# (Co)evolutionary methods for predicting exotic compounds and materials with optimal properties


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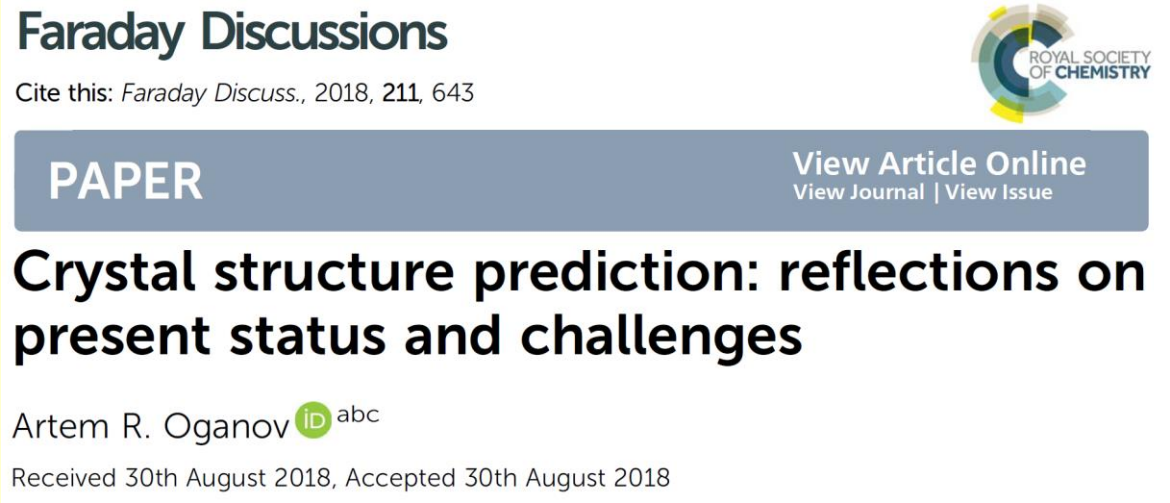
# Two roads in computational materials discovery

**Big data methods**
+Useful for high-throughput
-Crude
-Cannot predict completely new knowledge
-Database incompleteness is a problem

**Structure prediction:**
-Expensive calculations
+Reliable
+Can discover new things
+Do not require initial data

# Crystal Structure Can be Predicted for a Given Compound



Faraday Discussions

Cite this: *Faraday Discuss.*, 2018, **211**, 643

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## Crystal structure prediction: reflections on present status and challenges

Artem R. Oganov [abc]

Received 30th August 2018, Accepted 30th August 2018

# The USPEX project
# (Universal Structure Predictor: Evolutionary Xtallography)

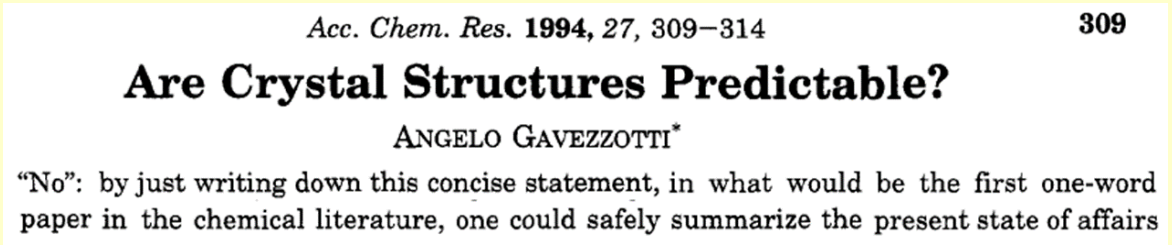
## http://uspex-team.org

[Oganov A.R., Glass C.W., *J.Chem.Phys.* 124, 244704 (2006)]

- **Combination of evolutionary algorithm and quantum-mechanical calculations.**
- **>7100 users.**
- **Solves «intractable» problem of structure prediction**

**-3D, 2D, 1D, 0D –systems,**

**-prediction of phase transition mechanisms.**

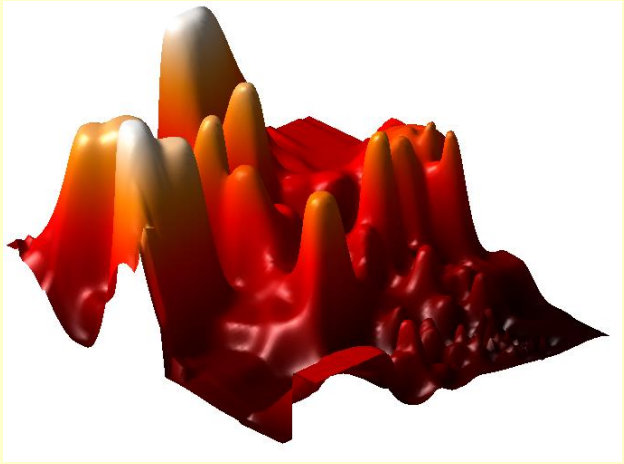


*Acc. Chem. Res.* **1994,** *27,* 309−314 **309**

**Are Crystal Structures Predictable?**

ANGELO GAVEZZOTTI*

"No": by just writing down this concise statement, in what would be the first one-word paper in the chemical literature, one could safely summarize the present state of affairs



**Energy landscape of $Au_8Pd_4$**

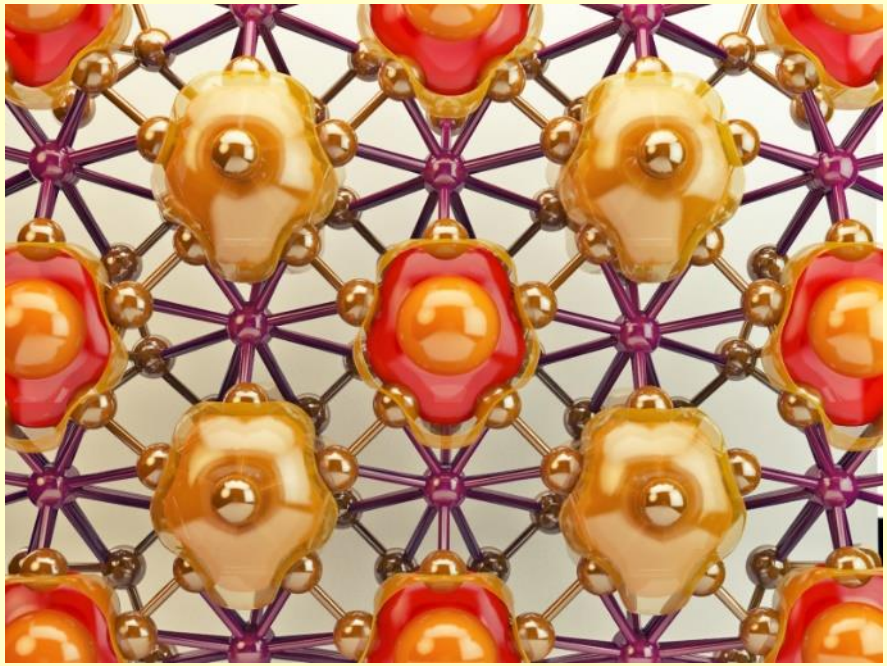
**W. Kohn**

**J. P. Perdew**

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

$$E_{GGA,xc} = \int d\mathbf{r}\, F_{xc}(\rho, \frac{|\nabla\rho|}{2k_F\rho(\mathbf{r})})\rho(\mathbf{r})e_x[\rho(\mathbf{r})]$$

# Predicting new crystal structures without empirical information

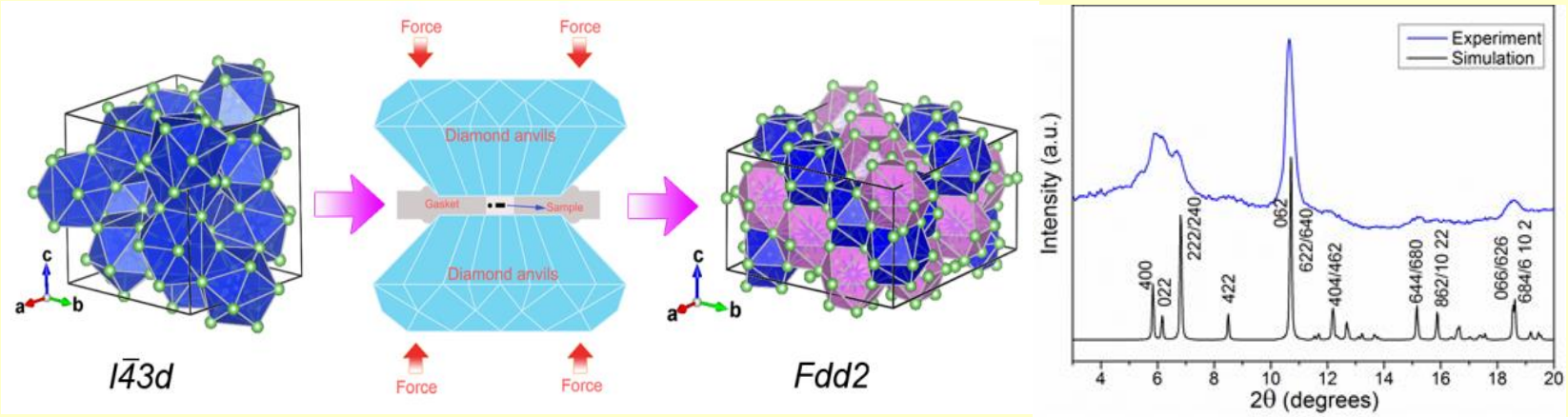


**New superhard structure of boron (Oganov et al., *Nature*, 2009)**

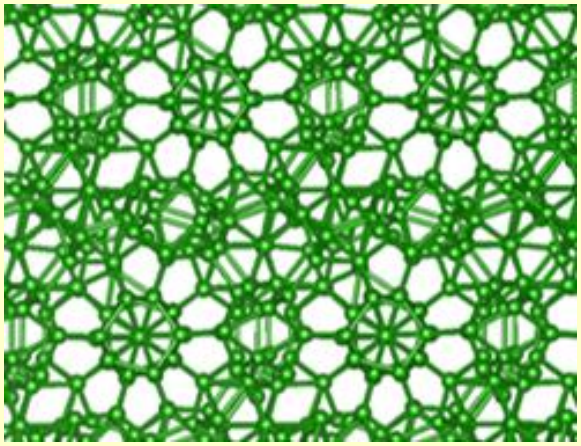

**High-pressure transparent allotrope of sodium (Ma, Eremets, Oganov, *Nature*, 2009)**

# Cases of record complexity:
# -$Li_{15}Si_4$ with 152 atoms/cell
# -disordered β-boron with 106 atoms/cell

Li-Si




**Structural transformation of $Li_{15}Si_4$ at 7 GPa. New phase has more attractive properties for use in Li-batteries. [Zeng & Oganov, *Adv. Energy Mat.*, 2015]**

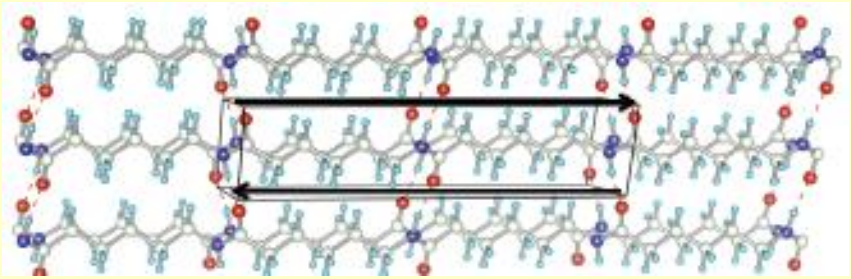


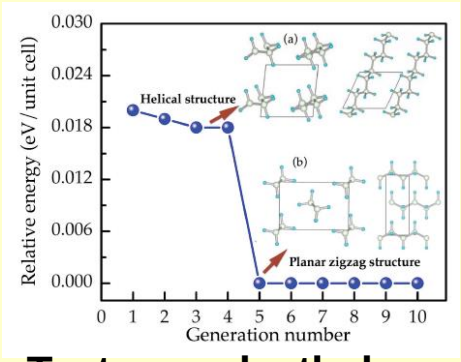
**Crystal structure of β-boron at ambient conditions.**
**[Podryabinkin, Shapeev & Oganov, *Phys. Rev. B*, 2019]**

