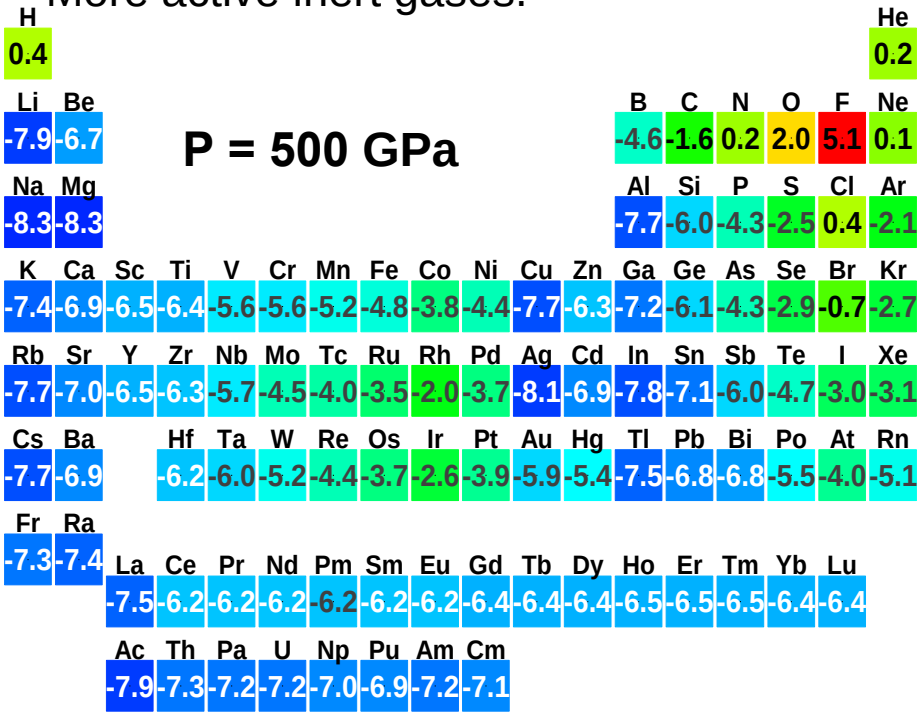
[Dong & Oganov, *PNAS* 2022]

- Chemical hardness decreases with pressure → multicenter bonds → metallization.

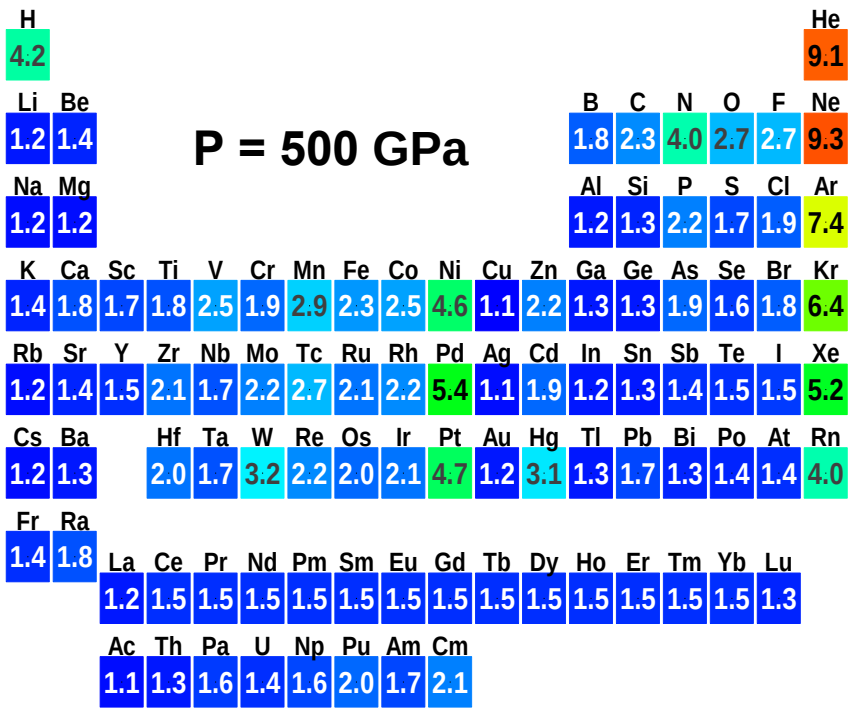
→"strange" compounds (Na_3Cl, ThH_{10},…).

→host-guest structures (Na, K, Rb, Ca, Sr).

- Elements under pressure behave as heavier analogs in the group
- Stabilization of high oxidation state (CsF_5, FeO_2,…).
- More active inert gases.



Electronegativity

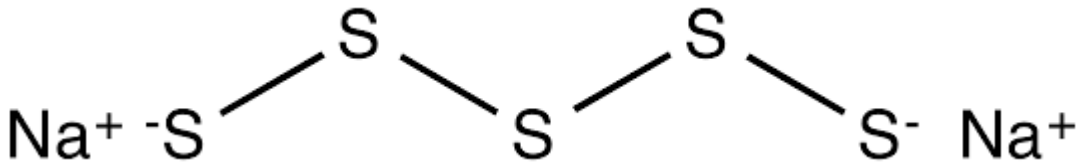


Chemical hardness

Some «strange» compounds exist without pressure: polysulfides

Na_2S_5 from our experiments

$$Na_2S + 4S = Na_2S_5$$



Coexistence of S^0 and S^- is possible due to low chemical hardness of S.

Our electronegativities and chemical hardnesses explain many phenomena under pressure

[Dong & Oganov, *PNAS* 2022]

- Chemical hardness decreases with pressure → multicenter bonds → metallization.

→"strange" compounds (Na_3Cl, ThH_{10},…).

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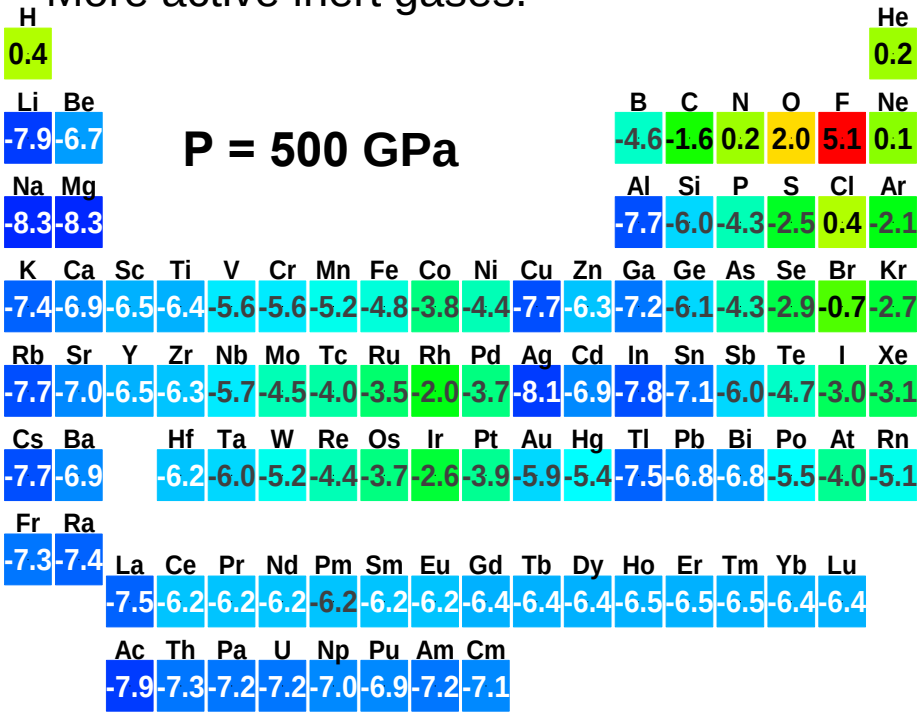
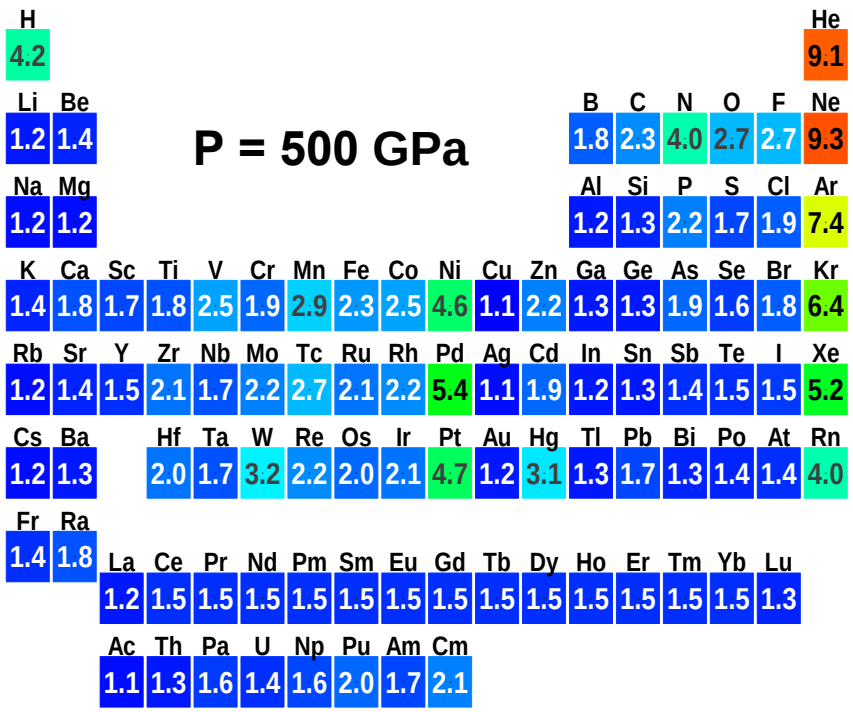


Electronegativity

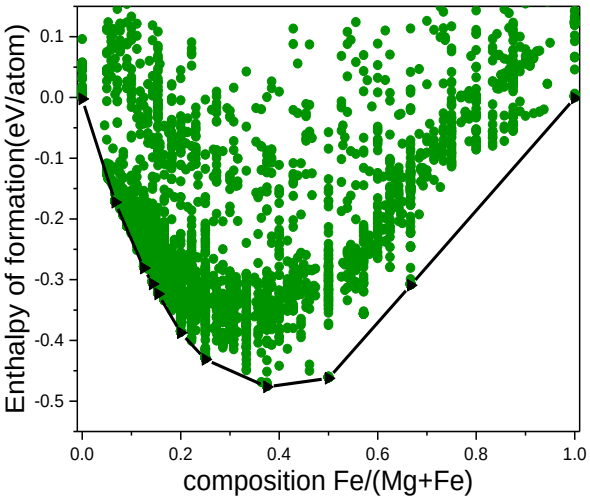


Chemical hardness

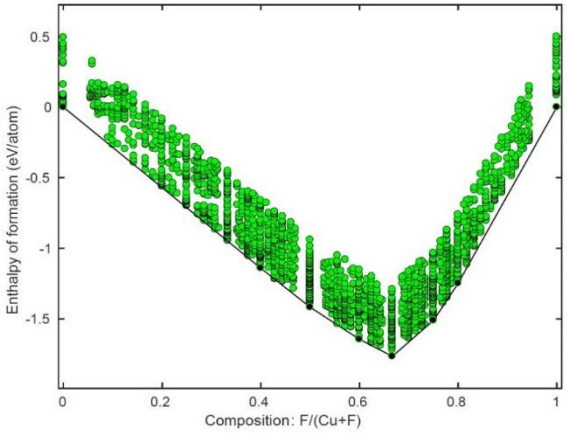
Our scale shows where to look for new compounds

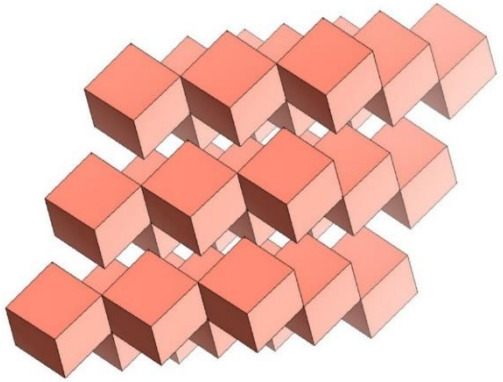
- Electronegativity difference Fe-Mg grows from 0.57 eV (0 GPa) to 2.25 eV (200 GPa) – and stable compounds appear.
- Electronegativity of high oxidation states becomes lower → these states become accessible. For example, in CuF_4.

$X(N) = X_0 - \eta N$



Enthalpies of formation in Mg-Fe system at 200 GPa





Enthalpies of formation in Cu-F system and structure of CuF_4 at 500 GPa

Simple questions

- **Why high-pressure chemistry is so different?**

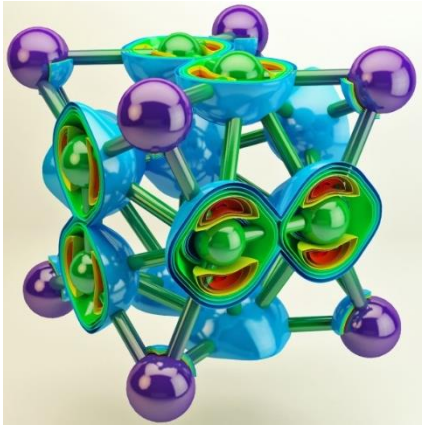
  -everything eventually becomes metallic.

  -strange structures of the elements (host-guest Na, K, Rb, Ca,…).

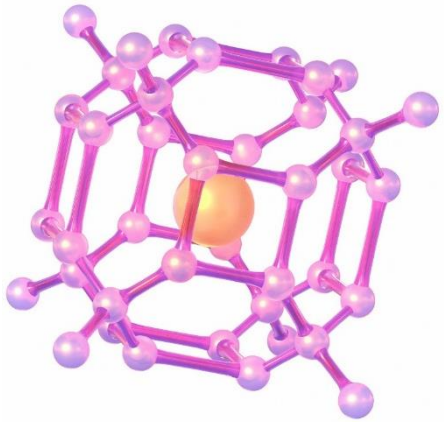
  -emergence of «strange» compounds Na_3Cl, ThH_{10}, etc.

  -«strange» CaS_5, Na_2S_5 exist already at normal conditions.

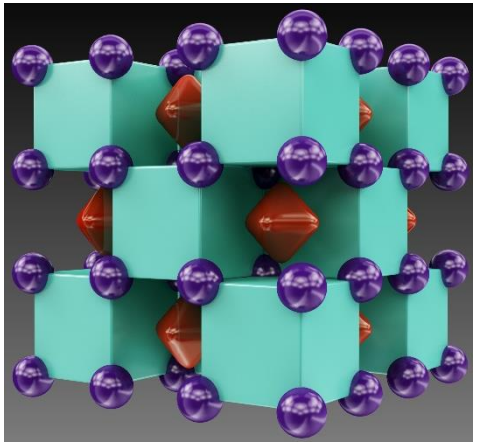
  -inert gases become more reactive.



$NaCl_3$ (*Science* 2013)



ThH_{10} (*Mat. Today* 2020)



Na_2He (*Nature Chemistry* 2017)

Simple questions

- **Why some elements vigorously react, while others don't?**
- **Why some compounds are stable, while others are not?**
- **Why some parageneses exist, while others don't?**
- **Why high-pressure chemistry is so different?**

-everything eventually becomes metallic.

-strange structures of the elements (host-guest Na, K, Rb, Ca,…).

-emergence of «strange» compounds Na_3Cl, ThH_{10}, etc.

-«strange» CaS_5, Na_2S_5 exist already at normal conditions.

-inert gases become more reactive.