# Prediction of new polymers for flexible capacitors

**(Zhu, Sharma, Oganov: *J.Chem.Phys.* 2014, *Nature Commun.* 2014)**

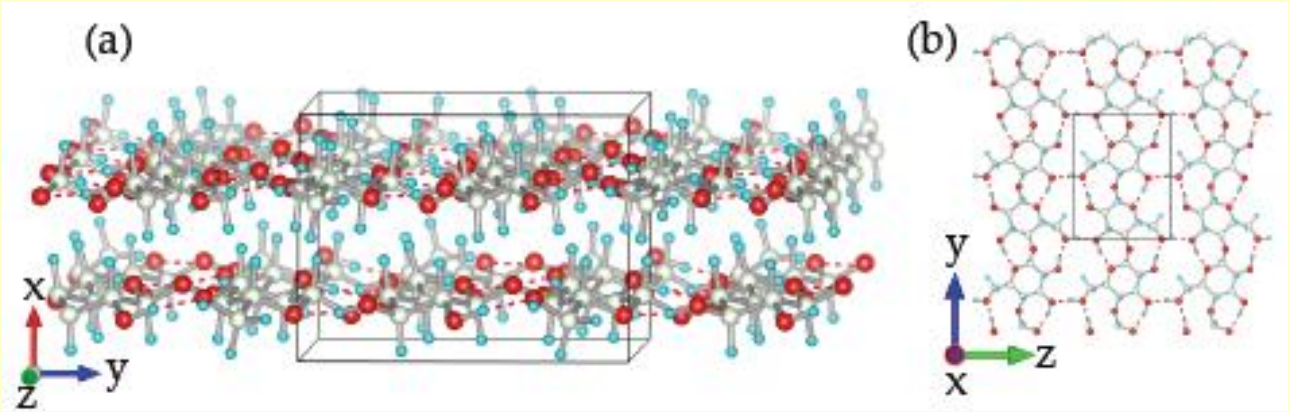
**Nylon-6 test**

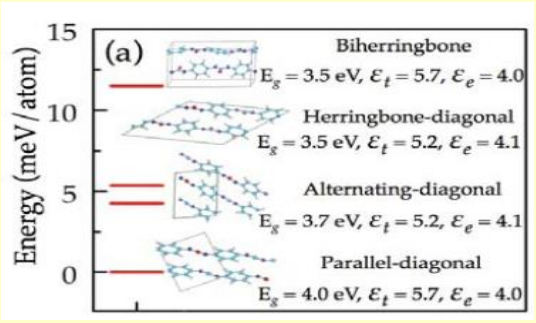




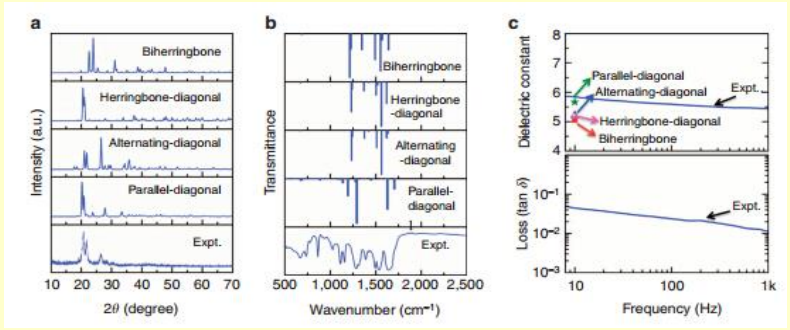

**Test on polyethylene**

**Cellulose test**




**Prediction of 3 new high-k polymers**

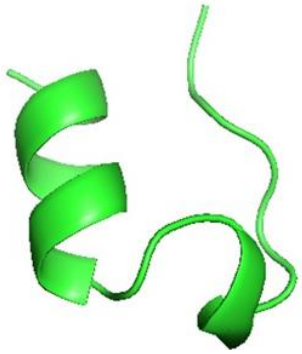



**Experimental proof**

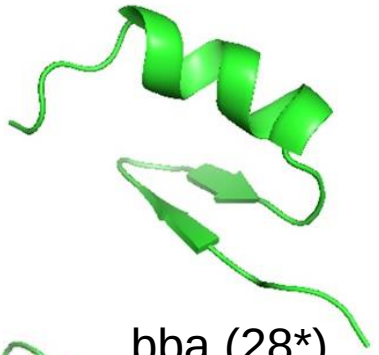
# Protein structure can also be predicted by USPEX

**[Rachitsky, Kruglov, Oganov, in prep.]**

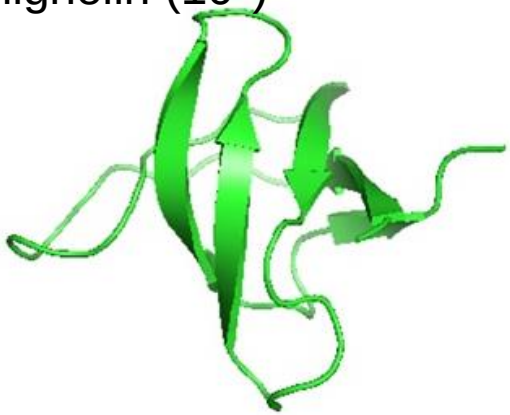
Chignolin (10*)



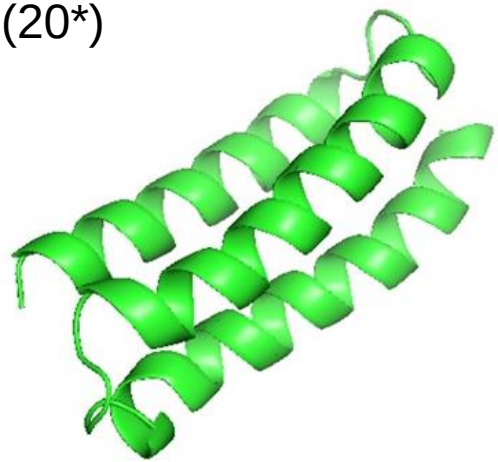
Trp-cage (20*)



bba (28*)



1shf (58*)

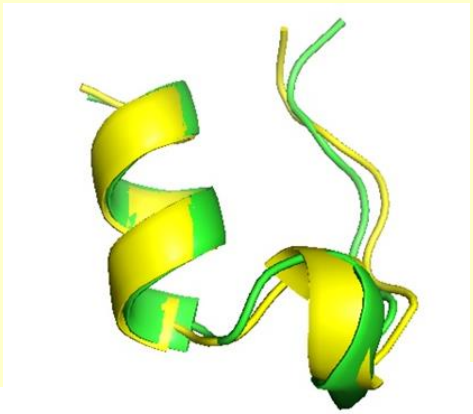


2a3d (73*)

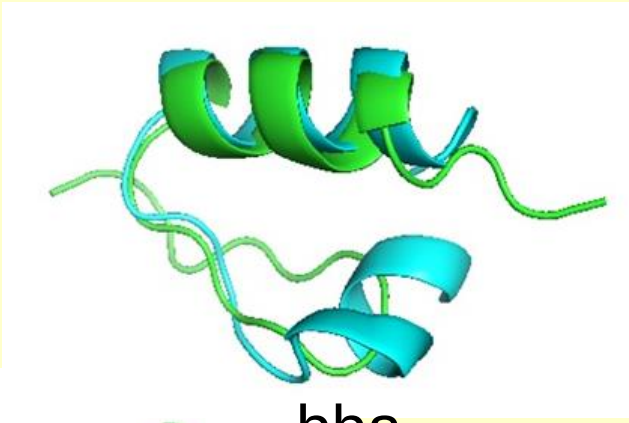
* Number of amino acid residues

# Comparing USPEX predictions with experimental protein structures

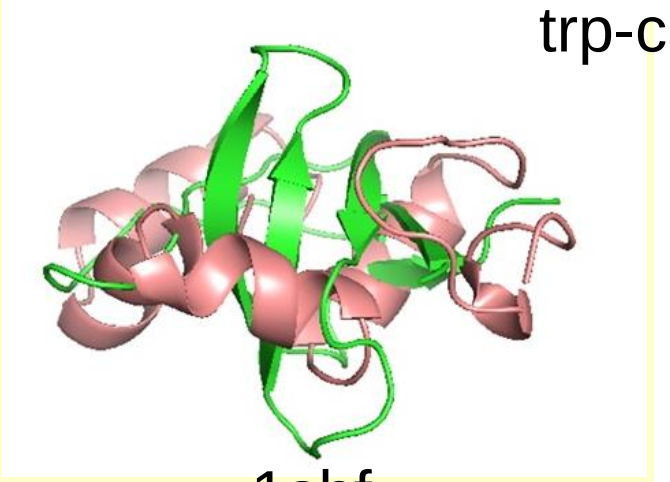
chignolin



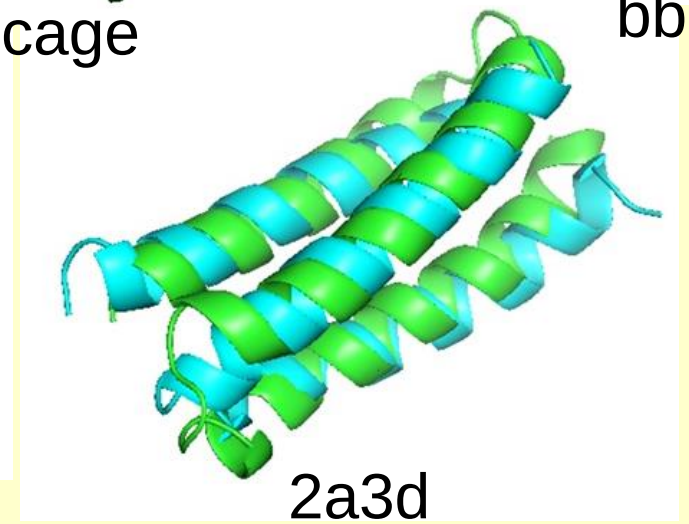
trp-cage



bba

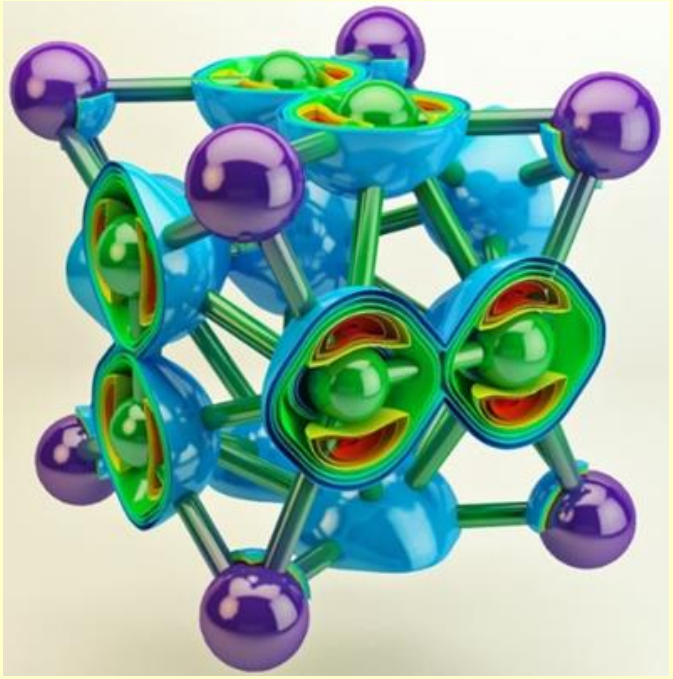


1shf



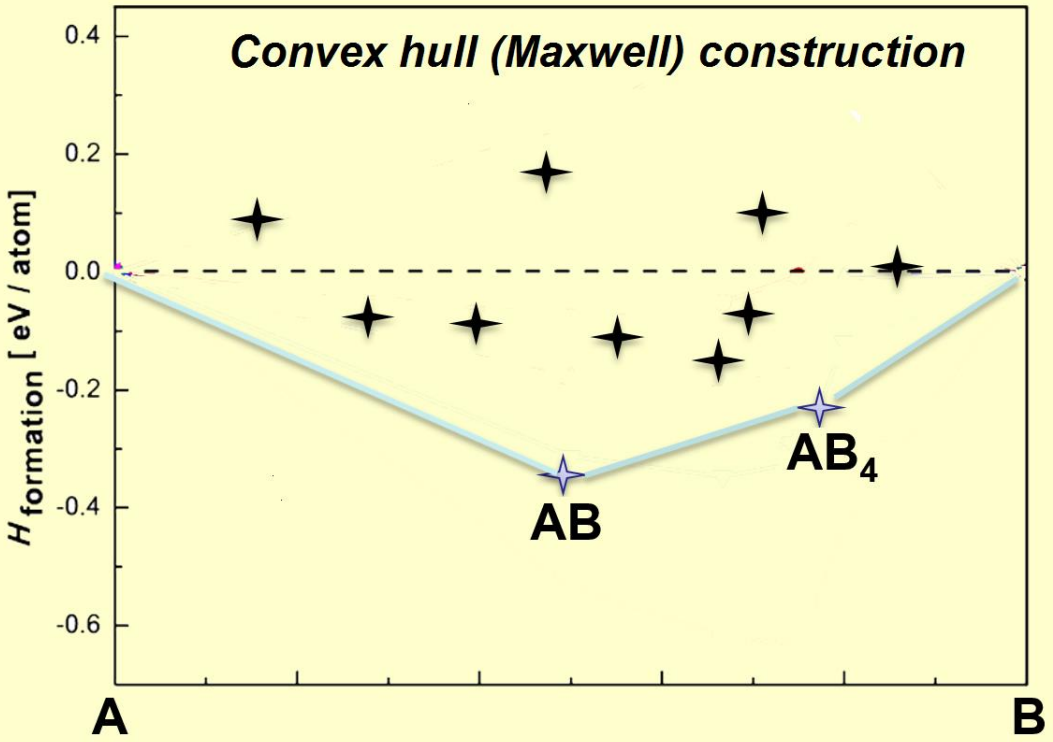
2a3d

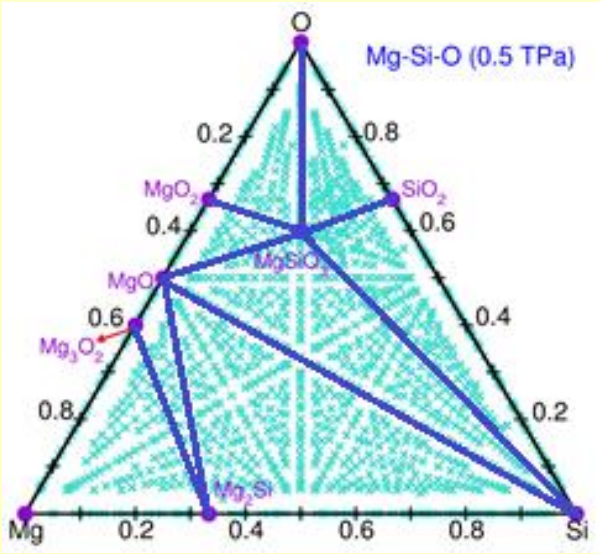
# USPEX Can Predict Stable Compounds



# To predict thermodynamic stability, we must use the Maxwell construction (the convex hull)

## Thermodynamic stability in variable-composition systems

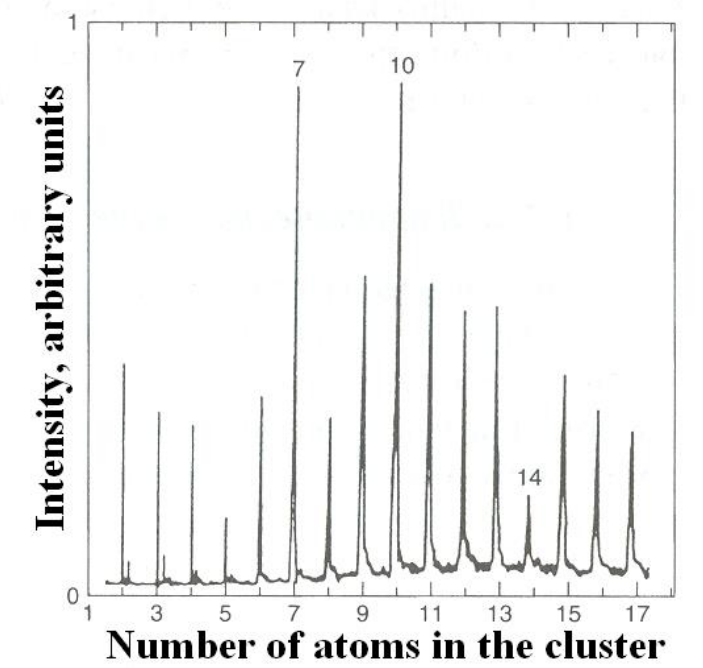


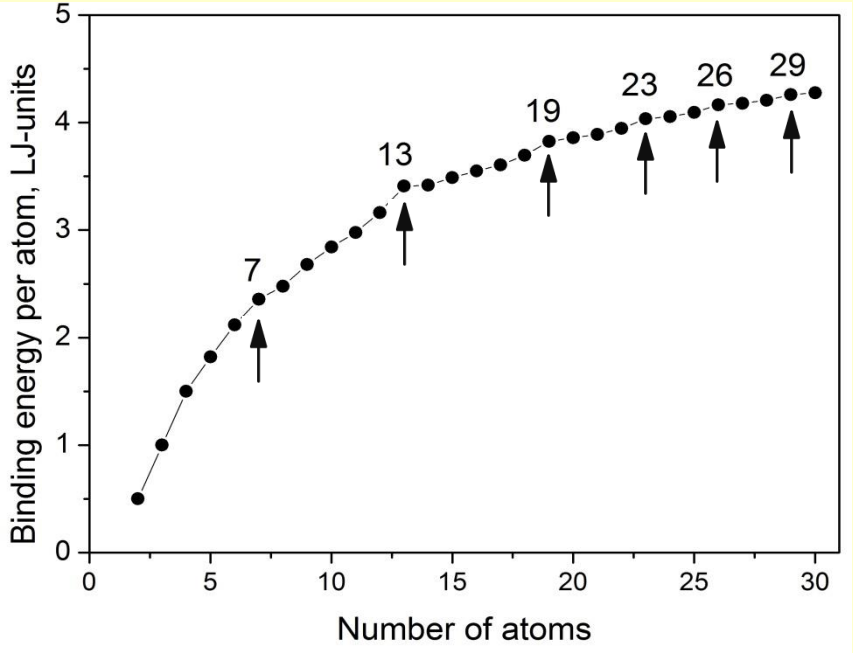

**3-component convex hull: Mg-Si-O system at 500 GPa (Niu & Oganov, *Sci. Rep.* 2015)**

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

# Stability of molecules: conventional, local

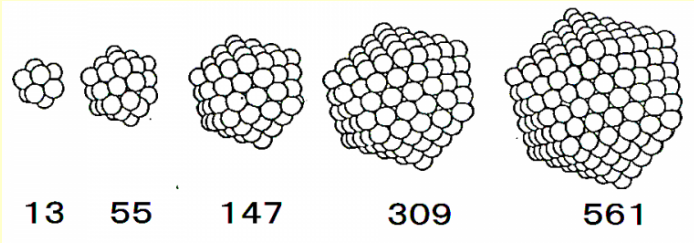



**Mass-spectrum of $Pb_n$ clusters (Poole & Owens, 2003)**




**Lennard-Jones clusters**

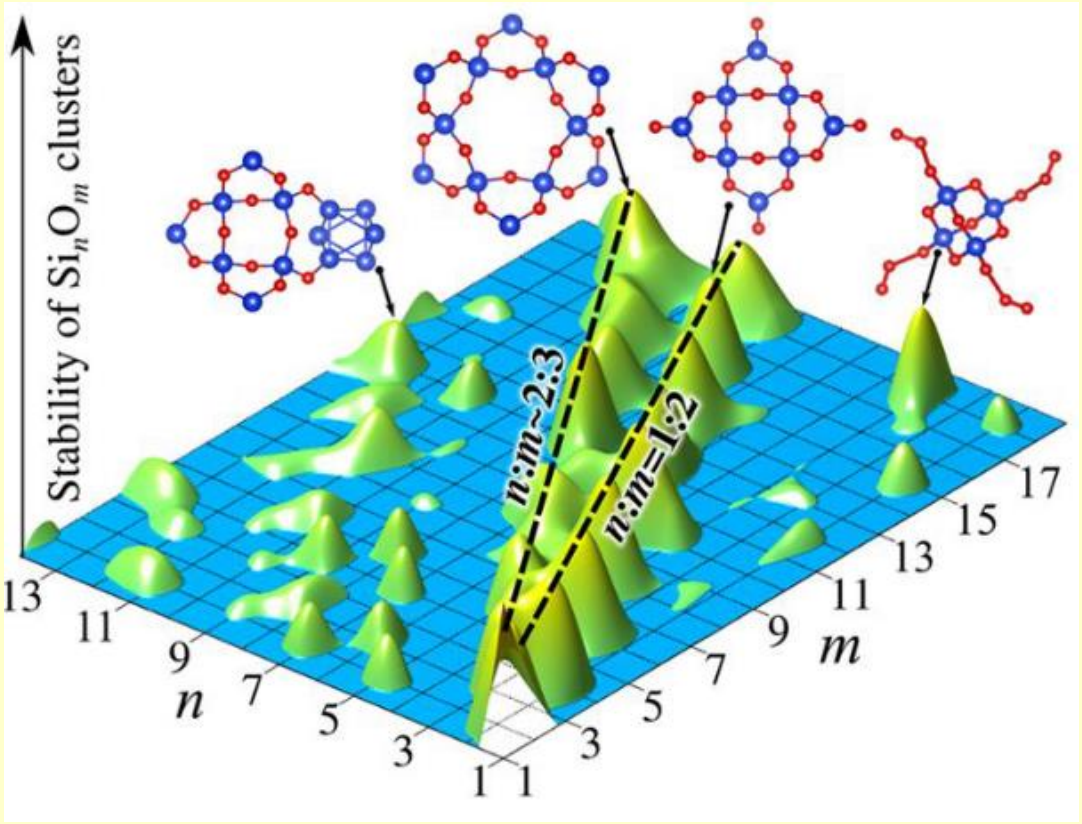
↑ – “magic” cluster



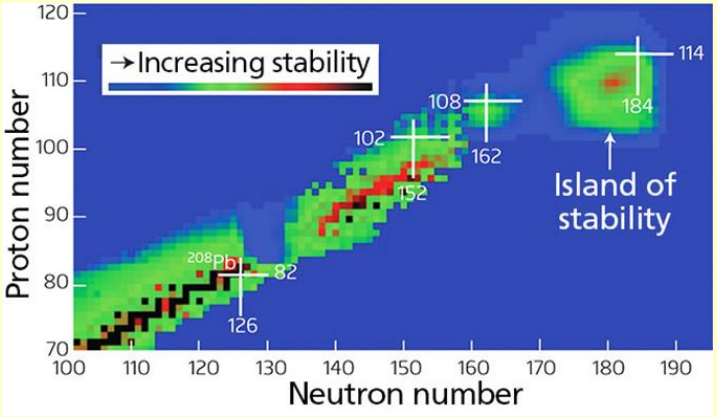

**Binding energy grows with the size of cluster. We define stability relative to neighboring compositions. Stability is due to filled shells (electronic, atomic).**