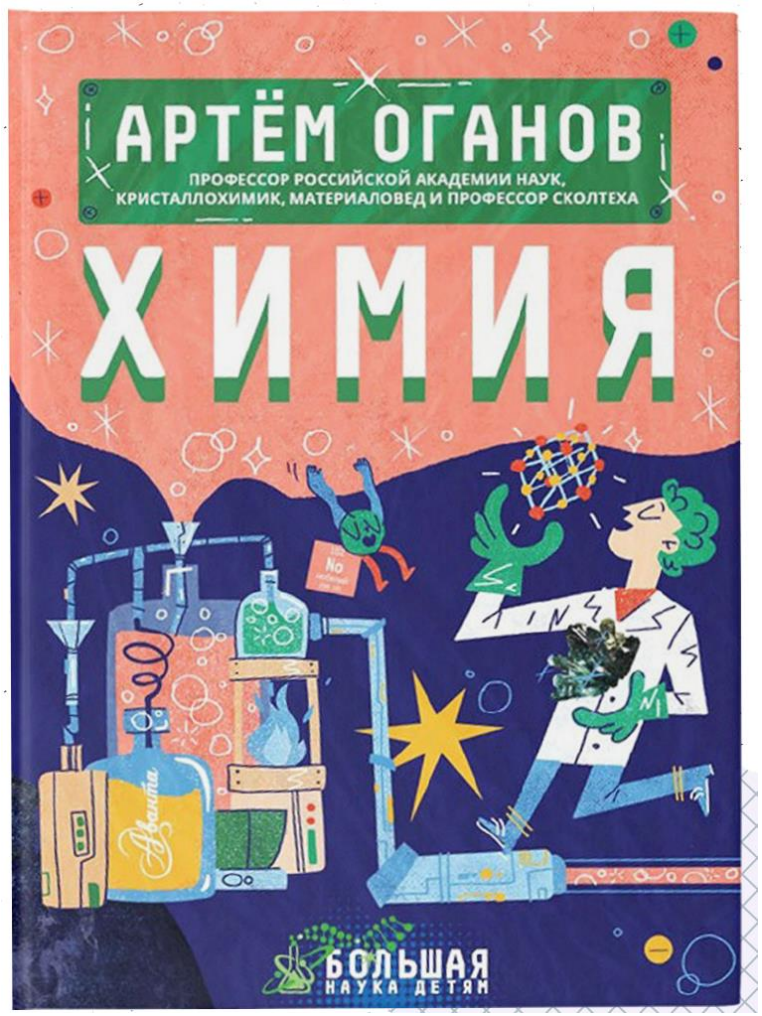
Ridges and islands of stability of molecules

Artem R. Oganov FRSC MAE

Skolkovo Institute of Science and Technology, Russia

My story

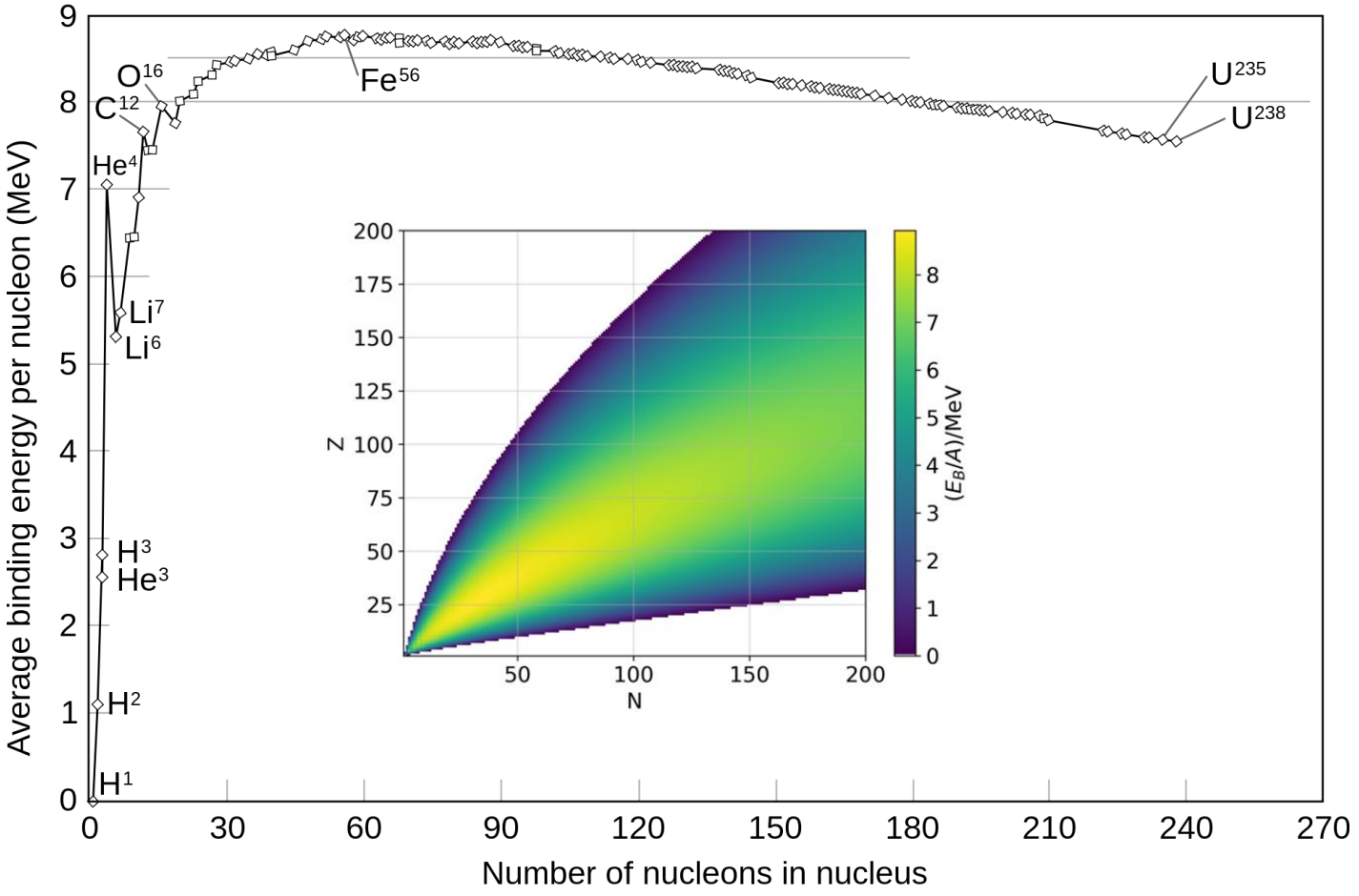
Once upon a time I was attracted to chemistry by a popular science book. I dreamed that I will grow up and work at JINR, discovering new elements.



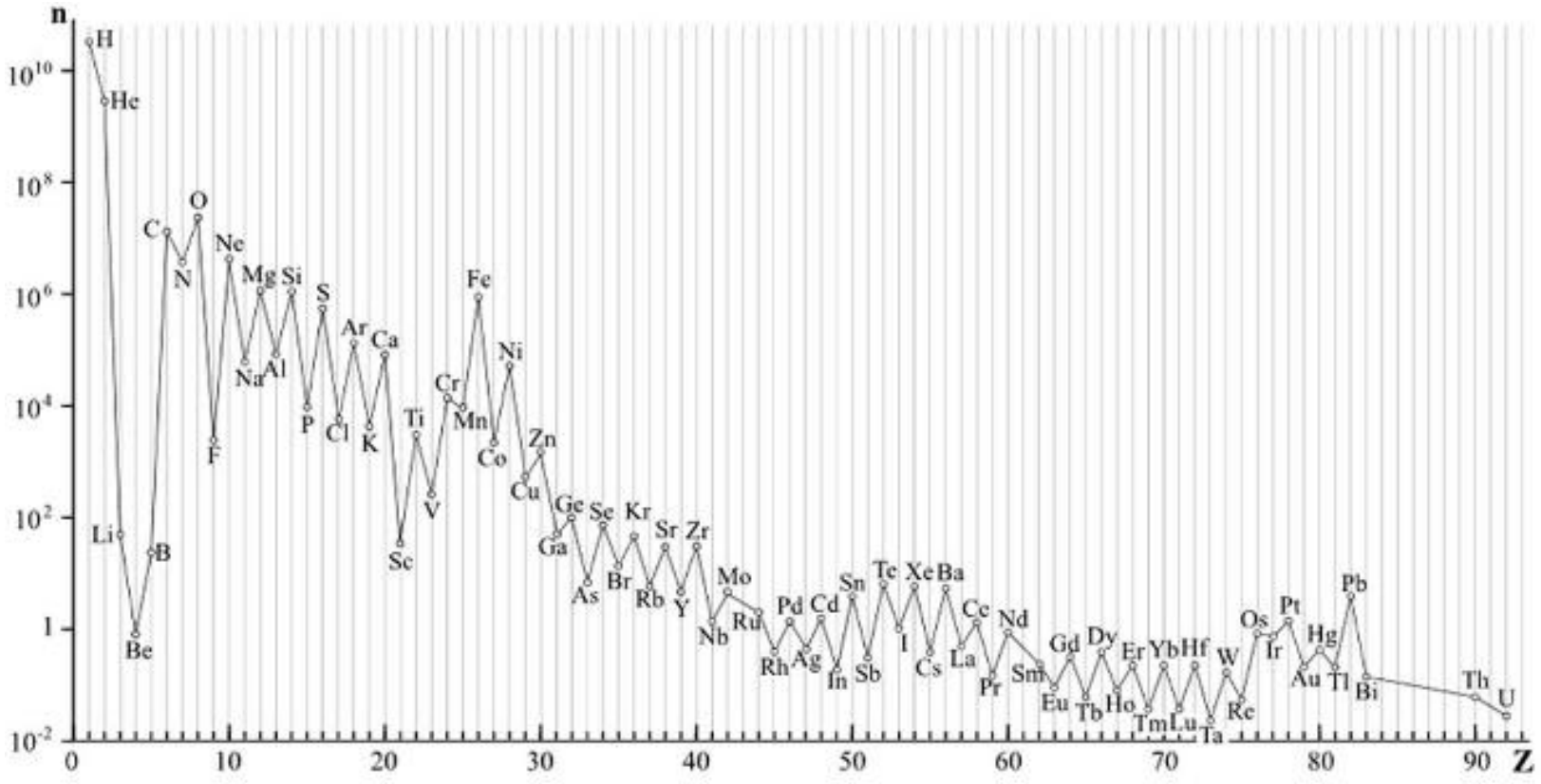
After 300 papers I wrote a book for children.

A Faraway Field: Nuclear Reactions

Some nuclei are better than others



Some elements are more abundant than others



Abundance of the elements in the Universe:

-Almost all atoms are H and He.

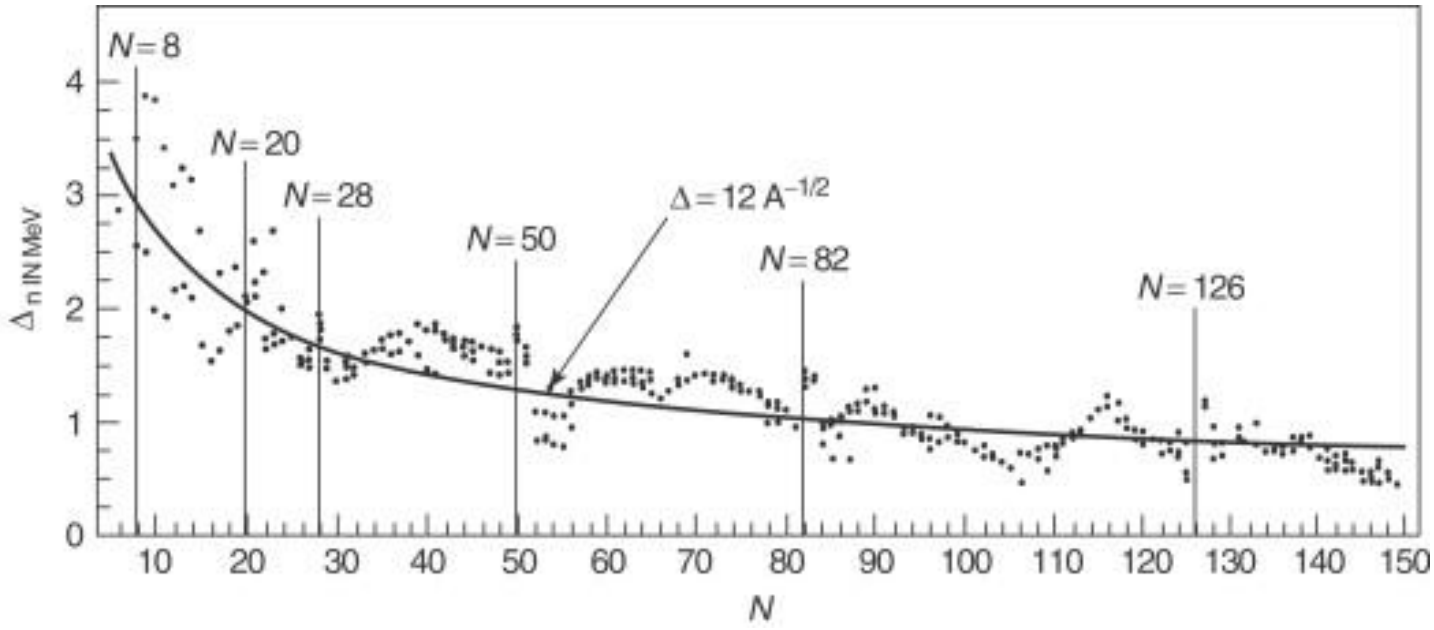
-Even-Z elements are more abundant than nearest odd-Z elements.

-Peaks at O, Fe, Xe, Pb.

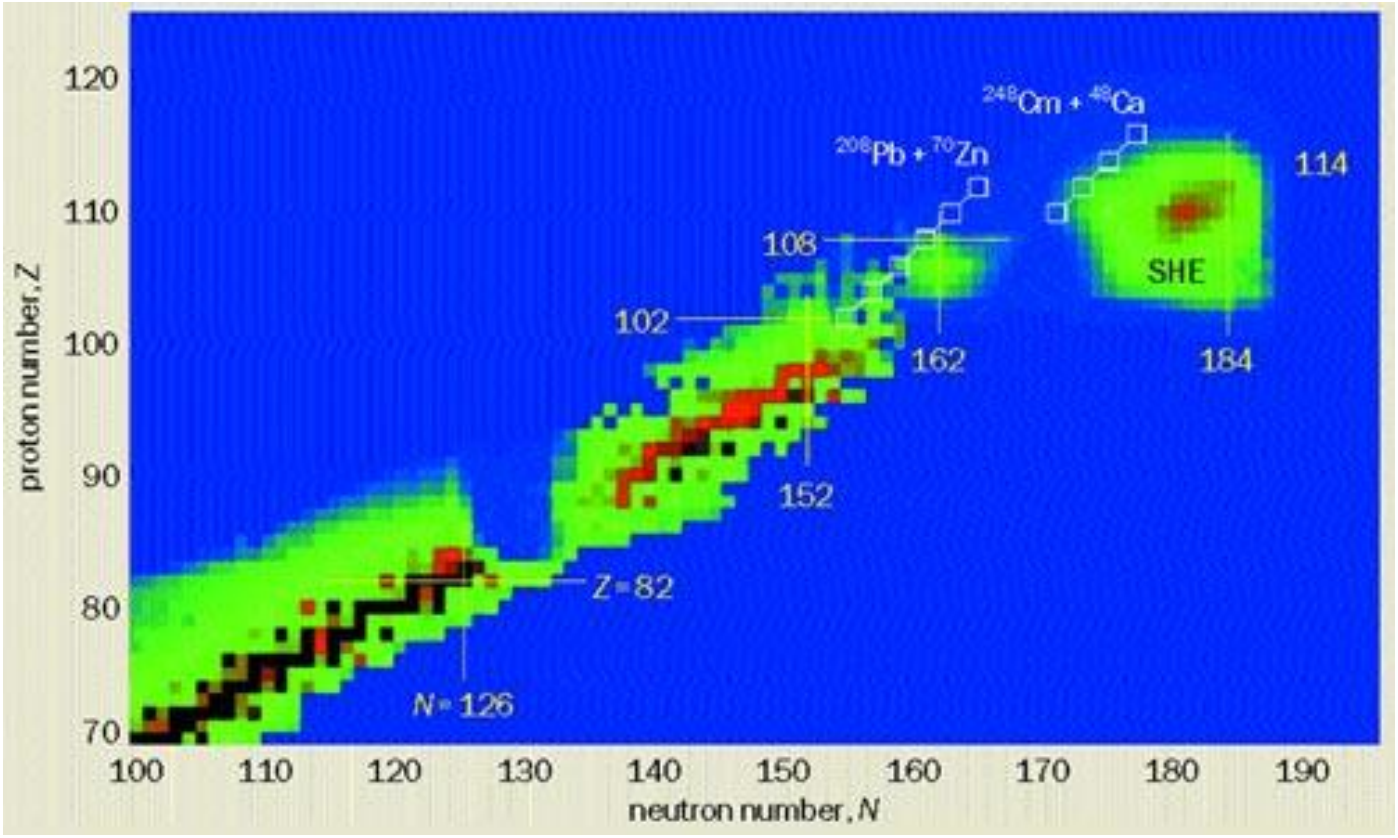
-Deep minima after He, O, Ca, Fe, Ni, Pb.