# 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., $Si_4O_{18}$**



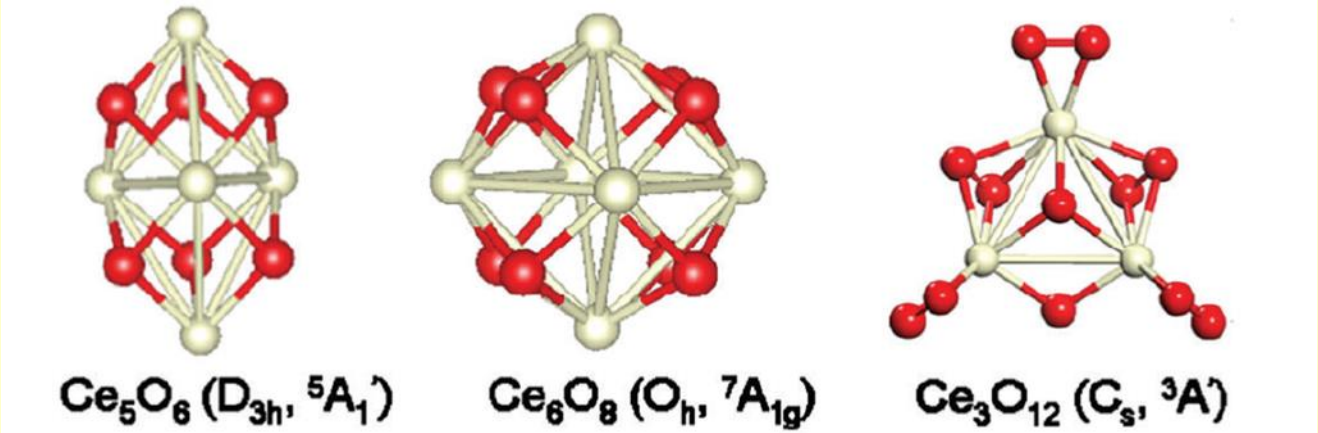

«Magic» nuclei: with filled proton or neutron shells (2, 8, 20, 28, 50, 82, 126 p or n)
($1s^2/2p^6/3d^{10}2s^2/4f^8/4f^63p^65g^{10}/5g^84d^{10}3s^26h^{12}$)

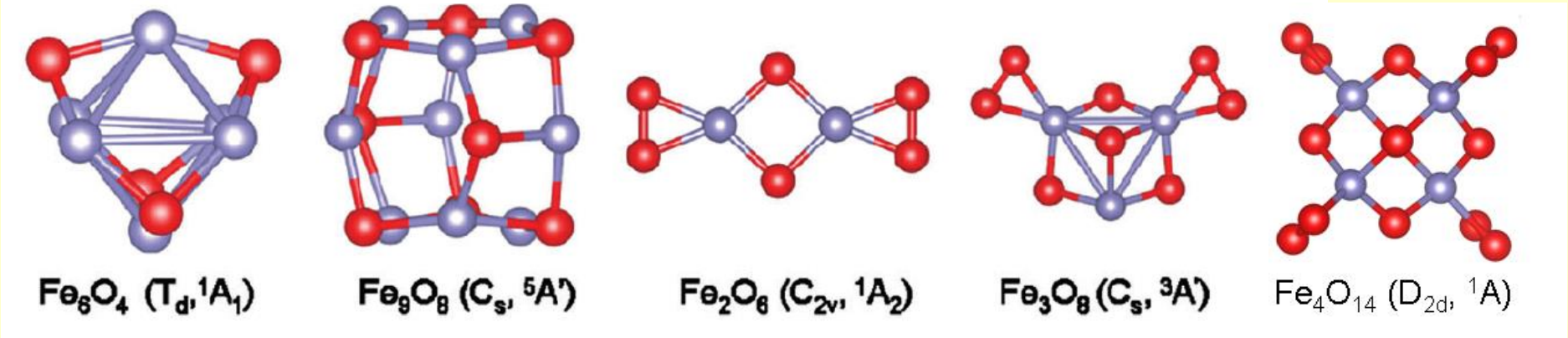
Magic numbers of electrons = 2, 10, 18, 36, 54, 86, 118)

**Analogy with magic atomic nuclei**

# Unusual compositions of transition metal oxide clusters

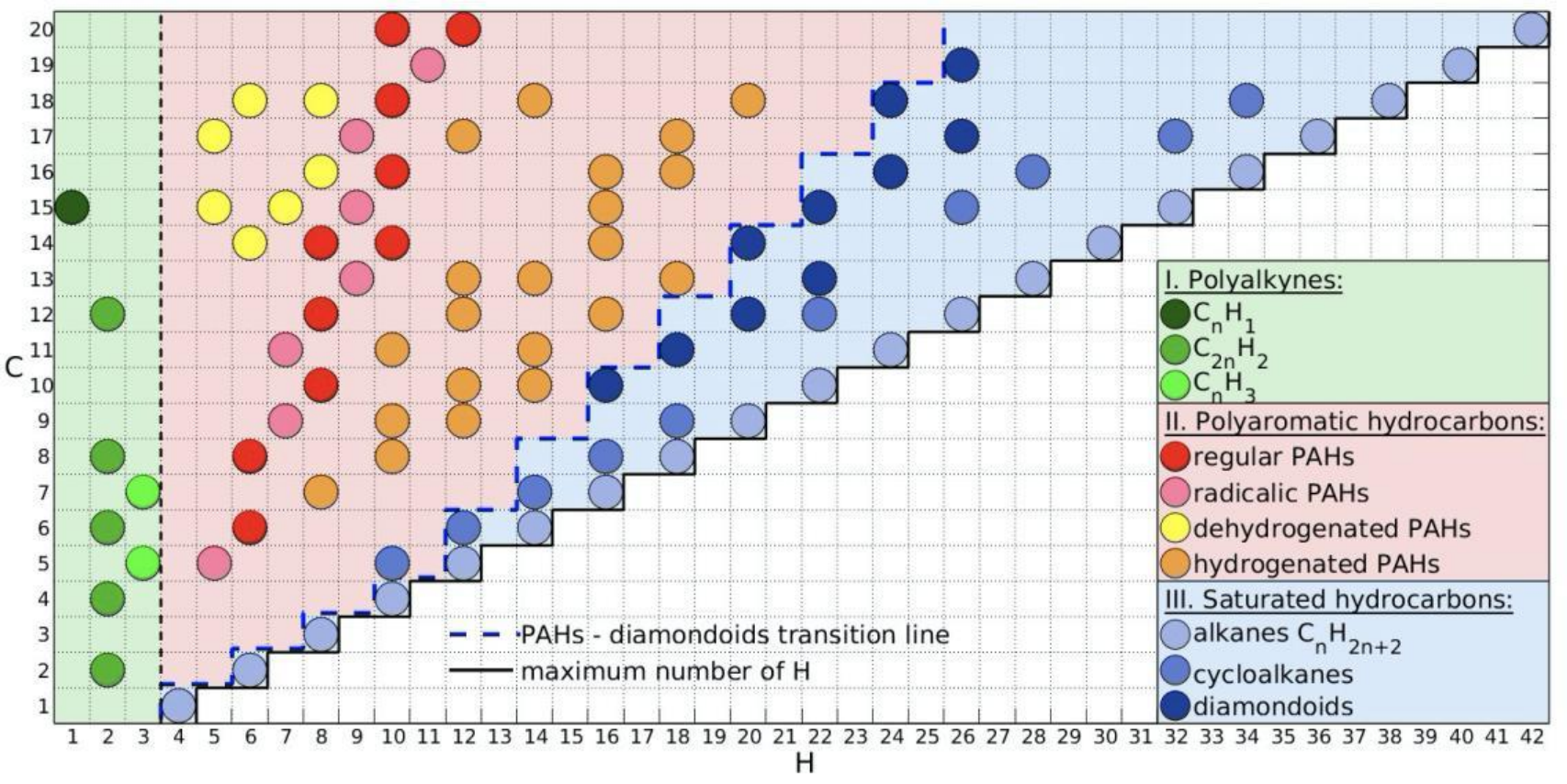
**[Yu & Oganov, *Phys. Chem. Chem. Phys.*, 2018]**



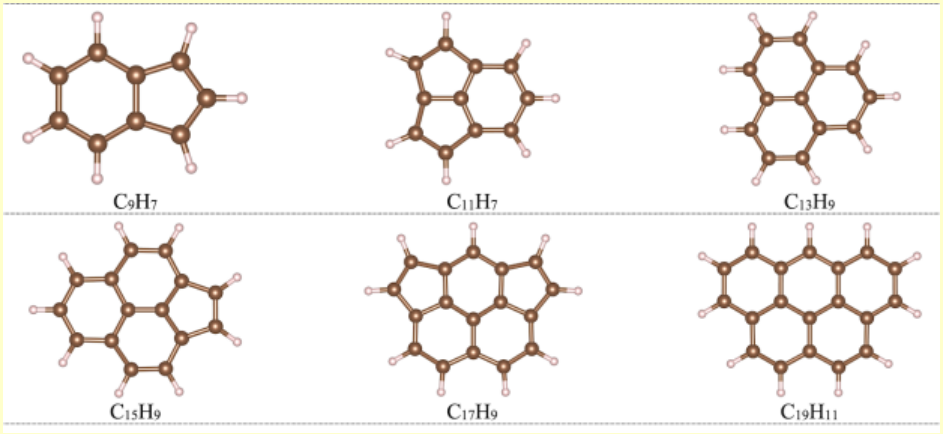

**Do crystals grow from such particles?**

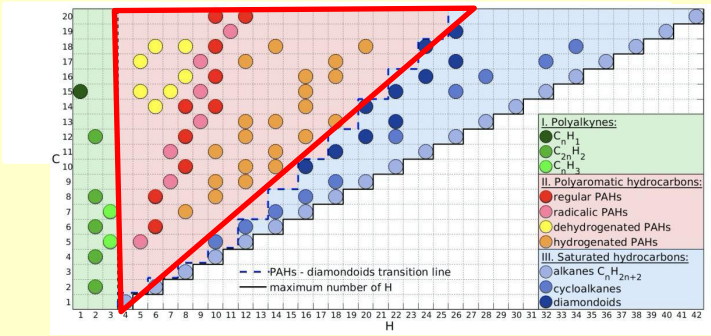
# Prediction of stable hydrocarbons: very diverse chemistry

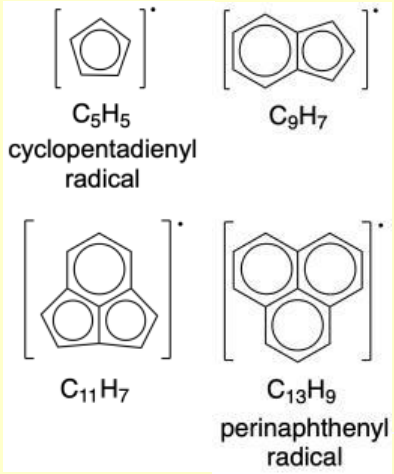



**Complex chemistry of hydrocarbons made simple:**
**-Rationalize which molecules are reactive and polymerize.**
**-Rationalize magnetic(!) hydrocarbons, which are known ($C_{13}H_9$ etc).**

# Stable magnetic hydrocarbons?



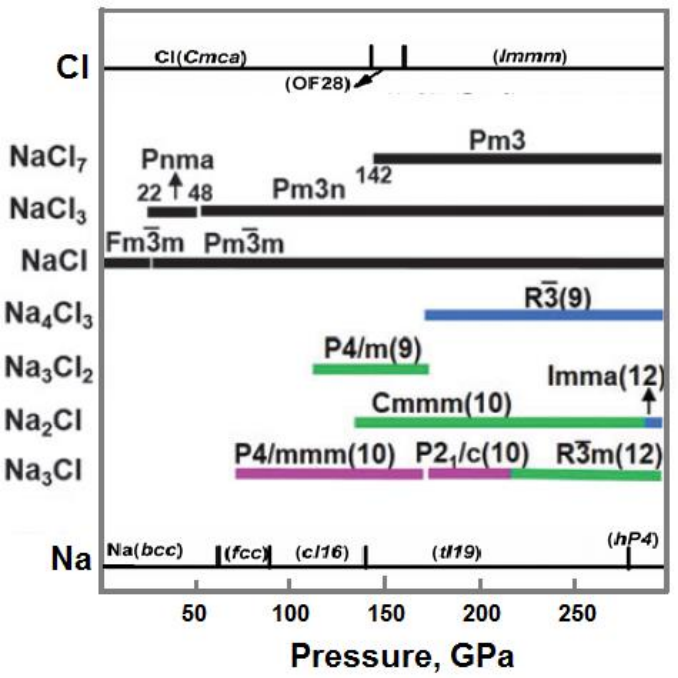




Such molecules are found in interstellar space and in the atmosphere of Titan

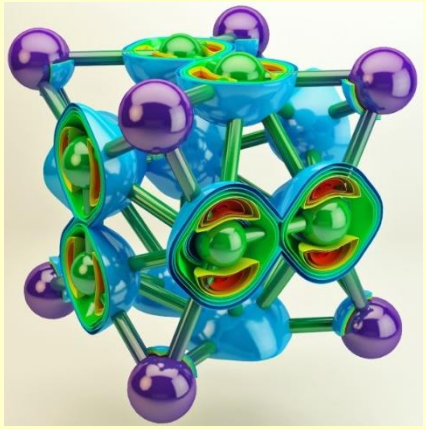
Na-Cl

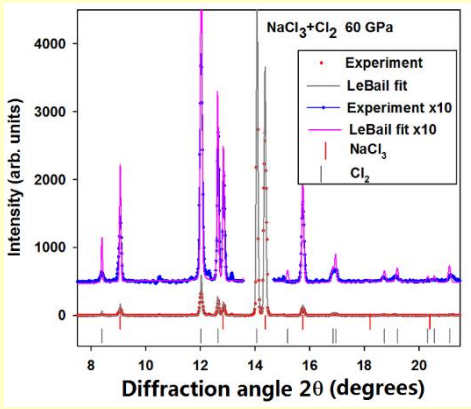
# Predictive power of modern methods:

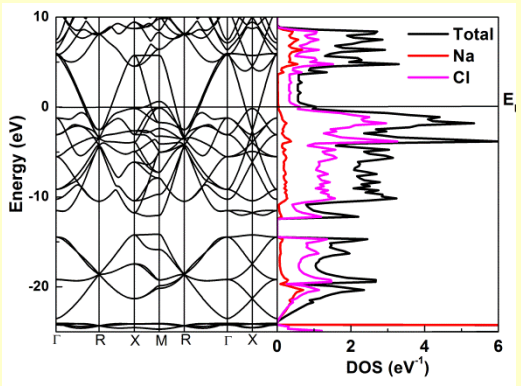
**$Na_3Cl$, $Na_2Cl$, $Na_3Cl_2$, NaCl, $NaCl_3$, $NaCl_7$ are stable under pressure [Zhang, Oganov, et al. *Science*, 2013].**

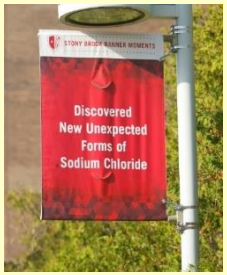



Stability fields of sodium chlorides






$NaCl_3$: atomic and electronic structure, and experimental XRD pattern

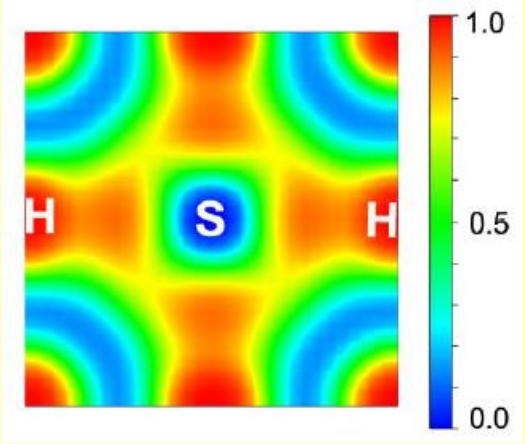
## Chemical anomalies:

- Divalent Cl in $Na_2Cl$!
- Coexistence of metallic and ionic blocks in $Na_3Cl$!
- Positively charged Cl in $NaCl_7$!

[Zhang, Oganov, et al., *Science* (2013)]
[Saleh & Oganov, *PCCP* (2015)]

# Highest-Tc superconductivity: new record, 203 Kelvin (Duan et al., *Sci. Rep.* 4, 6968 (2014))

**H-S**

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CONDENSED MATTER PHYSICS

Received
7 July 2014

Accepted
29 September 2014

Published
10 November 2014

Correspondence and requests for materials should be addressed to T.C. (cuitian@jlu.edu.cn)

## Pressure-induced metallization of dense $(H_2S)_2H_2$ with high-$T_c$ superconductivity

Defang Duan[1,2], Yunxian Liu[1], Fubo Tian[1], Da Li[1], Xiaoli Huang[1], Zhonglong Zhao[1], Hongyu Yu[1], Bingbing Liu[1], Wenjing Tian[2] & Tian Cui[1]

[1]State Key Laboratory of Superhard Materials, College of physics, Jilin University, Changchun, 130012, P. R. China, [2]State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun, 130012, P. R. China.

The high pressure structures, metallization, and superconductivity of recently synthesized $H_3$-containing compounds $(H_2S)_2H_2$ are elucidated by *ab initio* calculations. The ordered crystal structure with *P*1 symmetry is determined, supported by the good agreement between theoretical and experimental X-ray diffraction data, equation of states, and Raman spectra. The *Cccm* structure is favorable with partial hydrogen bond symmetrization above 37 GPa. Upon further compression, $H_2$ molecules disappear and two intriguing metallic structures with *R*3*m* and *Im*-3*m* symmetries are reconstructive above 111 and 180 GPa, respectively. The predicted metallization pressure is 111 GPa, which is approximately one-third of the currently suggested metallization pressure of bulk molecular hydrogen. Application of the Allen-Dynes-modified McMillan equation for the *Im*-3*m* structure yields high $T_c$ values of 191 K to 204 K at 200 GPa, which is among the highest values reported for $H_2$-rich van der Waals compounds and $MH_3$ type hydride thus far.



## Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system

A. P. Drozdov, M. I. Eremets, I. A. Troyan, V. Ksenofontov & S. I. Shylin

*Nature* (2015) | doi:10.1038/nature14964
Received 25 June 2015 | Accepted 22 July 2015 | Published online 17 August 2015

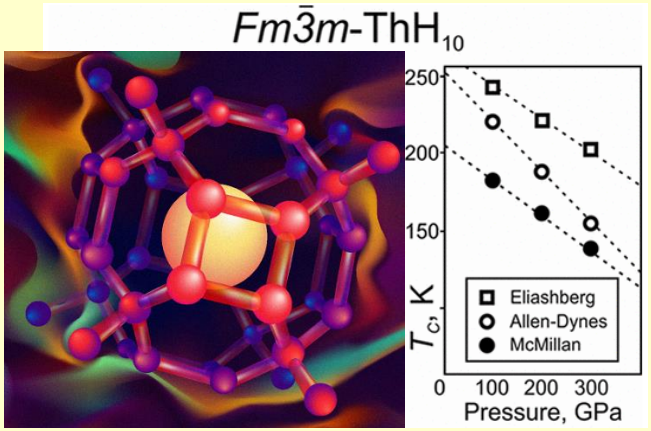
A superconductor is a material that can conduct electricity without resistance below a superconducting transition temperature, $T_c$. The highest $T_c$ that has been achieved to date is in the copper oxide system[1]: 133 kelvin at ambient pressure[2] and 164 kelvin at high pressures[3]. As the nature of superconductivity in these materials is still not fully understood (they are not conventional superconductors), the prospects for achieving still higher transition temperatures by this route are not clear. In contrast, the Bardeen–Cooper–Schrieffer theory of conventional superconductivity gives a guide for achieving high $T_c$ with no theoretical upper bound—all that is needed is a favourable combination of high-frequency phonons, strong electron–phonon coupling, and a high density of states[4]. These conditions can in principle be fulfilled for metallic hydrogen and covalent compounds dominated by hydrogen[5, 6], as hydrogen atoms provide the necessary high-frequency phonon modes as well as the strong electron–phonon coupling. Numerous calculations support this idea and have predicted transition temperatures in the range 50–235 kelvin for many hydrides[7], but only a moderate $T_c$ of 17 kelvin has been observed experimentally[8]. Here we investigate sulfur hydride[9], where a $T_c$ of 80 kelvin has been predicted[10]. We find that this system transforms to a metal at a pressure of approximately 90 gigapascals. On cooling, we see signatures of superconductivity: a sharp drop of the resistivity to zero and a decrease of the transition temperature with magnetic field, with magnetic susceptibility measurements confirming a $T_c$ of 203 kelvin. Moreover, a pronounced isotope shift of $T_c$ in sulfur deuteride is suggestive of an electron–phonon mechanism of superconductivity that is consistent with the Bardeen–Cooper–Schrieffer scenario. We argue that the phase responsible for high-$T_c$ superconductivity in this system is likely to be $H_3S$, formed from $H_2S$ by decomposition under pressure. These findings raise hope for the prospects for achieving room-temperature superconductivity in other hydrogen-based materials.

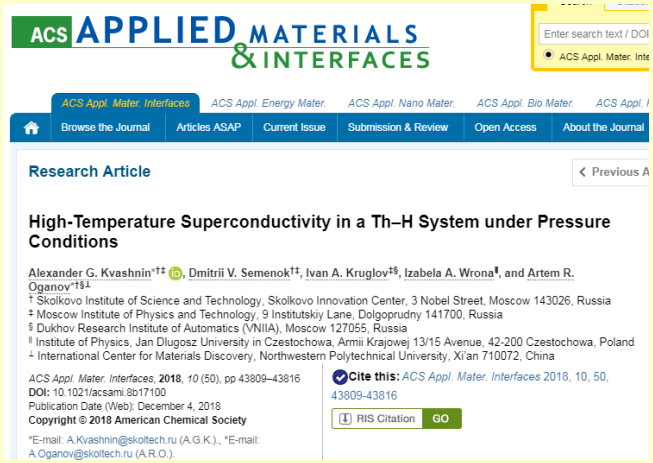
- **Old record Tc=135 K (Schilling, 1993) is broken: theorists (T. Cui, 2014) predicted new compound $H_3S$ with Tc~200 K.**
- **Confirmed by A. Drozdov et al. (*Nature* 525, 73 (2015)).**

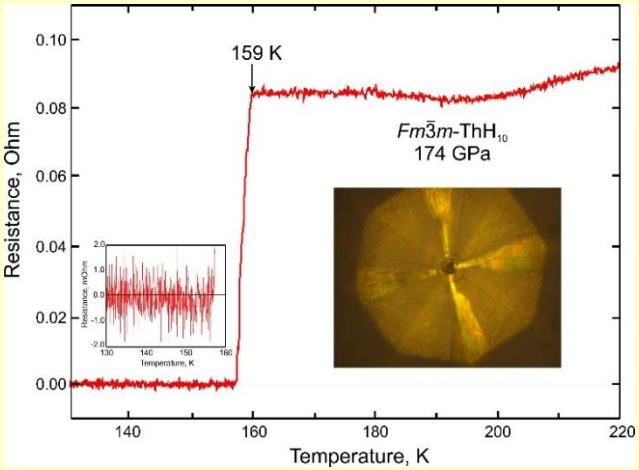
# Thorium superhydride $ThH_{10}$ ($T_C$ = 159-161 K)
## [Semenok, Troyan, Oganov, Materials Today 2020]

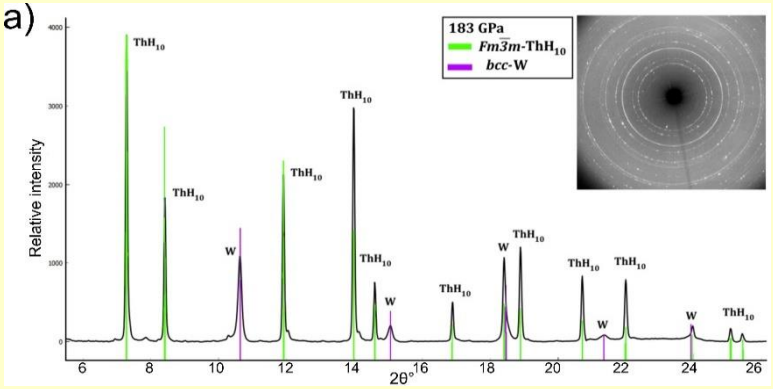
Predicted by us in 2018, synthesized by us in 2019 at 174 GPa!

Theory at 174 GPa gives Tc=167-183 K. Experiment: Tc = 161 K.