Shell structure effects: closed-shell nuclei are particularly stable

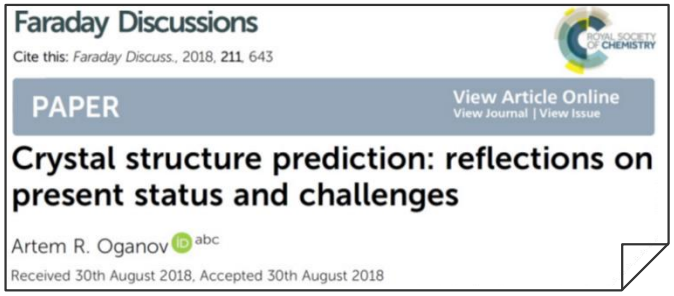
$$\Delta = -\tfrac{1}{2}\{\mathscr{B}(N-1,Z) + \mathscr{B}(N+1,Z) - 2\mathscr{B}(N,Z)\}$$



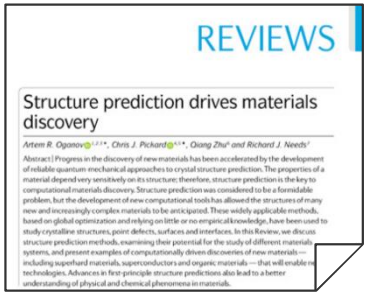
The landscape: sea of instability, ridge(s) of stability, island(s) of stability



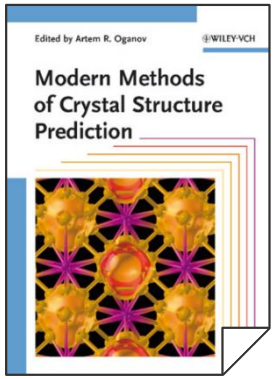
Our Field: Crystal Structure Prediction



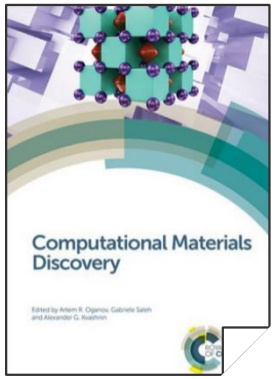
Faraday Discussions (2018)



Nature Reviews Materials (2019)



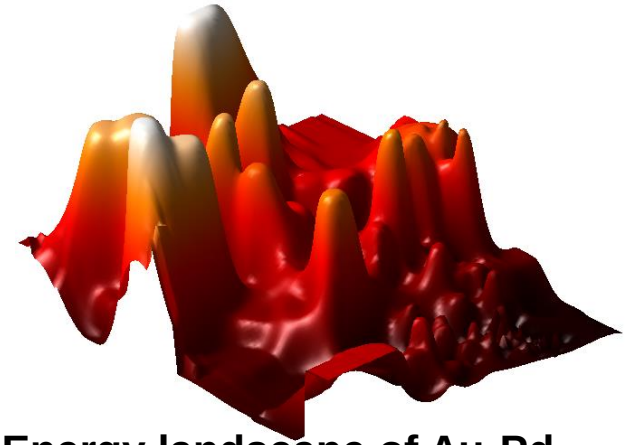
2011



2018

USPEX (Universal Structure Predictor: Evolutionary Xtallography)

- **Combination of evolutionary algorithm and quantum-mechanical calculations.**
- **>8500 users.**
- **Solves “formidable” problem of crystal structure prediction.**



Energy landscape of Au_8Pd_4

uspex-team.org

Samrath Lal Chaplot

RESEARCH NEWS

Crystal structure prediction – evolutionary or revolutionary crystallography?

S. L. Chaplot and K. R. Rao CURRENT SCIENCE, VOL. 91, NO. 11, 10 DECEMBER 2006

- Early article about our work

Quantum-mechanical calculations (using density functional theory

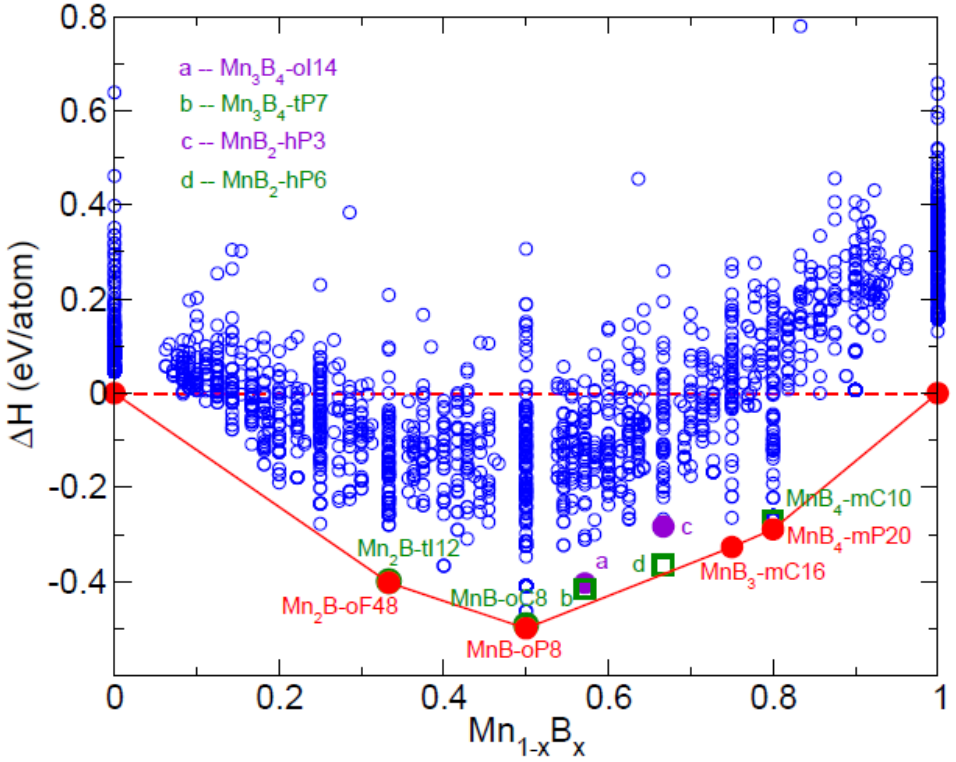
$$(-\frac{\nabla^2}{2}+v_{e\text{-}n}[\rho(\mathrm{r})]+v_H[\rho(\mathrm{r})]+v_{xc}[\rho(\mathrm{r})])\phi_i(\mathrm{r})=\varepsilon_i\phi_i(\mathrm{r})$$

W. Kohn
Nobel Prize in Chemistry 1998

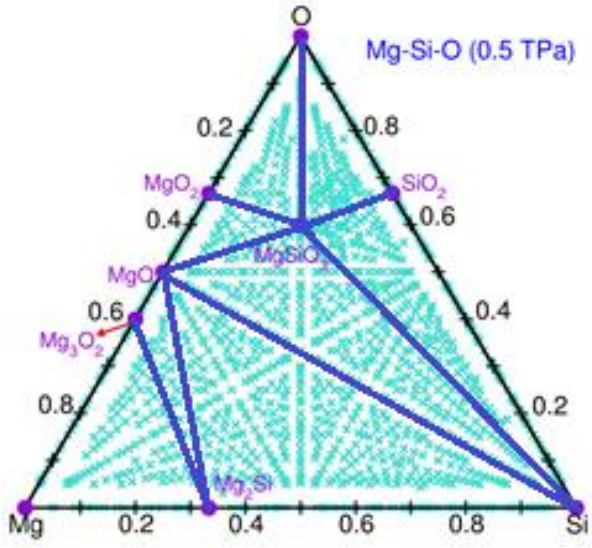
E. Schroedinger
Nobel Prize in Physics 1933

Global minimization of the energy gives structure (and composition) of stable crystals

Thermodynamic stability in variable-composition systems



2-component convex hull: Mn-B system (Niu & Oganov, PCCP 2014)



3-component convex hull: Mg-Si-O system at 500 GPa (Niu & Oganov, *Sci. Rep.* 2015)

Stable structure must be below all the possible decomposition lines !!

For molecules, things are not so simple: The curious case of graphane and benzene.

Wen X.D., Hoffmann R., Oganov A.R. (PNAS 108, 6833-6837, 2011).

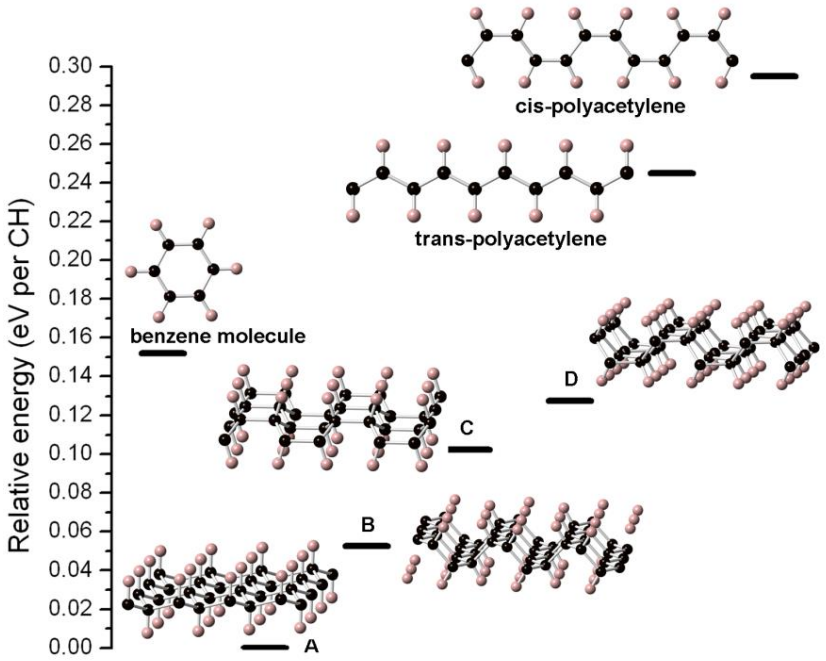


Fig. 3. The relative energy (in eV per CH; relative to single-sheet graphane A, 0 K) of some CH structures.

1825: M. Faraday discovers benzene C_6H_6.

1865: A. Kekule proposes cyclic structure of benzene.

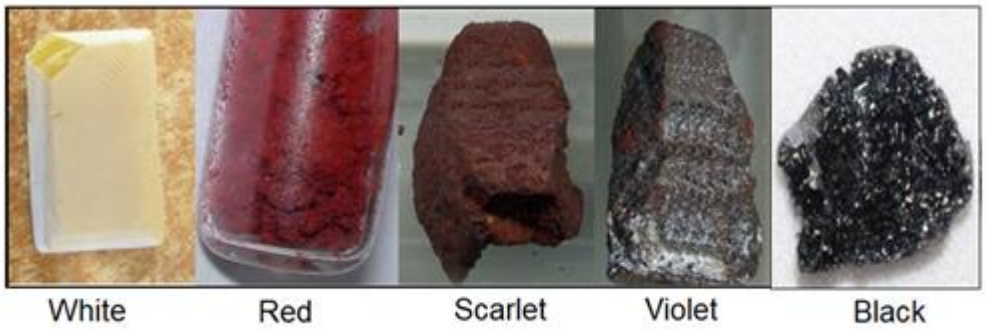
1958: G. Natta synthesized polyacetylene $C_{2n}H_{2n}$.

2007: Sofo et al. found graphane to be more stable than benzene.

2009: Elias et al. synthesized graphane.

2011: Wen, Hoffmann, Oganov proved that graphane-A has the lowest energy among all CH phases. Four graphanes are more favorable than benzene.

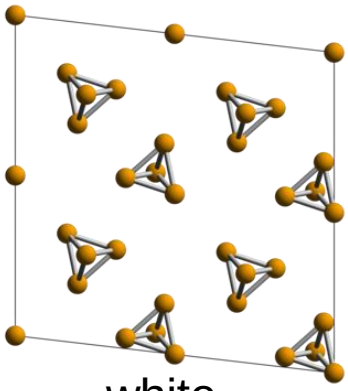
The puzzle of phosphorus

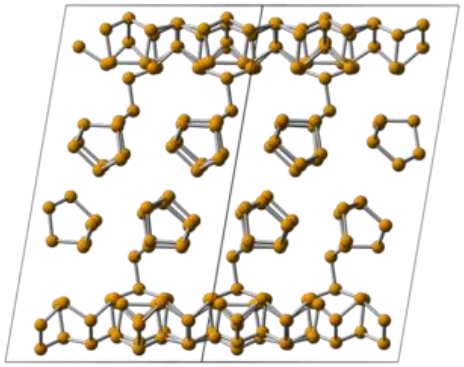


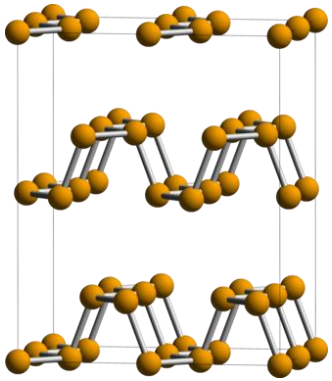
1669: alchemist H. Brand discovers white phosphorus. Least stable, most reactive and most toxic.

1847-1914: red, violet and black phosphorus discovered.