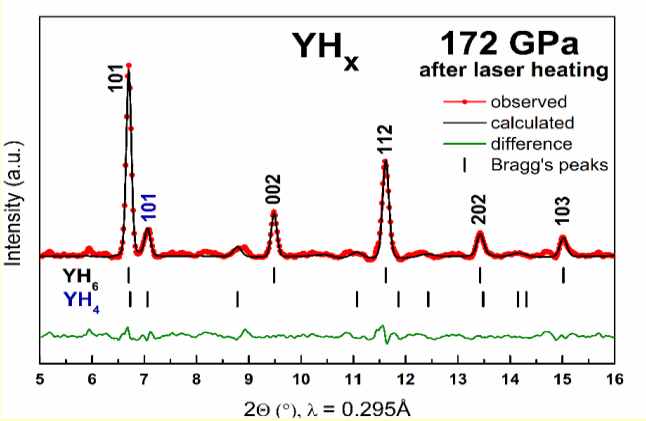



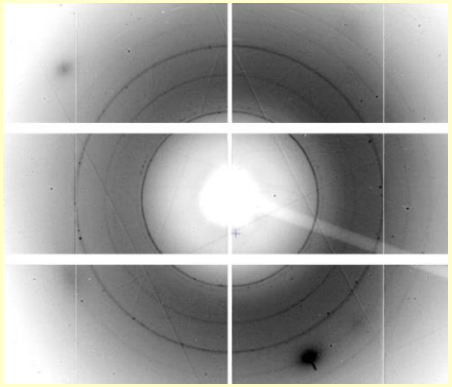



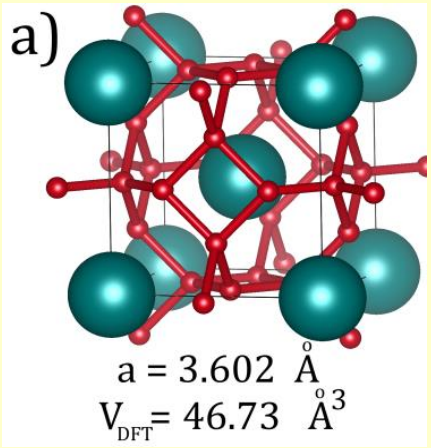



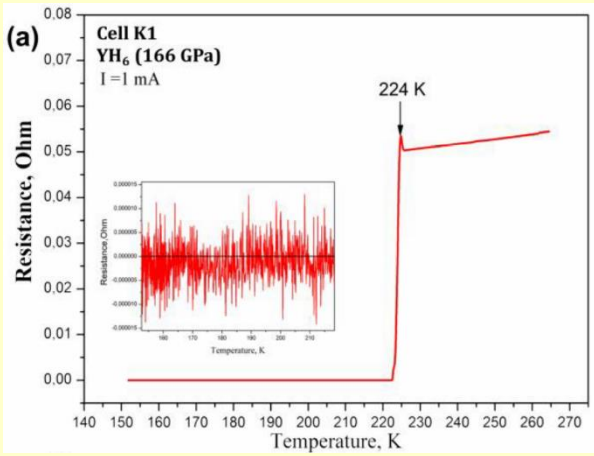
# Yttrium hydride $YH_6$ ($T_C$ = 224 K, $B_C$ = 116-158 T)

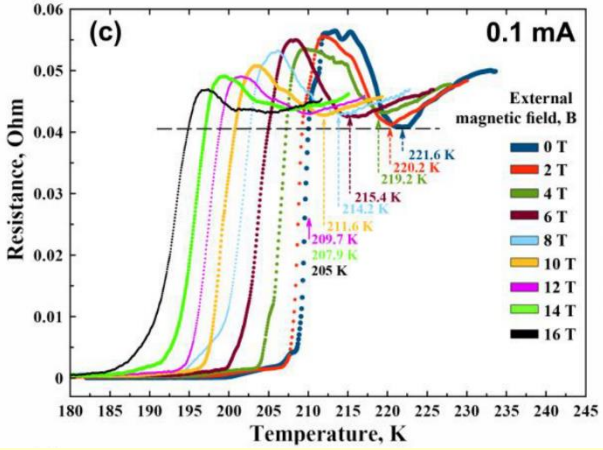
**[Semenok, Troyan, Oganov, *Advanced Materials*, 2021]**

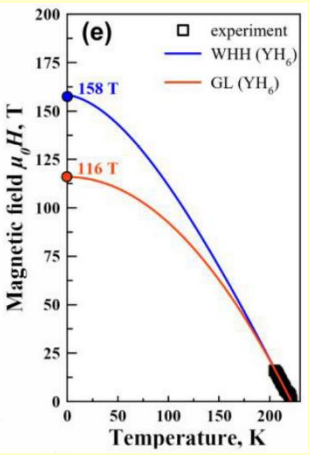


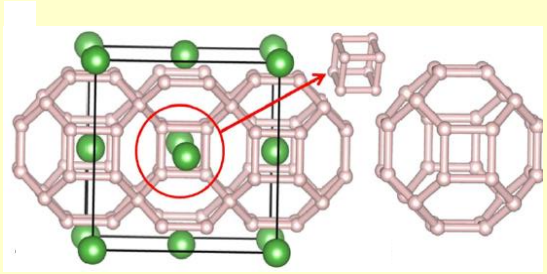


# And the record is broken again: $LaH_{10}$ (Tc = 250-260 K at 170 GPa)



The maximum $T_C$ ~ 250-260 K

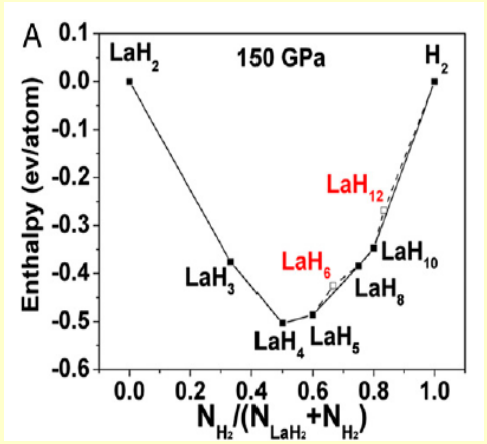
PNAS

## Potential high-$T_c$ superconducting lanthanum and yttrium hydrides at high pressure

Hanyu Liu[a], Ivan I. Naumov[a], Roald Hoffmann[b], N. W. Ashcroft[c], and Russell J. Hemley[d,e,1]

[a]Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015; [b]Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853; [c]Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY 14853; [d]Department of Civil and Environmental Engineering, The George Washington University, Washington, DC 20052; and [e]School of Applied and Engineering Physics, Cornell University, Ithaca, NY 14853

Contributed by Russell J. Hemley, May 5, 2017 (sent for review March 20, 2017; reviewed by Panchapakesan Ganesh, Jeffrey M. McMahon, and Dimitrios Papaconstantopoulos)




Cornell University Library

## Evidence for superconductivity above 260 K in lanthanum superhydride at megabar pressures

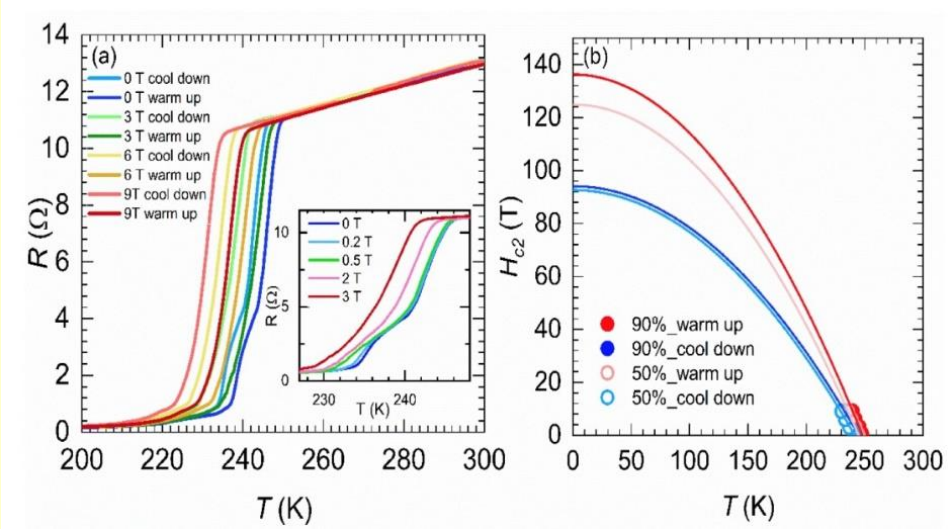
Maddury Somayazulu, Muhtar Ahart, Ajay K Mishra, Zachary M. Geballe, Maria Baldini, Yue Meng, Viktor V. Struzhkin, Russell J. Hemley

*(Submitted on 23 Aug 2018 (v1), last revised 29 Aug 2018 (this version, v3))*

## Superconductivity at 250 K in lanthanum hydride under high pressures

A. P. Drozdov, P. P. Kong, V. S. Minkov, S. P. Besedin, M. A. Kuzovnikov, S. Mozaffari, L. Balicas, F. Balakirev, D. Graf, V. B. Prakapenka, E. Greenberg, D. A. Knyazev, M. Tkacz, M. I. Eremets

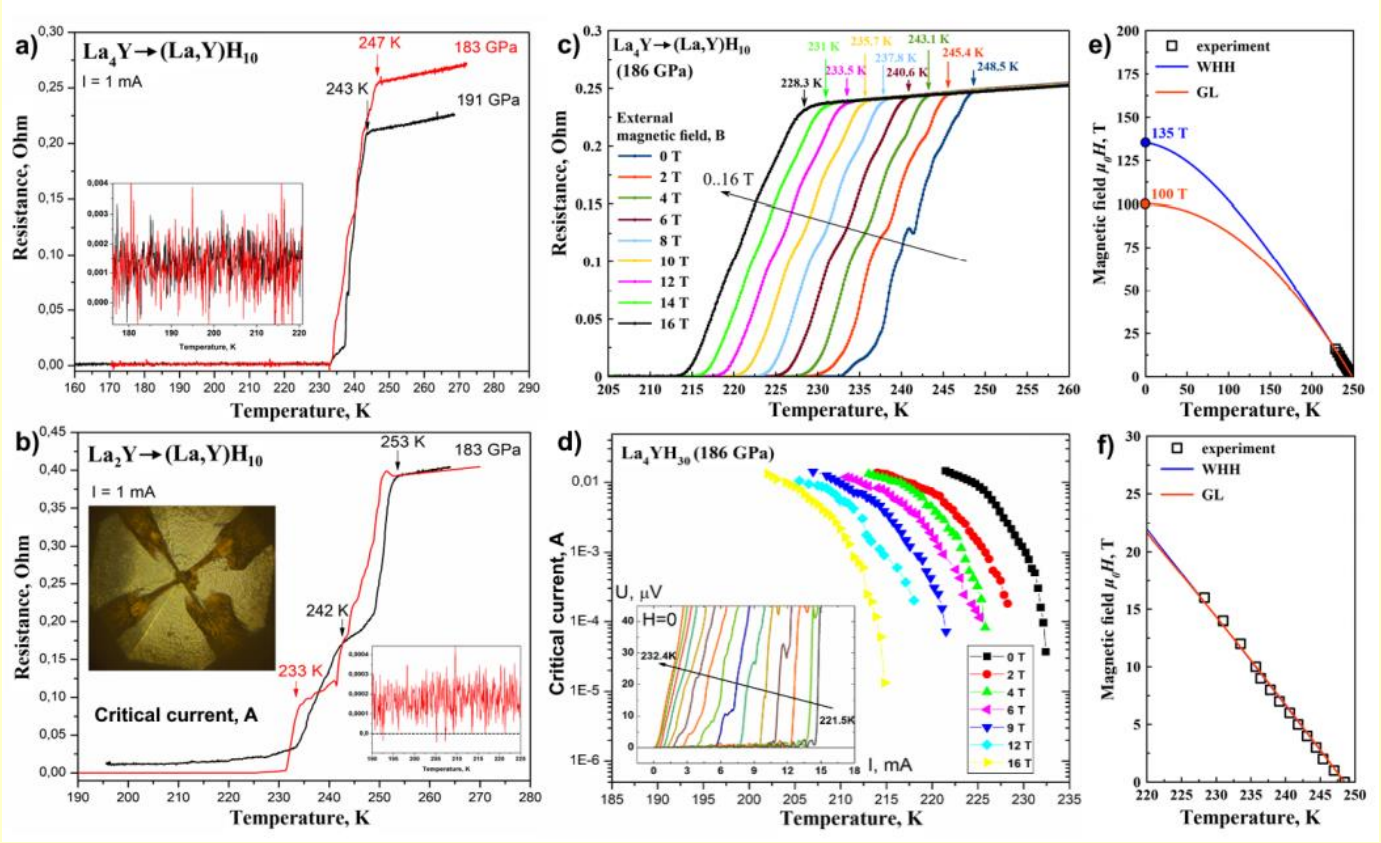
*(Submitted on 4 Dec 2018)*



# $(La,Y)H_{10}$: Superconductivity at 253 K

**[Semenok, Troyan, Oganov, *Materials Today*, in press]**

- **$(La,Y)H_6$ $T_C$ = 237 K.**
- **$(La,Y)H_{10}$ $T_C$ = 253 K. $Bc_2$ = 135 Tesla. $J_C$ = 2500 A/mm$^2$ at 4.2 K.**