White phosphorus is easiest to make, but least stable.
Violet (or black?) phosphorus are hardest to make, but most stable.


white


violet

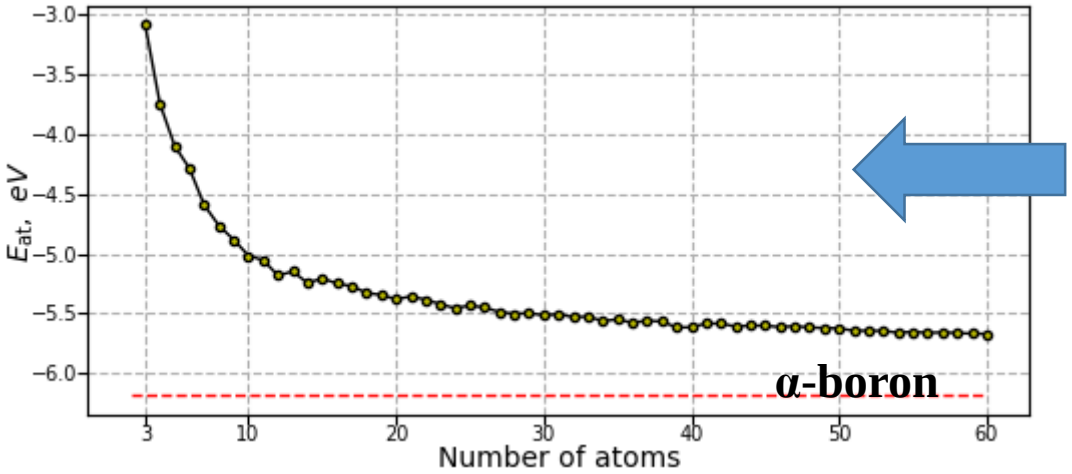

red

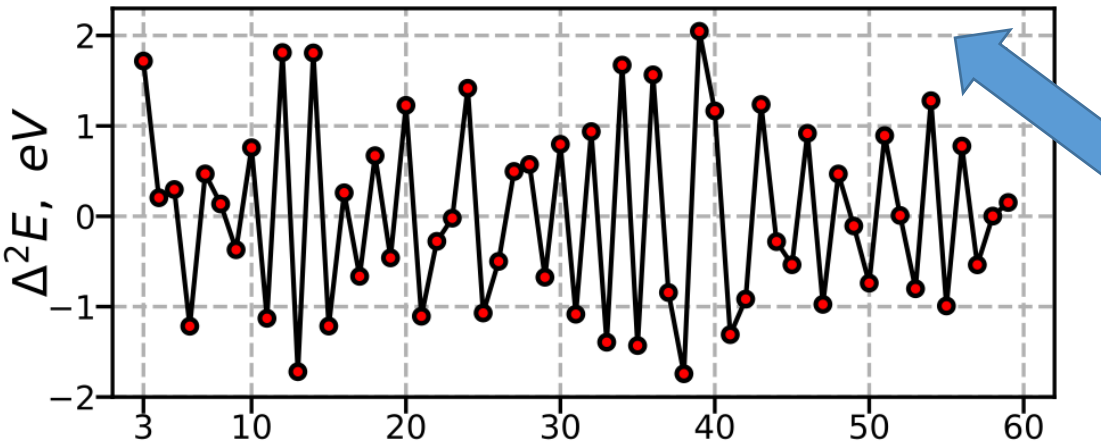
Decay of other phases of phosphorus gives off white phosphorus (P_4 molecules)

Prediction of Stable Molecules

Stability of molecules does not follow from straight comparison of energies

Example of boron clusters (Anisimova & Oganov, submitted.)





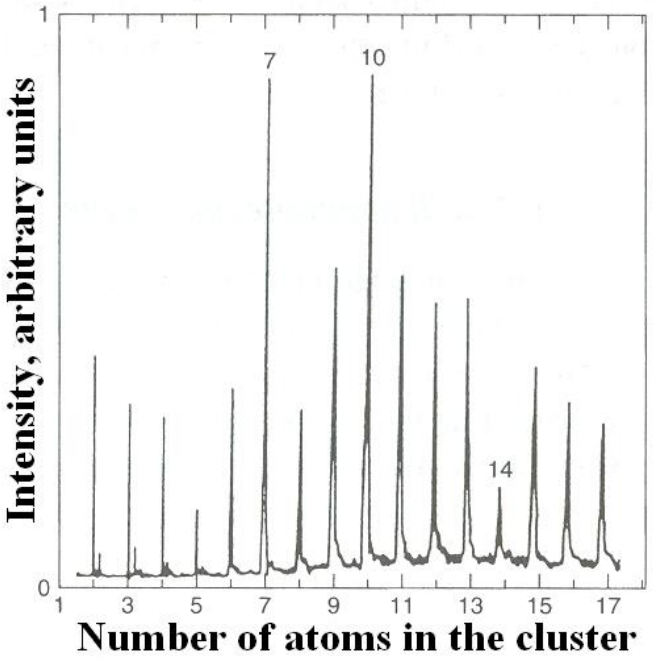
1. Energy falls almost monotonically with number of atoms.

2. Infinite crystal always wins by energy.

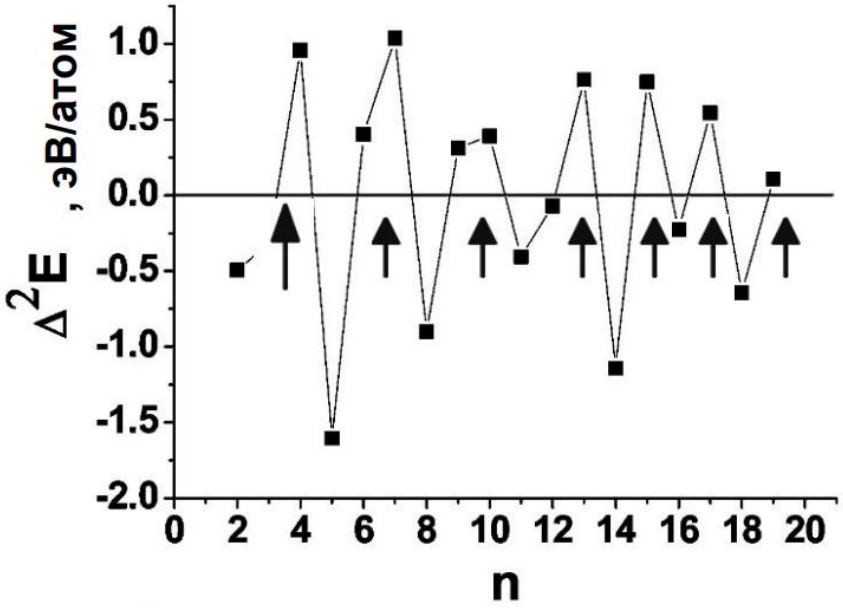
3. Correct comparison of energies – only with neighbor compositions.

4. Δ^2E is a proper measure.

$\Delta^2 E > 0$ indicates the most abundant ("magic") molecules



Mass-spectrum of Pb_n clusters (Poole & Owens, 2003)



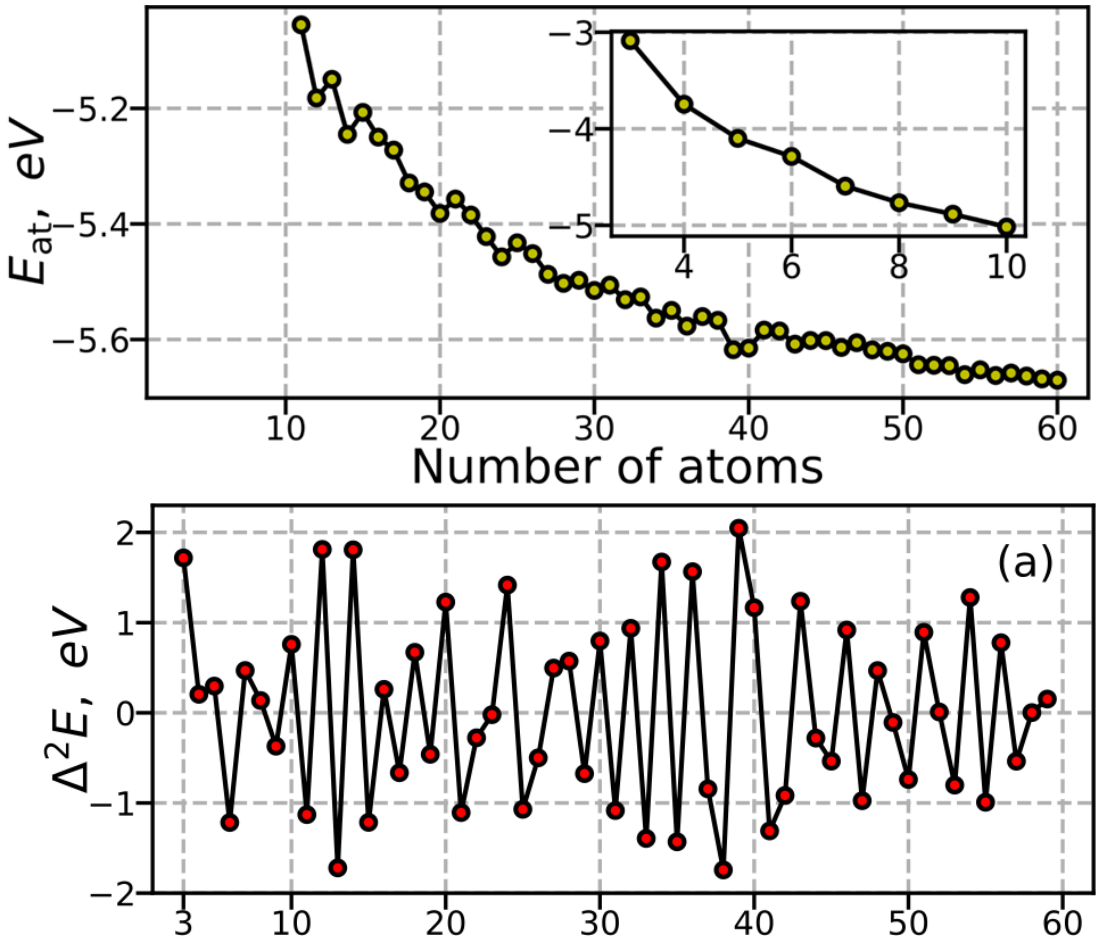
$\Delta^2 E$ for Pb_n clusters (Li et al., 2009)

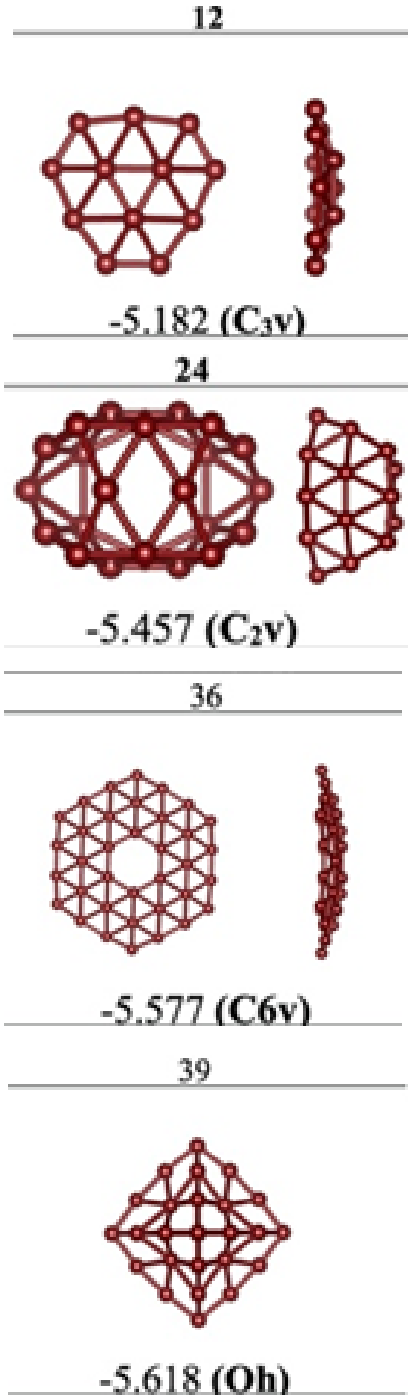
↑ – "magic" cluster

Binding energy grows with the size of cluster. We define stability relative to neighboring compositions. Stability is due to filled shells (electronic, atomic).

Let's look at pure elements: Boron

(Anisimova & Oganov, submitted)





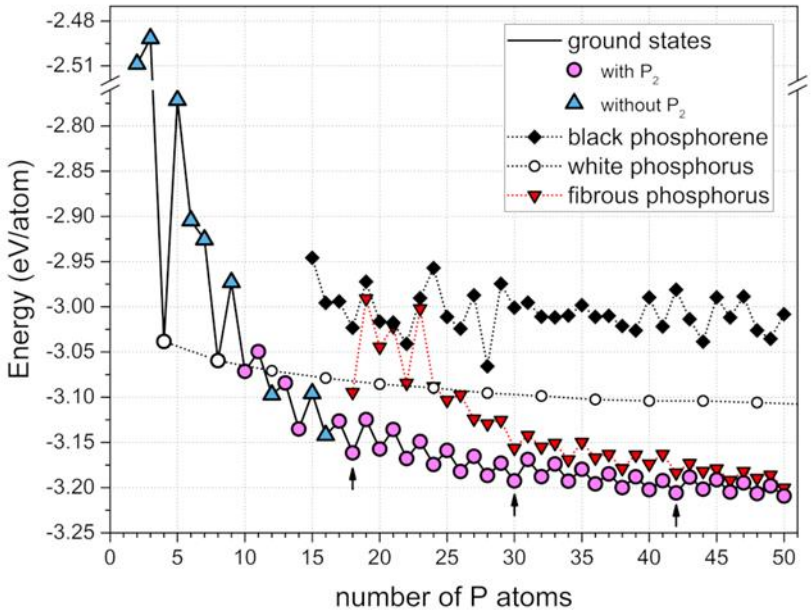
- **Magic – mostly even clusters.**
- **Results similar to Wu et al. (2020), but often with lower energy**

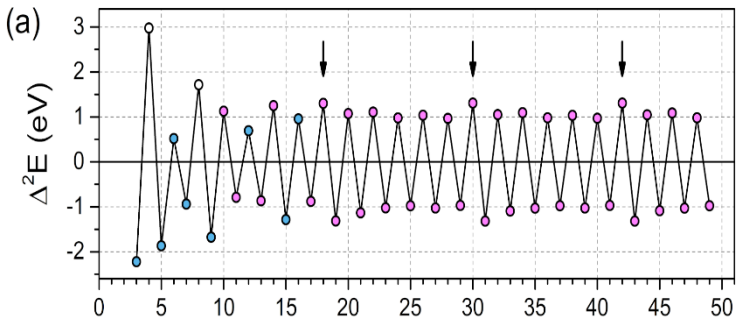
Let's look at pure elements: Phosphorus

(Rybkovskiy & Oganov, submitted)

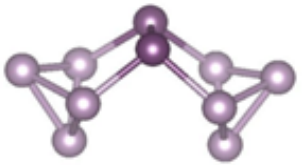
- **Magic – ONLY even clusters (electronic).**
- **Structural magic numbers k = 18+12n.**

One-dimensional quasiperiodic structures.

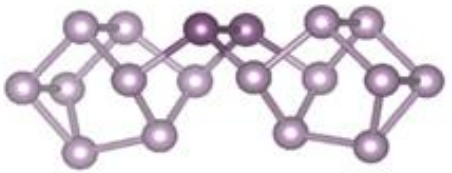




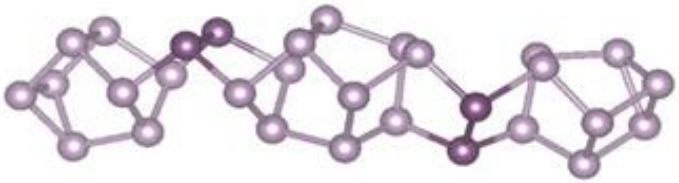
P_4



P_{10} ($P_4^*P_2P_4^*$)



P_{18} ($P_8^*P_2P_8^*$)

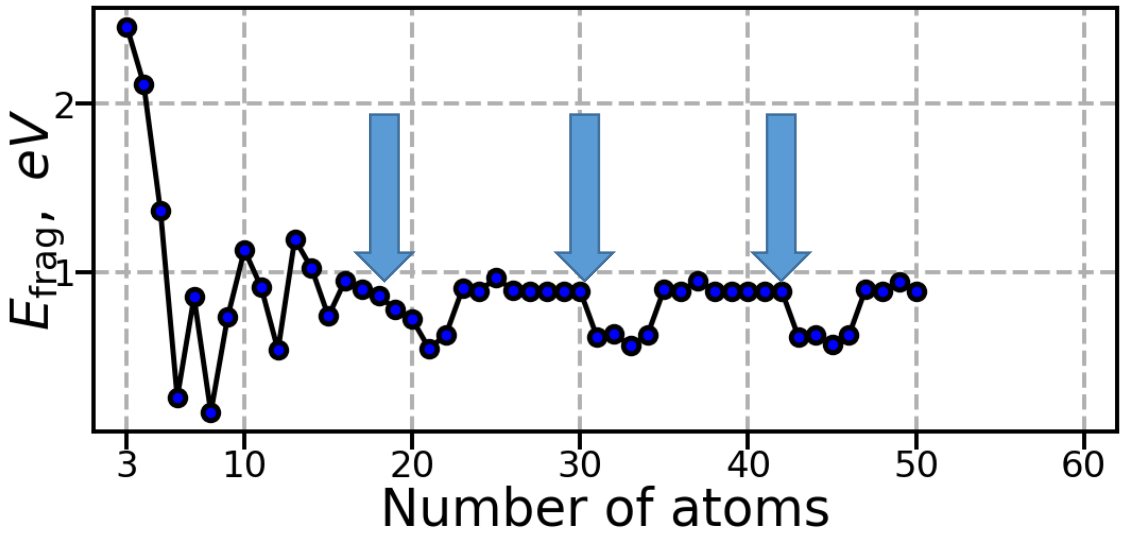


P_{30} ($P_8^*P_2P_{10}P_2P_8^*$)

P_{42} ($P_8^*P_2P_{10}P_2P_{10}P_2P_8^*$)

Fission of large clusters produces P_4 cluster. This explains why white phosphorus is easily formed.

Structural magic numbers k = 18+12n.

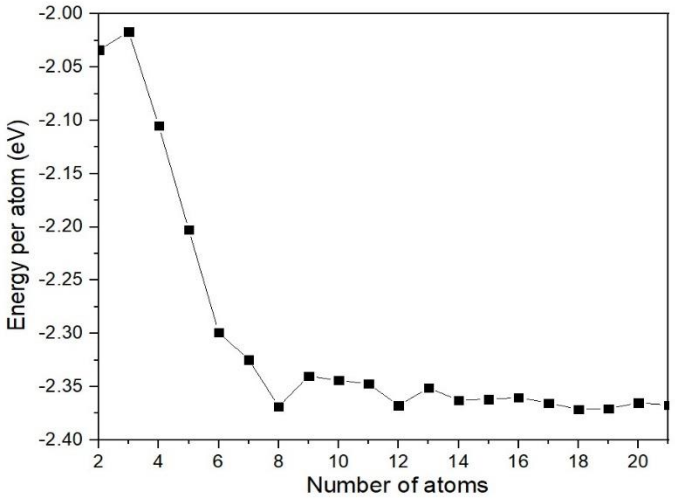


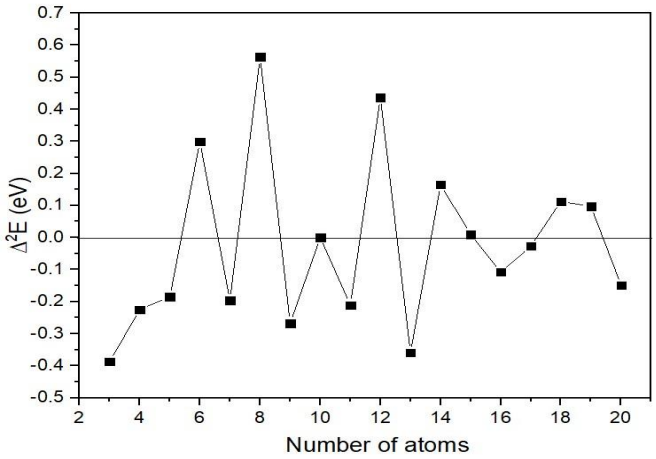
$P_2 \rightarrow P + P$, E_{frag} = 5.018
$P_3 \rightarrow P + P_2$, E_{frag} = 2.457
$P_4 \rightarrow P_2 + P_2$, E_{frag} = 2.118
$P_5 \rightarrow P_2 + P_3$, E_{frag} = 1.365
$P_6 \rightarrow P_2 + P_4$, E_{frag} = 0.256
$P_7 \rightarrow P_3 + P_4$, E_{frag} = 0.852
$P_8 \rightarrow P_4 + P_4$, E_{frag} = 0.168
$P_9 \rightarrow P_5 + P_4$, E_{frag} = 0.734
$P_{10} \rightarrow P_6 + P_4$, E_{frag} = 1.132
$P_{11} \rightarrow P_7 + P_4$, E_{frag} = 0.911

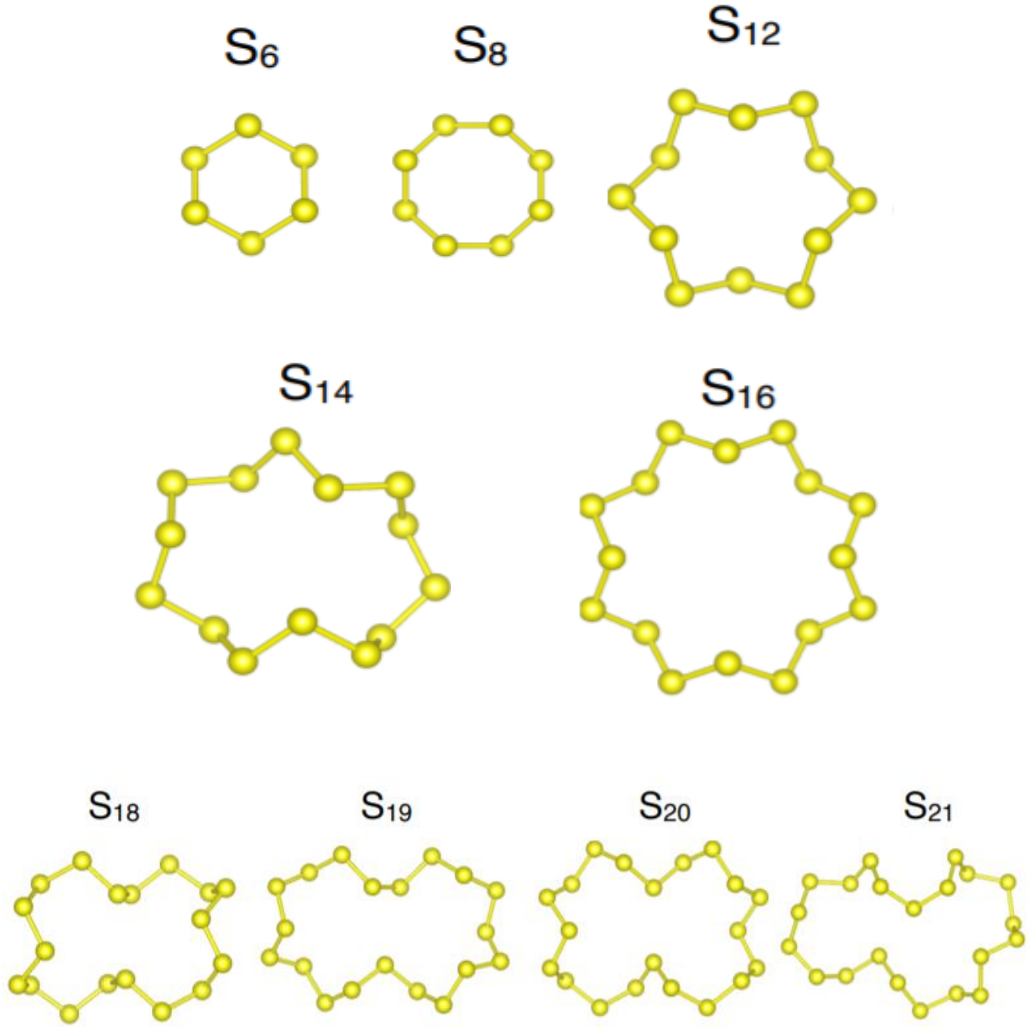
Let's look at pure elements: Sulfur

(Fedyaeva & Oganov, submitted)

- **Magic – mostly even clusters (structural).**
- **Starting from S_5, ring structures evolving towards spiral chains.**
- **S_8 is special.**





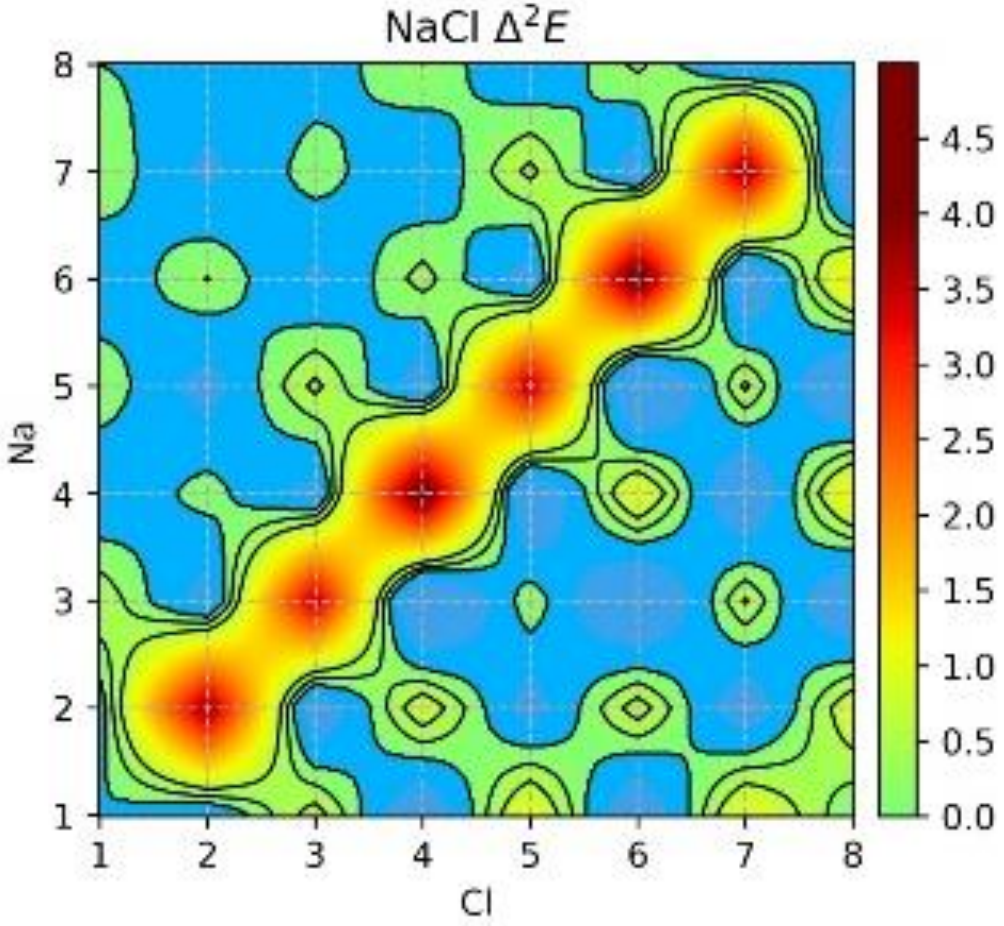


Na-Cl

Predicting stable Na-Cl molecules

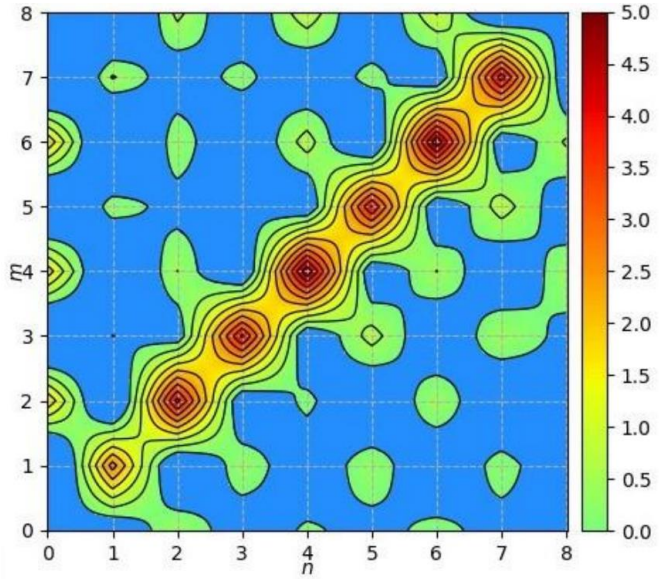
$(NaCl)_n$ ridge of stability.

Numerous minor islands of stability.

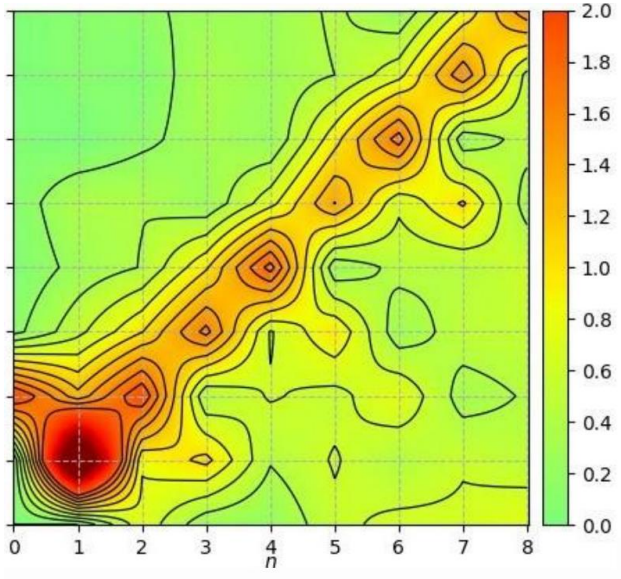


(result of M. Fedyaeva and S.V. Lepeshkin)