# ...and the record is broken again, reaching room-temperature superconductivity in an unknown S-C-H compound (Tc = 288 K at 267 GPa)

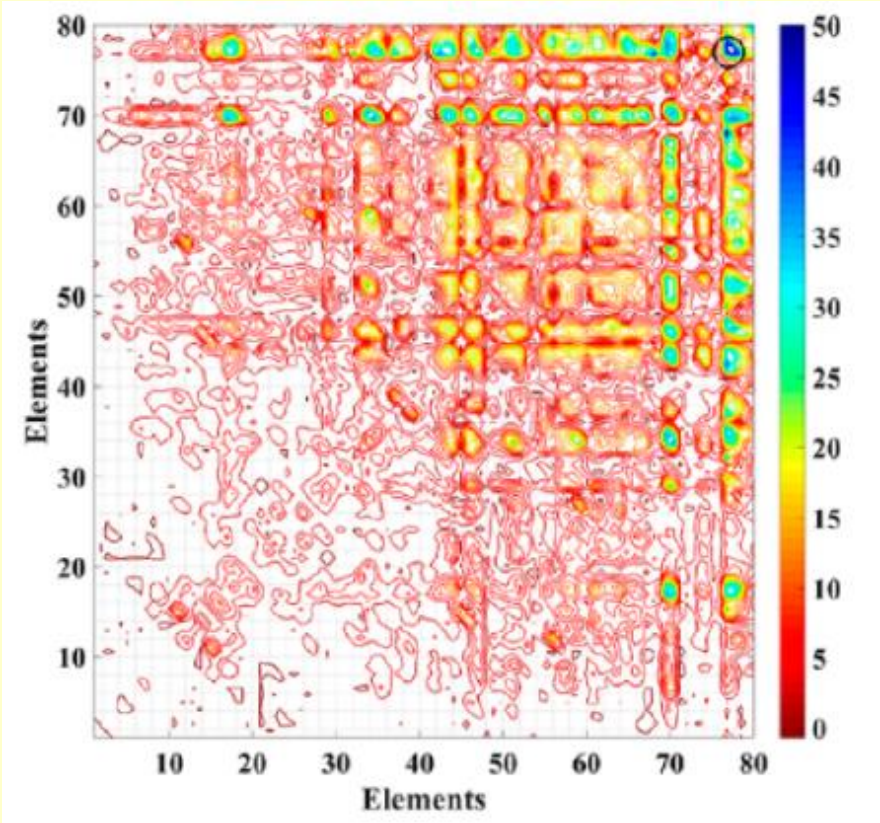
## Room-temperature superconductivity in a carbonaceous sulfur hydride

Elliot Snider, Nathan Dasenbrock-Gammon, Raymond McBride, Mathew Debessai, Hiranya Vindana, Kevin Vencatasamy, Keith V. Lawler, Ashkan Salamat & Ranga P. Dias

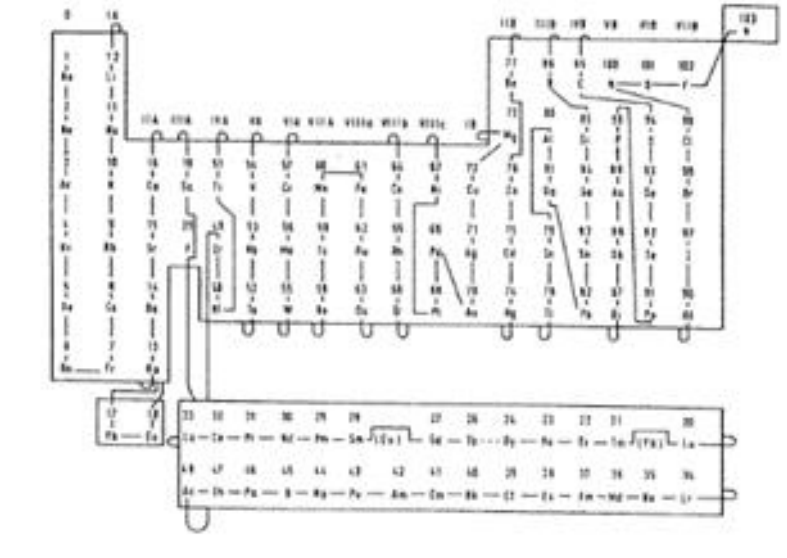
*Nature* **586**, 373–377(2020) | Cite this article

One of the long-standing challenges in experimental physics is the observation of room-temperature superconductivity[1,2]. Recently, high-temperature conventional superconductivity in hydrogen-rich materials has been reported in several systems under high pressure[3,4,5]. An important discovery leading to room-temperature superconductivity is the pressure-driven disproportionation of hydrogen sulfide ($H_2S$) to $H_3S$, with a confirmed transition temperature of 203 kelvin at 155 gigapascals[3,6]. Both $H_2S$ and $CH_4$ readily mix with hydrogen to form guest–host structures at lower pressures[7], and are of comparable size at 4 gigapascals. By introducing methane at low pressures into the $H_2S + H_2$ precursor mixture for $H_3S$, molecular exchange is allowed within a large assemblage of van der Waals solids that are hydrogen-rich with $H_2$ inclusions; these guest–host structures become the building blocks of superconducting compounds at extreme conditions. Here we report superconductivity in a photochemically transformed carbonaceous sulfur hydride system, starting from elemental precursors, with a maximum superconducting transition temperature of 287.7 ± 1.2 kelvin (about 15 degrees Celsius) achieved at 267 ± 10 gigapascals. The superconducting state is observed over a broad pressure range in the diamond anvil cell, from 140 to 275 gigapascals, with a sharp upturn in transition temperature above 220 gigapascals. Superconductivity is established by the observation of zero resistance, a magnetic susceptibility of up to 190 gigapascals, and reduction of the transition temperature under an external magnetic field of up to 9 tesla, with an upper critical magnetic field of about 62 tesla according to the Ginzburg–Landau model at zero temperature. The light, quantum nature of hydrogen limits the structural and stoichiometric determination of the system by X-ray scattering techniques, but Raman spectroscopy is used to probe the chemical and structural transformations before metallization. The introduction of chemical tuning within our ternary system could enable the preservation of the properties of room-temperature superconductivity at lower pressures.

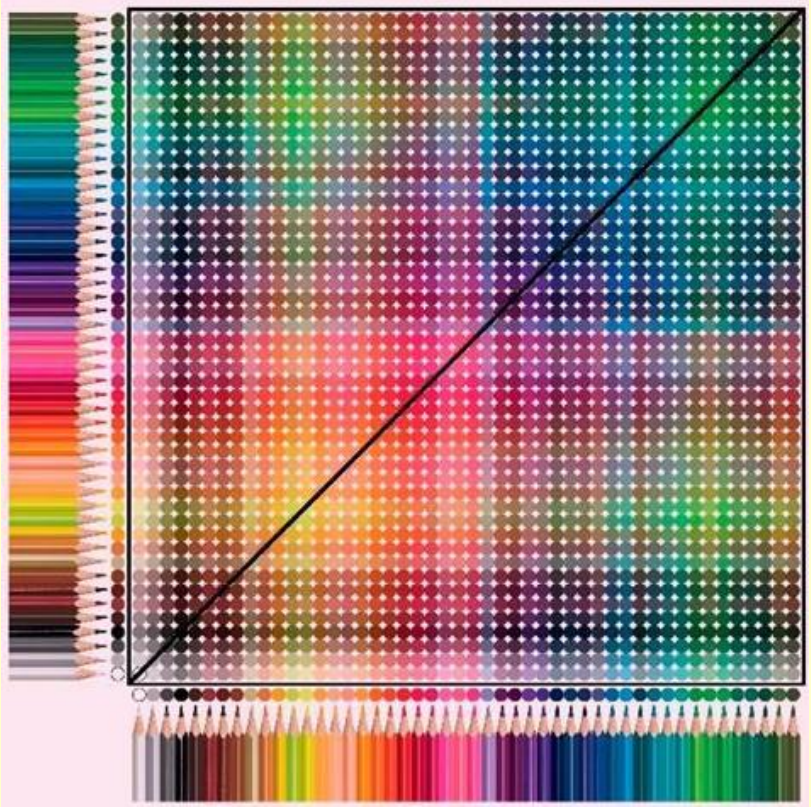
# USPEX Can Predict Optimal Material Among All Possible Compounds



# Mendeleev number (Pettifor, 1984) allows to predict stability, structure and properties of compounds.



Mendeleev numbers of the elements



Colored pencil analogy

# Mendeleev number is a way to organize elements and compounds by their properties

**[Pettifor, 1984; Allahyari & Oganov, *J. Phys. Chem. C*, 2020]**

| Mendeleev Number | Atom | Mendeleev Number | Atom | Mendeleev Number | Atom |
|---|---|---|---|---|---|
| 1 | Fr | 32 | Tl | 62 | Po |
| 2 | Cs | 33 | U | 63 | Fe |
| 3 | Rb | 34 | Pa | 64 | Cu |
| 4 | K | 35 | Zr | 65 | Co |
| 5 | Ra | 36 | Pu | 66 | As |
| 6 | Ba | 37 | Np | 67 | Ni |
| 7 | Sm | 38 | Nb | 68 | Kr |
| 8 | Gd | 39 | Ta | 69 | Mo |
| 9 | Eu | 40 | In | 70 | I |
| 10 | Sr | 41 | Pb | 71 | Pd |
| 11 | Tm | 42 | Cd | 72 | Ir |
| 12 | Pm | 43 | Xe | 73 | Os |
| 13 | Ca | 44 | Ti | 74 | P |
| 14 | Na | 45 | Al | 75 | Ru |
| 15 | Ac | 46 | Bi | 76 | Pt |
| 16 | La | 47 | Sn | 77 | At |
| 17 | Yb | 48 | Hg | 78 | Rh |
| 18 | Tb | 49 | Zn | 79 | W |
| 19 | Y | 50 | Ga | 80 | Rn |
| 20 | Dy | 51 | V | 81 | Se |
| 21 | Ho | 52 | Mn | 82 | B |
| 22 | Ce | 53 | Sb | 83 | Au |
| 23 | Er | 54 | Te | 84 | S |
| 24 | Li | 55 | Cr | 85 | Br |
| 25 | Th | 56 | Ag | 86 | H |
| 26 | Lu | 57 | Be | 87 | C |
| 27 | Pr | 58 | Ge | 88 | Cl |
| 28 | Nd | 59 | Re | 89 | N |
| 29 | Mg | 60 | Si | 90 | O |
| 30 | Sc | 61 | Tc | 91 | F |
| 31 | Hf | | | | |