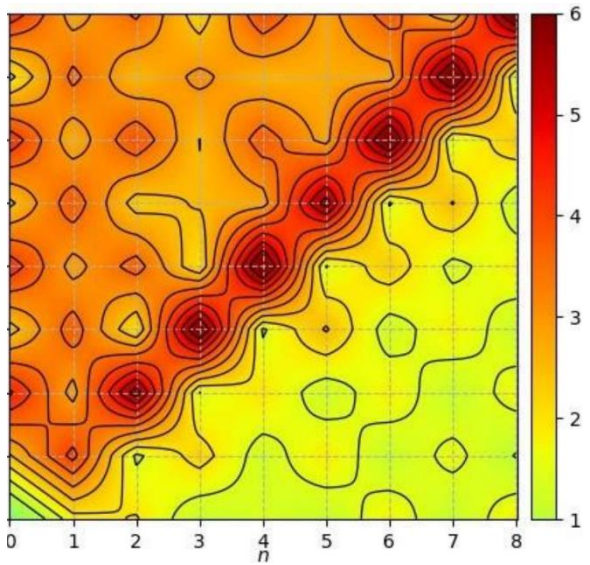
Three measures of stability



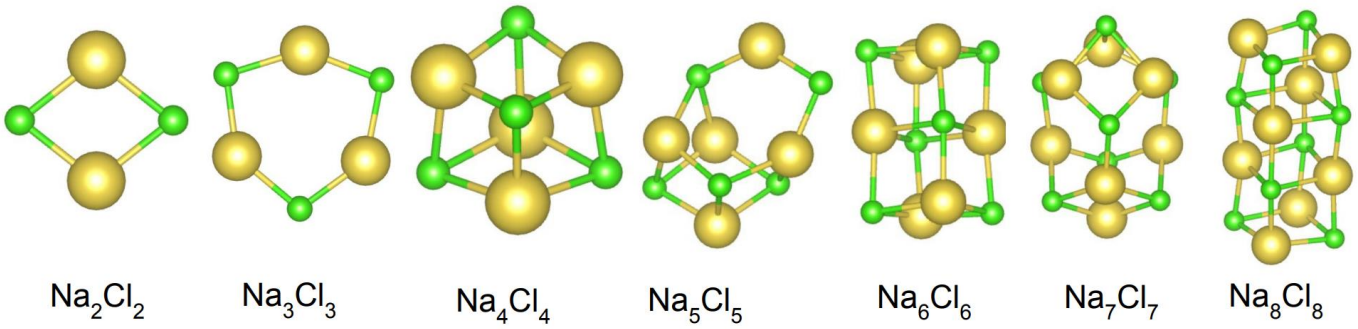
$\Delta^2 E$



E_{frag}

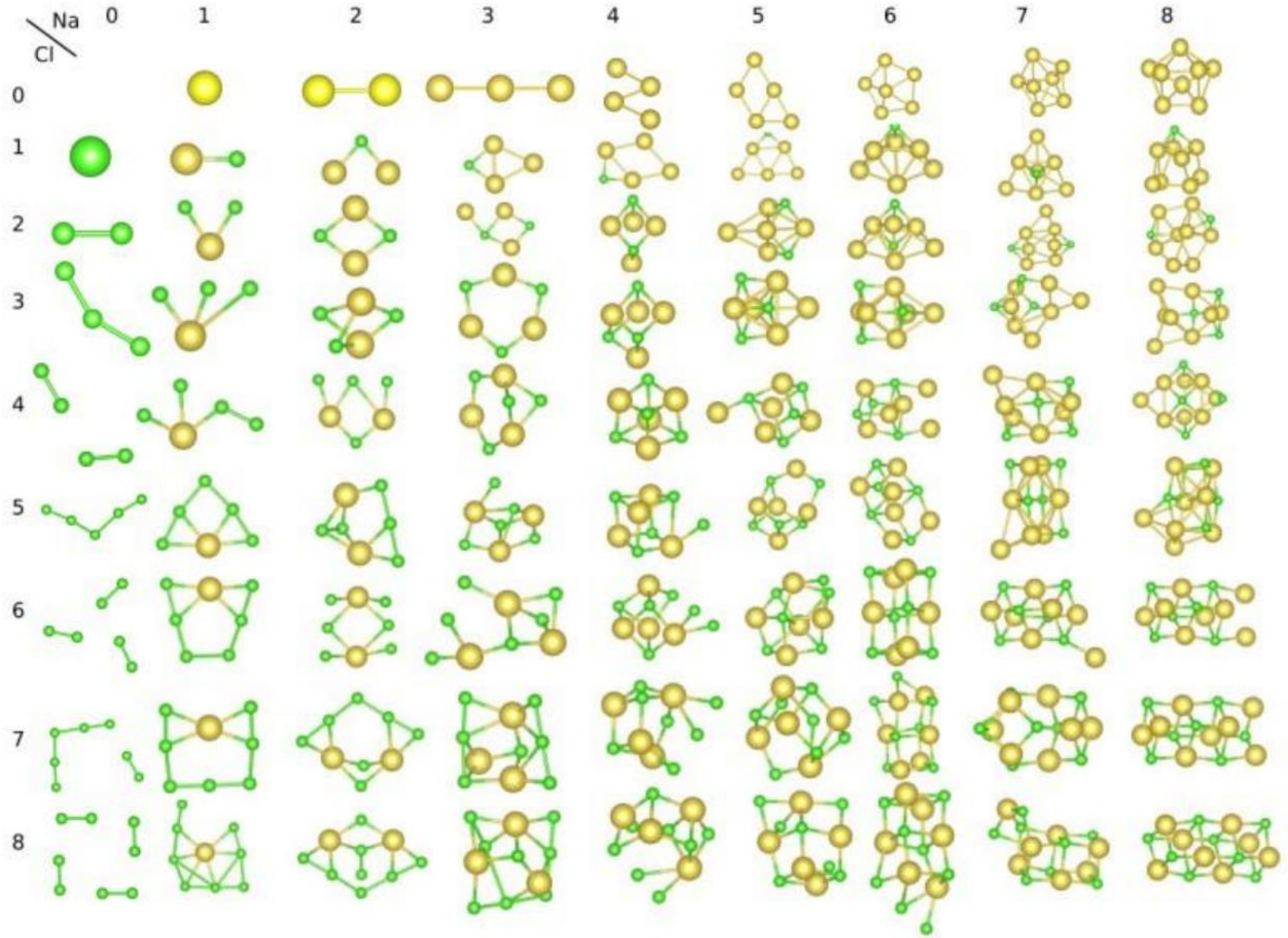


HOMO-LUMO gap



Na_2Cl_2 Na_3Cl_3 Na_4Cl_4 Na_5Cl_5 Na_6Cl_6 Na_7Cl_7 Na_8Cl_8

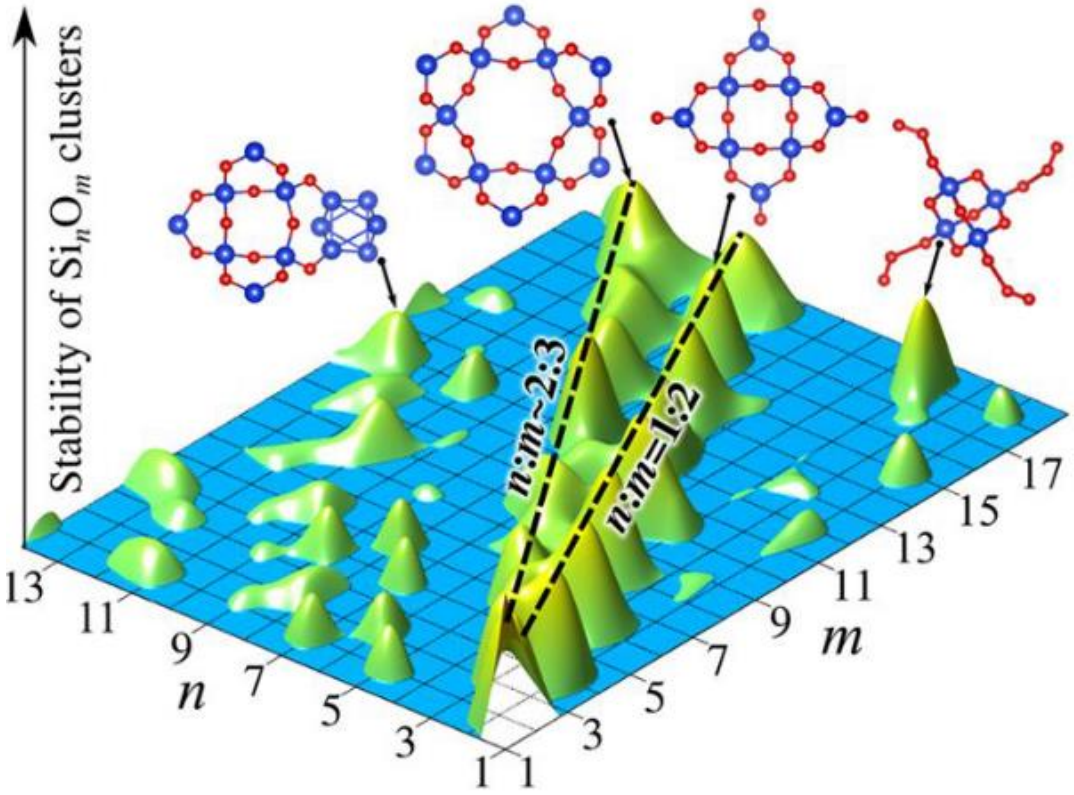
Na_mCl_n, (n,m=0-8)



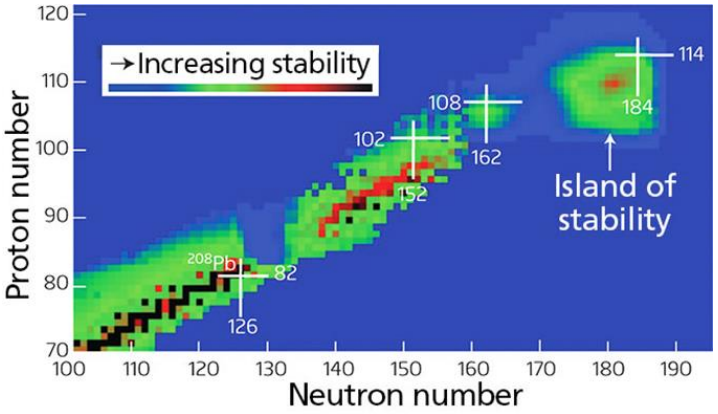
Map of stability of Si-O clusters

[Lepeshkin & Oganov, *J. Phys. Chem. Lett.* 2019]

Si-O



Ridges of stability: SiO_2, Si_2O_3
Islands of stability: e.g., Si_4O_{18}



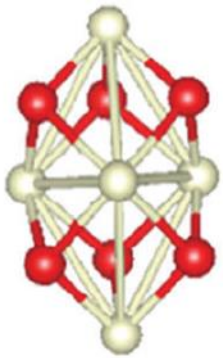
«Magic» nuclei: with filled proton or neutron shells (2, 8, 20, 28, 50, 82, 126 p or n)
($1s^2/2p^6/3d^{10}2s^2/4f^8/4f^63p^65g^{10}/5g^84d^{10}3s^26h^{12}$)

Magic numbers of electrons = 2, 10, 18, 36, 54, 86, 118)

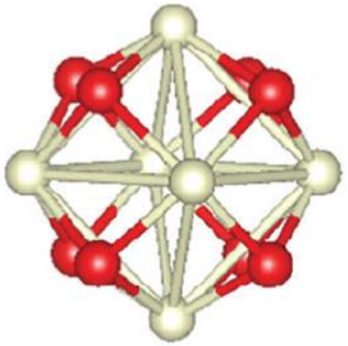
Analogy with magic atomic nuclei

Unusual compositions of transition metal oxide clusters

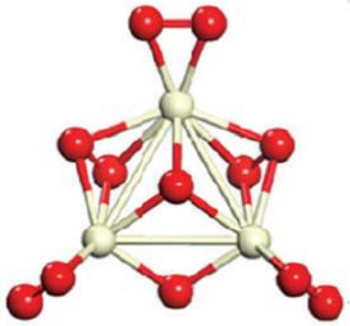
[Yu & Oganov, *Phys. Chem. Chem. Phys.*, 2018]



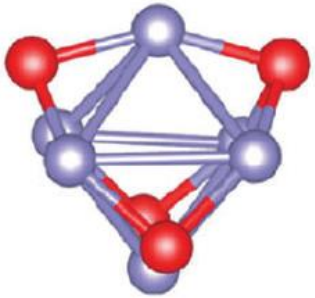
Ce_5O_6 (D_{3h}, $^5A_1'$)



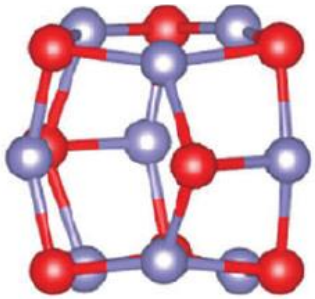
Ce_6O_8 (O_h, $^7A_{1g}$)



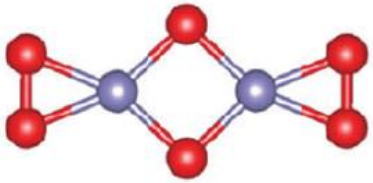
Ce_3O_{12} (C_s, $^3A'$)



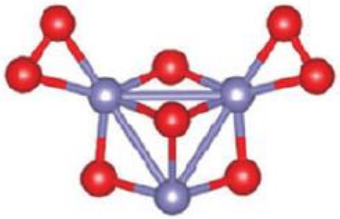
Fe_6O_4 (T_d, $^1A_1$)



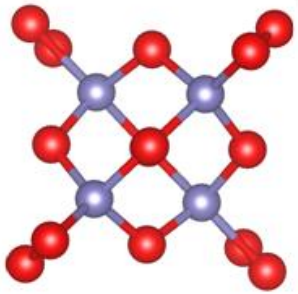
Fe_9O_8 (C_s, $^5A'$)



Fe_2O_6 (C_{2v}, $^1A_2$)



Fe_3O_8 (C_s, $^3A'$)

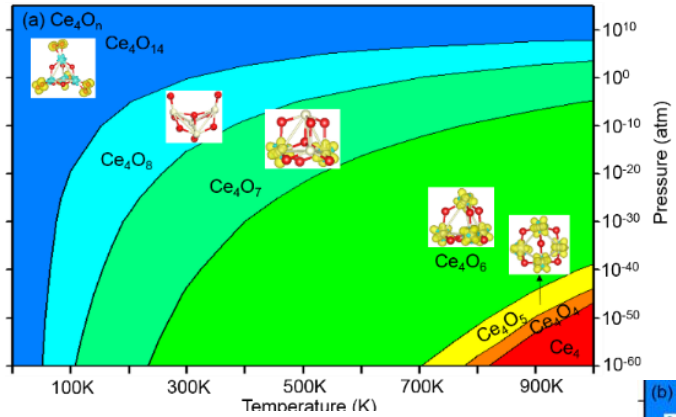


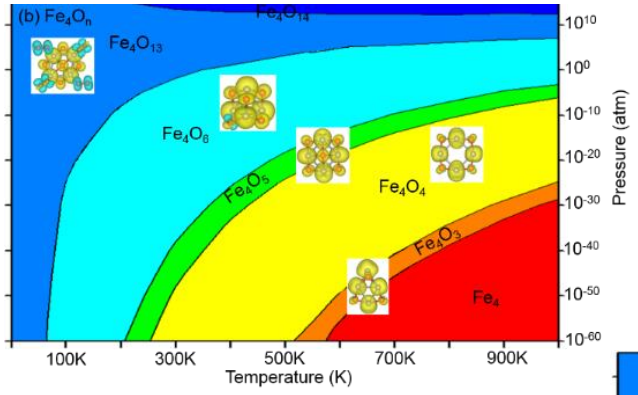
Fe_4O_{14} (D_{2d}, ^1A)

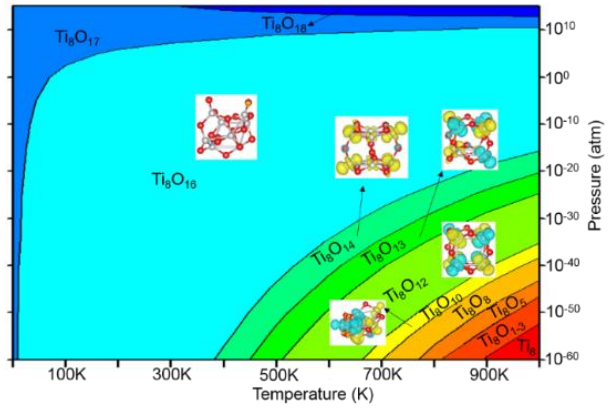
Do crystals grow from such particles (“inorganic synthons”)?

“Phase diagrams” of oxide clusters. Example of Ce_6O_n, Fe_4O_n, Ti_8O_n clusters.

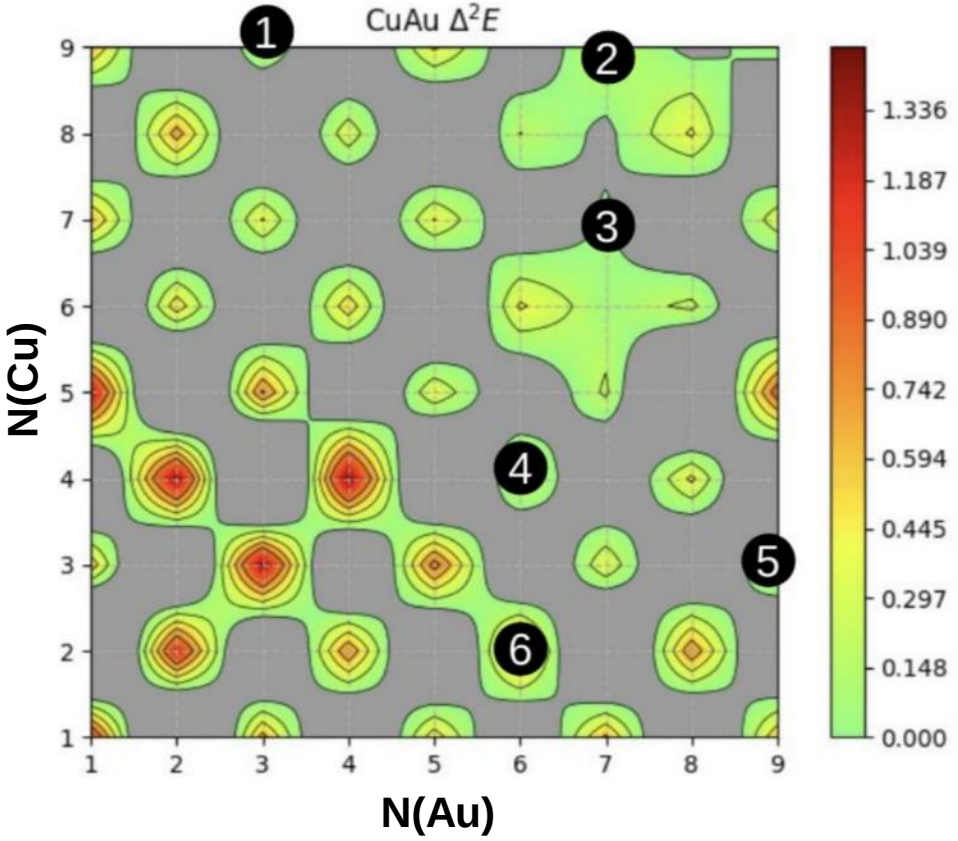
[Yu & Oganov, *Phys. Chem. Chem. Phys.*, 2018]



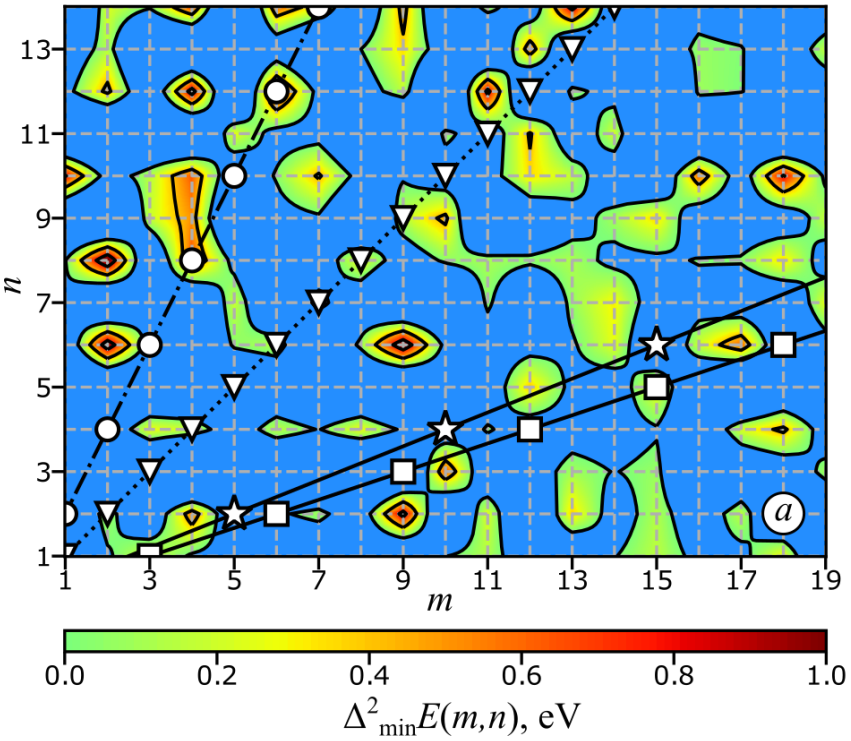




New tool: map of stability of molecules



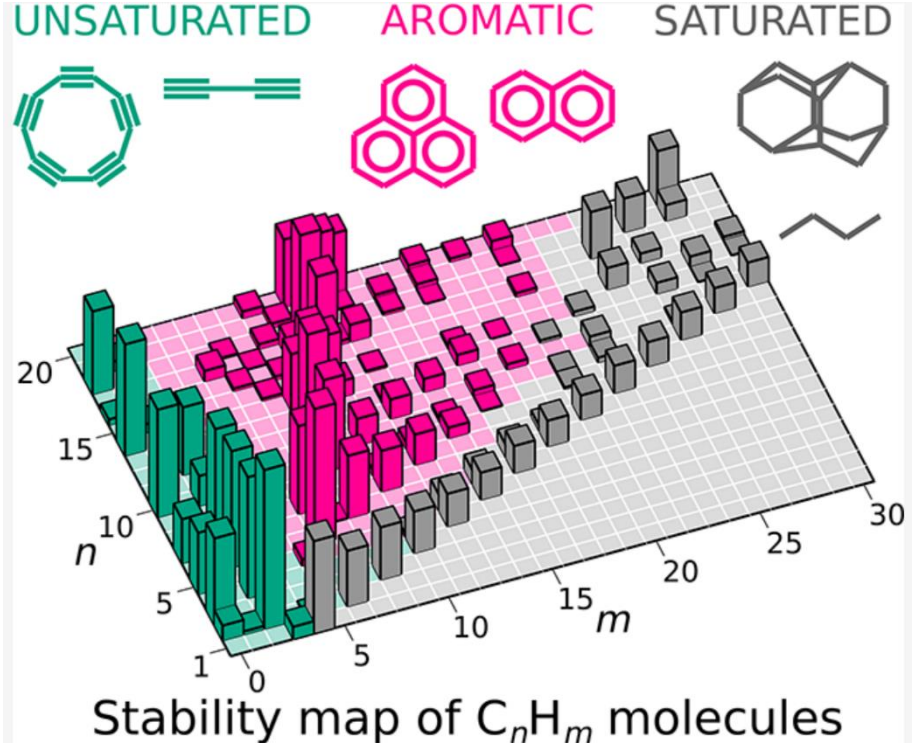
Map of stability of Cu-Au clusters (result of A. Mikhaylova).



Map of stability of Pd_mBi_n clusters (Sandu et al., PCCP, 2021)

Why is organic chemistry so diverse?

(Lepeshkin & Oganov, *J. Phys. Chem. Lett.* 2022)



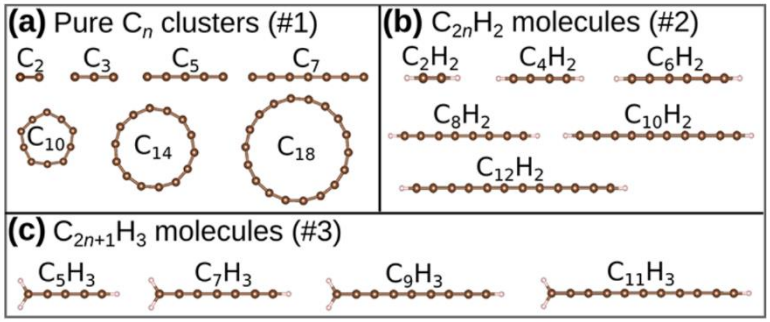


Figure 3. Structures of magic (poly)unsaturated HCs.

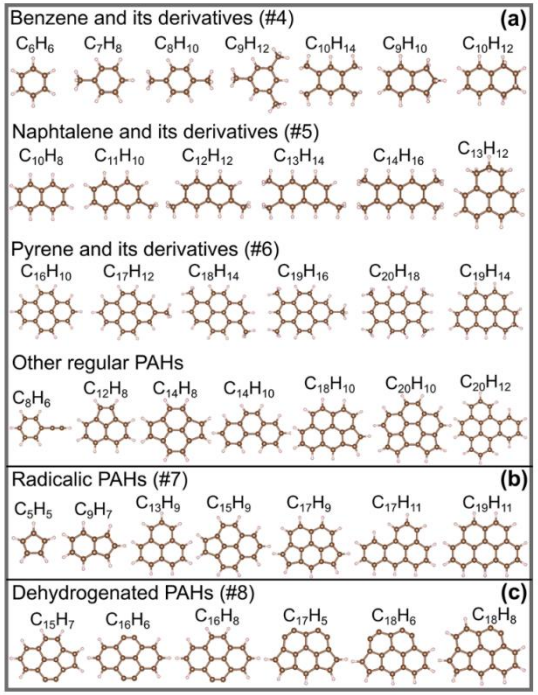


Figure 4. Structures of magic (poly)aromatic HCs.

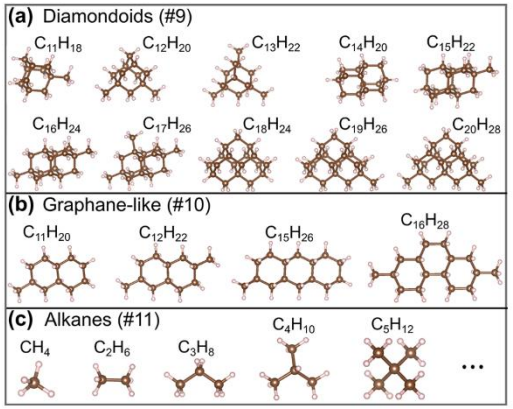


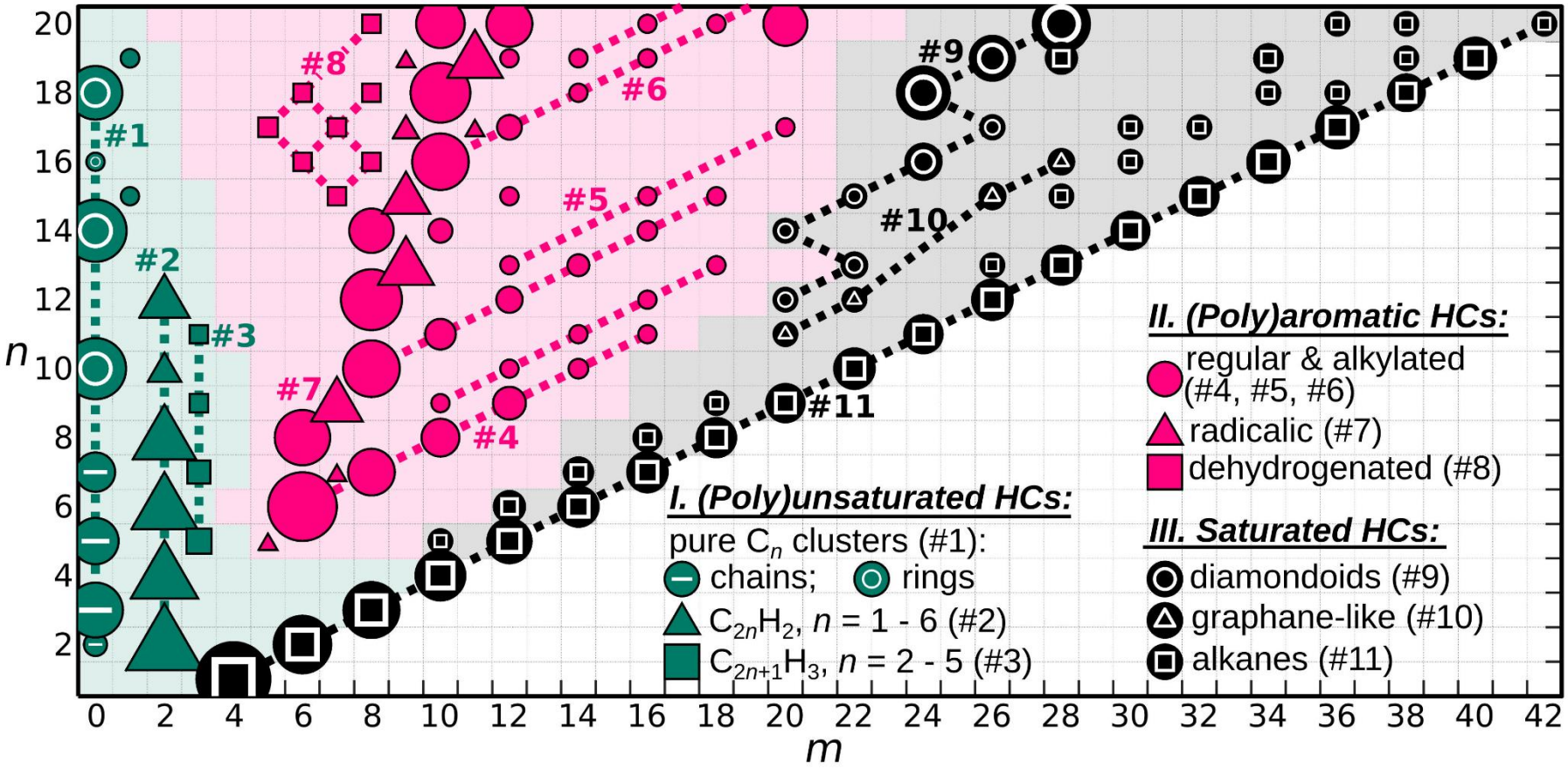
Figure 5. Structures of magic saturated HCs.

Which hydrocarbons are stable?

(Lepeshkin & Oganov, *J. Phys. Chem. Lett.* 2022)

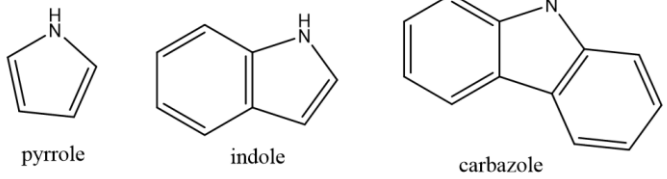
-Homologous series: alkanes etc.

-Huge diversity, explaining the diversity of organic chemistry.

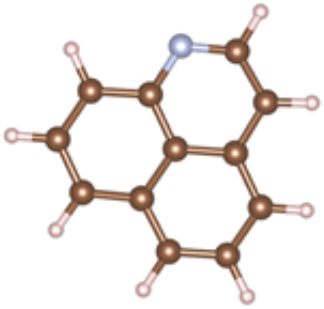


Towards greater complexity and molecules of life: C-H-N system

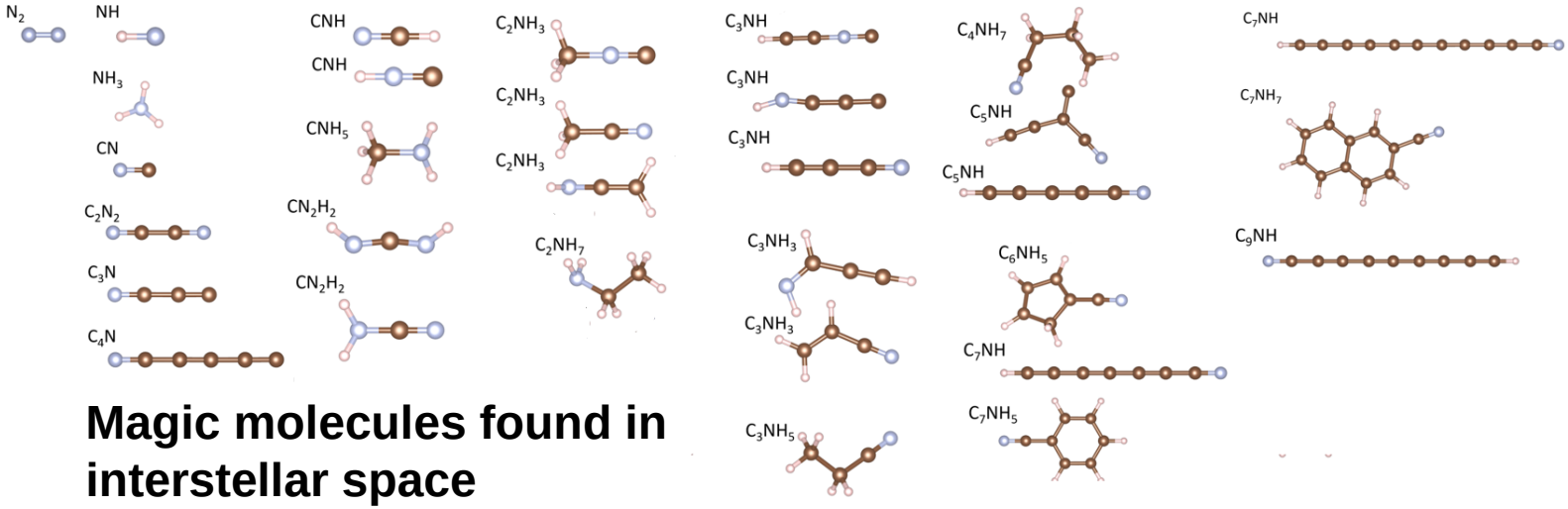
(Vaneeva & Oganov, *in prep.*)



Magic molecules found in crude oil

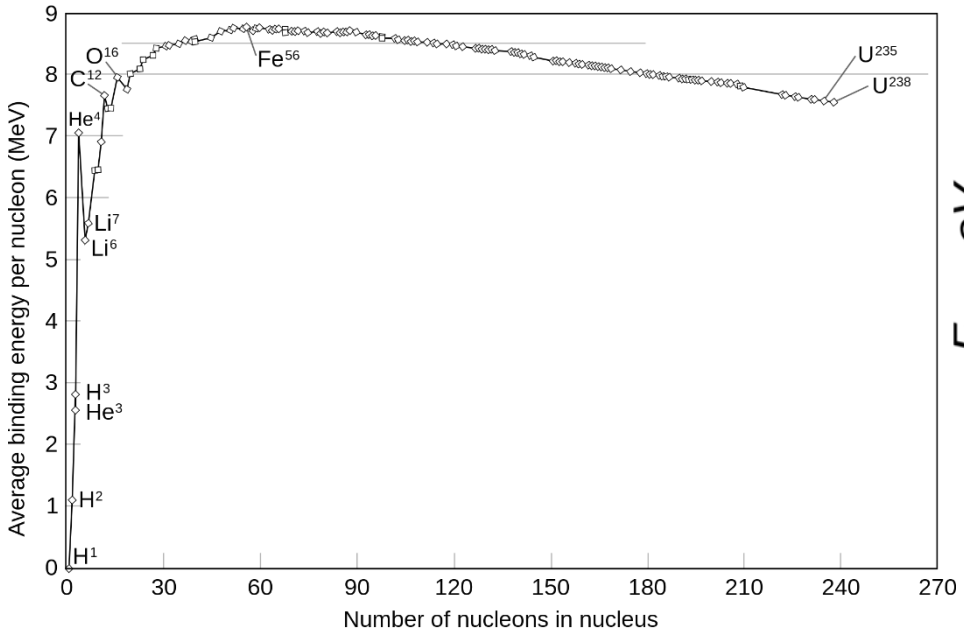


Newly predicted almost magic molecule $C_{12}NH_8$

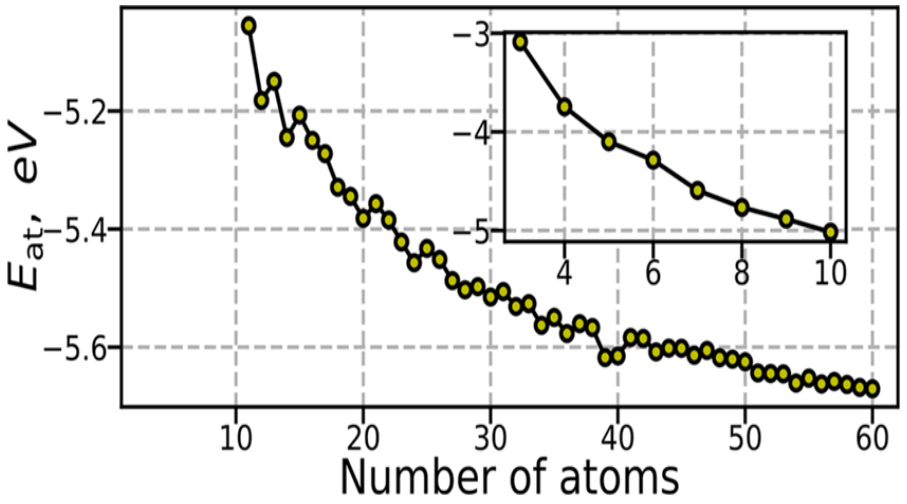


Magic molecules found in interstellar space

We've seen the similarities, but there are also differences:
1. Long-range interactions stabilize large molecules, destabilize heavy nuclei

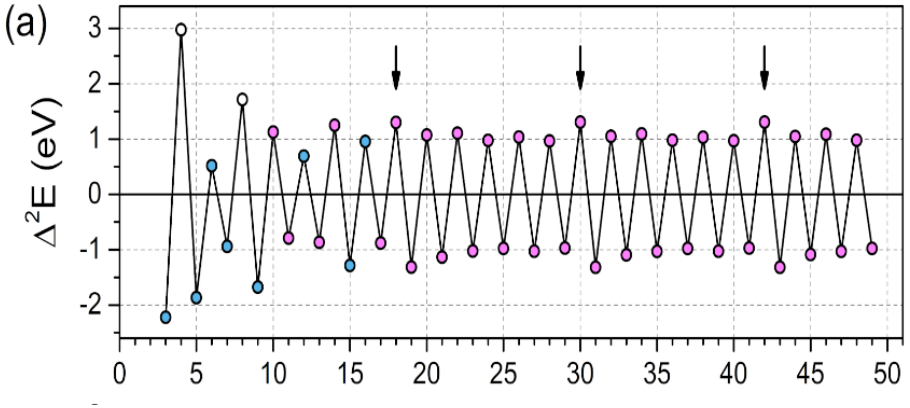


Binding energy of nuclei

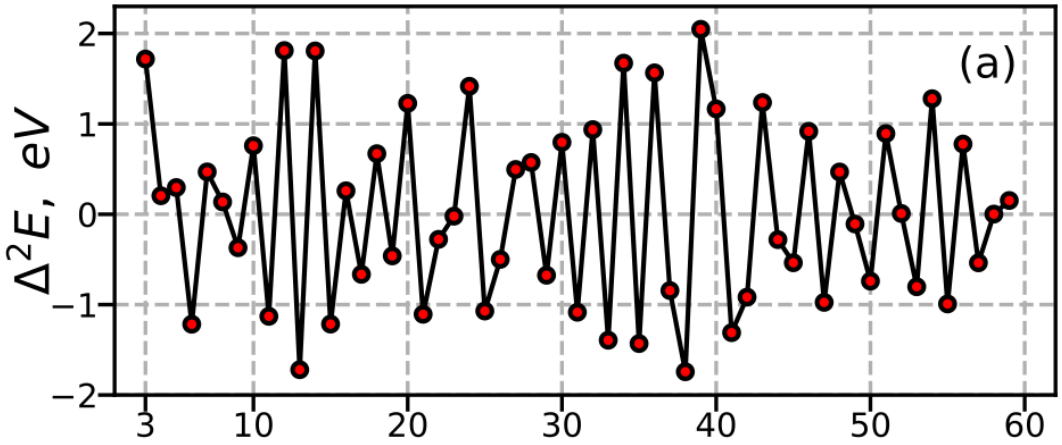


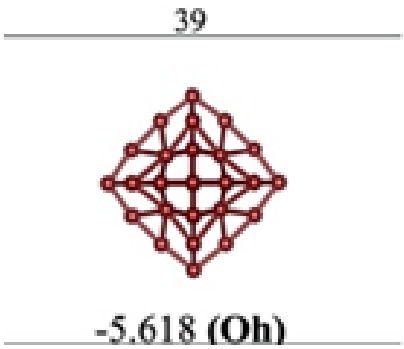
Atomization energy of molecules

We've seen the similarities, but there are also differences:
2. Two types of closed shells in molecules: electronic and structural



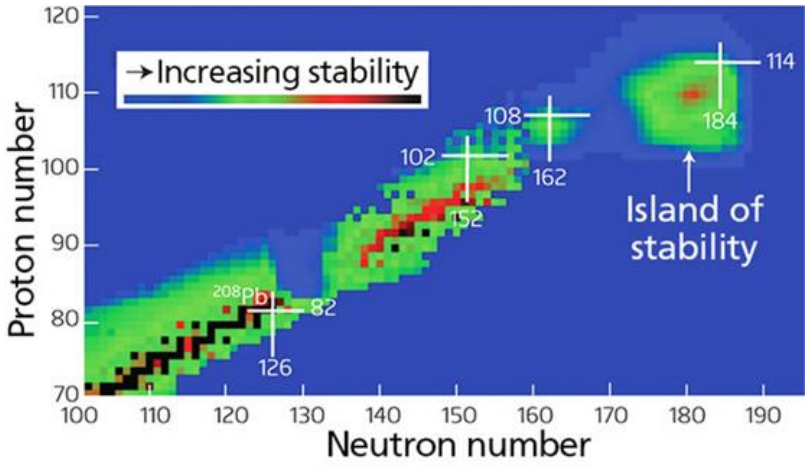
Dominance of electronic magic numbers in phosphorus

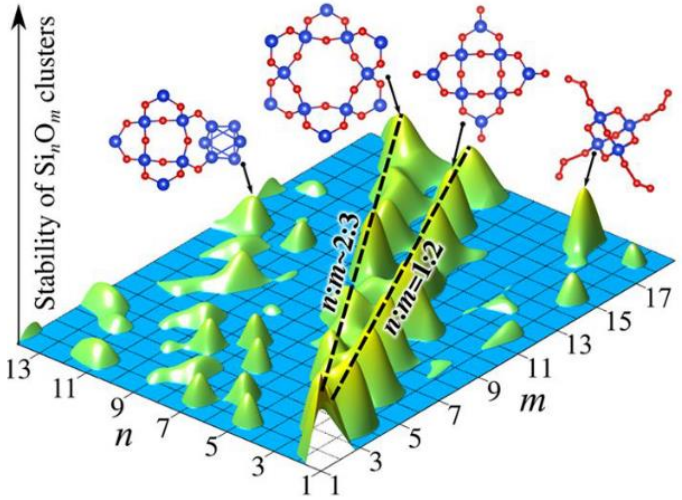


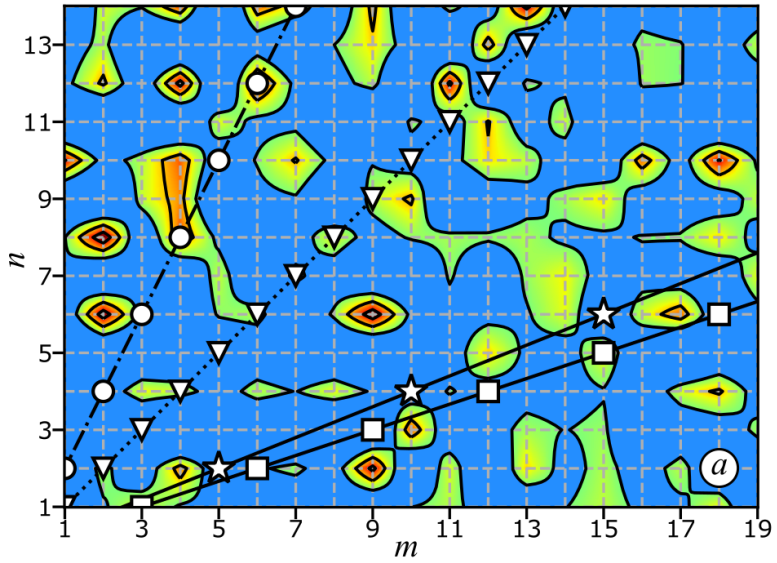


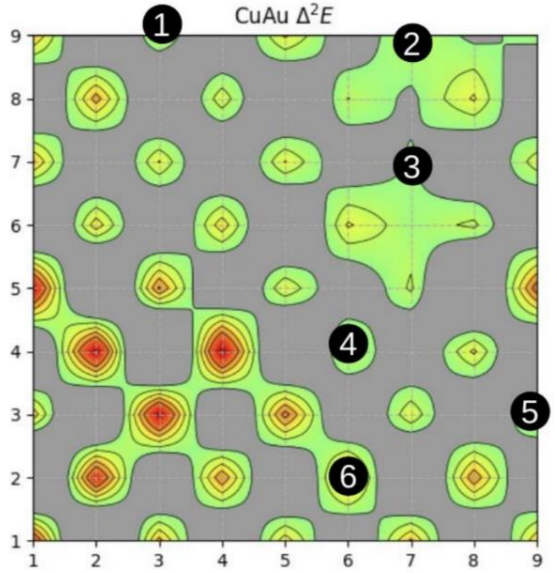
Competition between electronic and structural magic numbers in boron

We've seen the similarities, but there are also differences: 3. Molecular diagrams of stability can have different topologies









Simple questions

- **Why some elements vigorously react, while others don't?**
- **Why some compounds are stable, while others are not?**
- **Why some parageneses exist, while others do not?**
- **Why high-pressure chemistry is so different?**

  -everything eventually becomes metallic.

  -strange structures of the elements (host-guest Na, K, Rb, Ca,…).

  -emergence of «strange» compounds Na_3Cl, ThH_{10}, etc.

  -«strange» CaS_5, Na_2S_5 exist already at normal conditions.

  -inert gases become more reactive.

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- **Why some molecules are easily formed and other are not? ("Can anyone explain P_4O_{18}?").**
- **Why is symmetry so prevalent among non-biological molecules?**

USPEX Computational Materials Discovery

Our team. Where great minds do NOT think alike.

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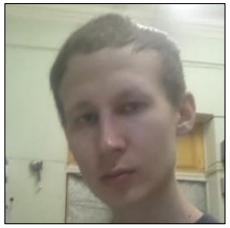

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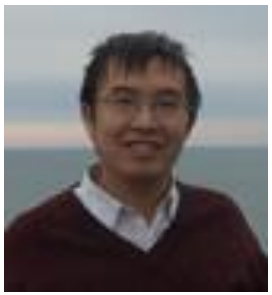

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