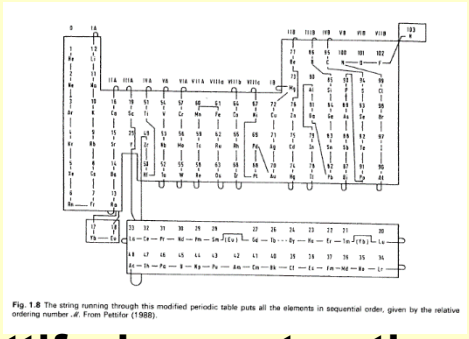
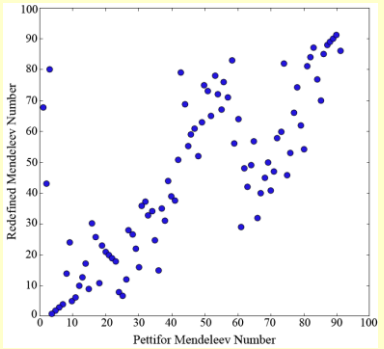
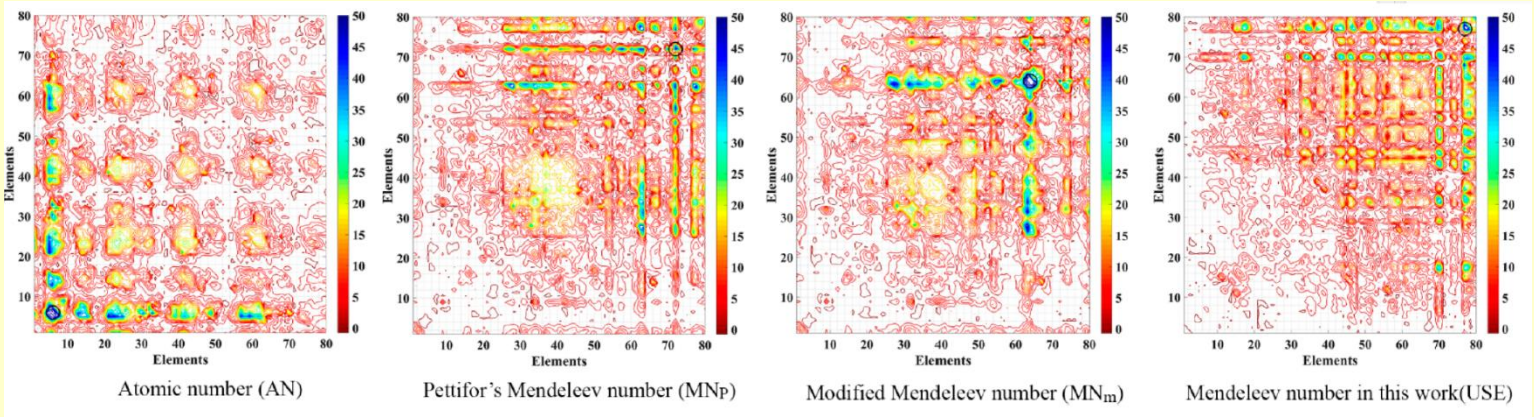


Fig. 1.8 The string running through this modified periodic table puts all the elements in sequential order, given by the relative ordering number, $A^r$. From Pettifor (1988).

**Pettifor's construction**




**Comparison with Pettifor's numbers**

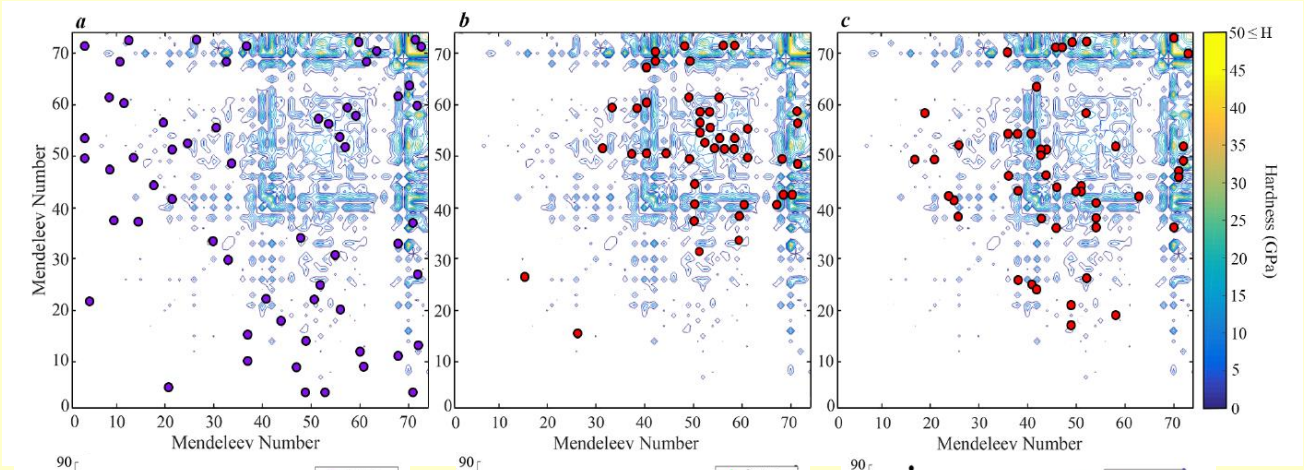


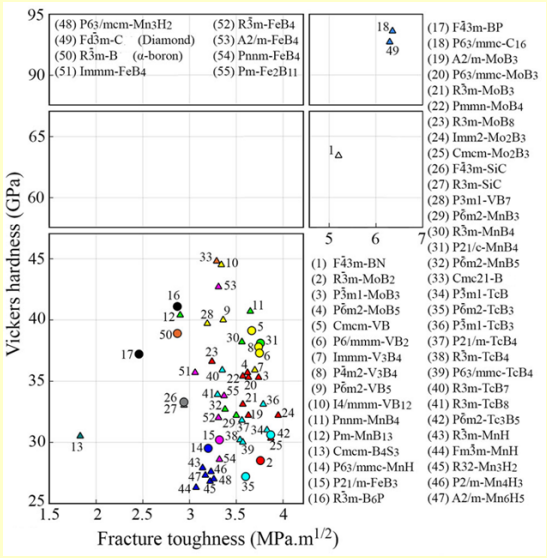

**Grouping of compounds by hardness using: (a) atomic numbers and Mendeleev numbers of (b) Pettifor, (c) Glawe, (d) ours.**

# Mendelevian search for the hardest possible material: diamond and lonsdaleite are found!

**[Allahyari & Oganov, *NPJ Comp. Mat.*, 2020]**

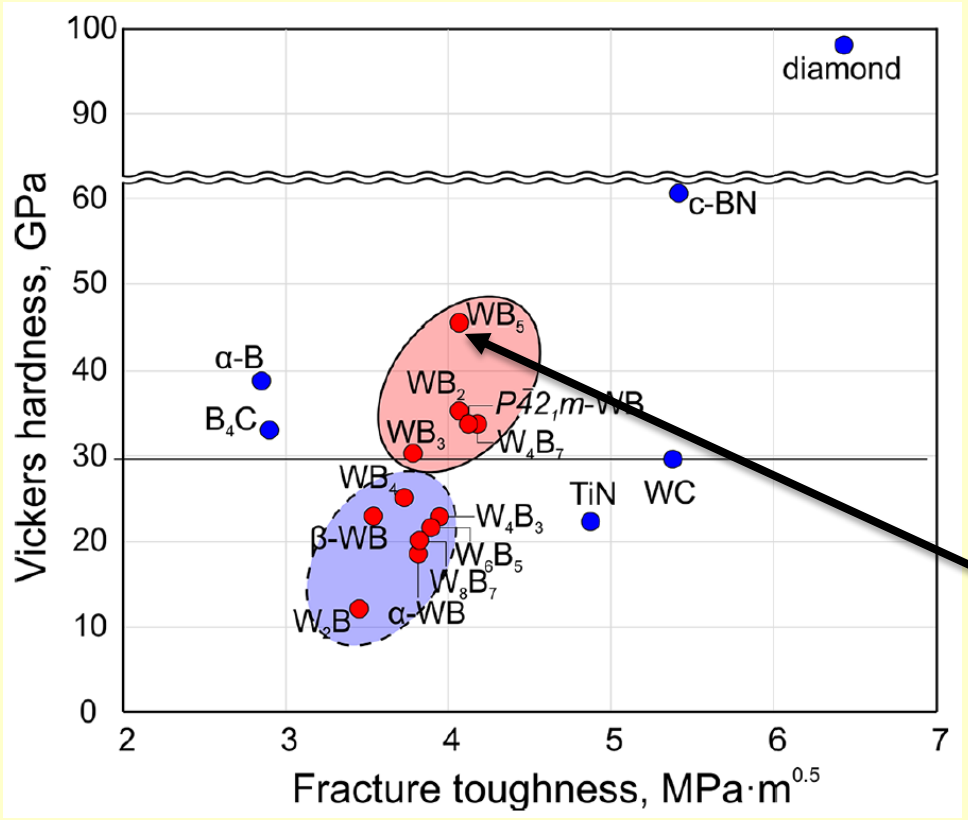
**1st generation** **5th generation** **10th generation**

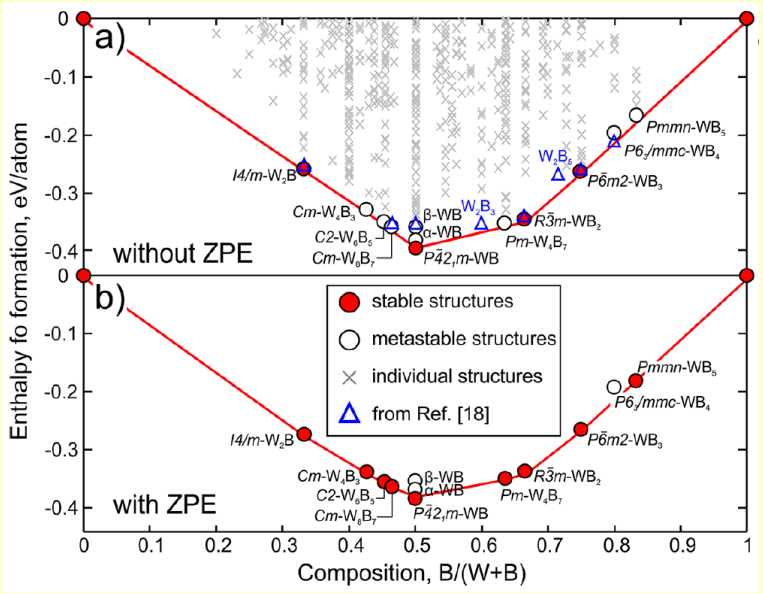


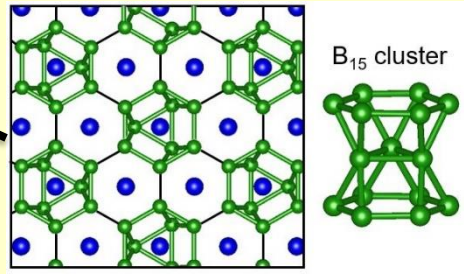



# $WB_{5-x}$: remarkable material

## [Kvashnin & Oganov, *J. Phys. Chem. Lett.*, 2018; *Adv. Science*, 2020]




**New material $WB_5$**

**Tungsten carbide WC - standard**

**Synthesized by V. Filonenko**

# Bonus: very recent story of a material harder than diamond

- **Fujii (PRL, 2020) claimed “pentadiamond” to have unique elastic moduli.**
- **Both machine learning and DFT calculations prove this wrong (Brazhkin & Oganov, arxiv.org).**

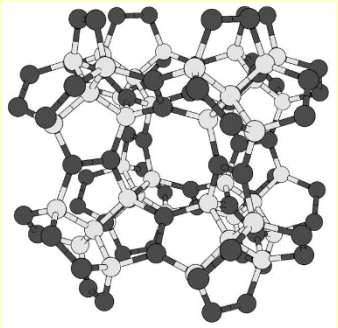



Table 1. Calculated elastic properties of pentadiamond in comparison with Y. Fujii et al. [1].

| Property | Y. Fujii et al. [1] | This work (Quantum ESPRESSO) | This work (VASP) | This work (machine learning) |
|---|---|---|---|---|
| a, Å | 9.195 | 9.184 | 9.191 | 9.195 |
| E-E(diam), meV/atom | 275 | 263 | 267 | - |
| $C_{11}$, GPa | 1715.3 | 539 | 537 | 409 |
| $C_{12}$, GPa | -283.5 | 105 | 106 | 118 |
| $C_{44}$, GPa | 1187.5 | 141 | 143 | 200 |
| B, GPa | 381 | 250 | 249 | 215 |
| G, GPa | 1113 | 172 | 169 | 176 |
| Y, GPa | 1691 | 420 | 413 | 415 |
| σ | -0.241 | 0.22 | 0.22 | 0.18 |
| $H_v$, GPa | 210 | 20 | 20 | 26 |

# Fast and reliable calculations of thermoelectric properties are enabled by AICON program (Fan & Oganov, 2020; Fan & Oganov, submitted).

Computer Physics Communications
Volume 251, June 2020, 107074
ELSEVIER

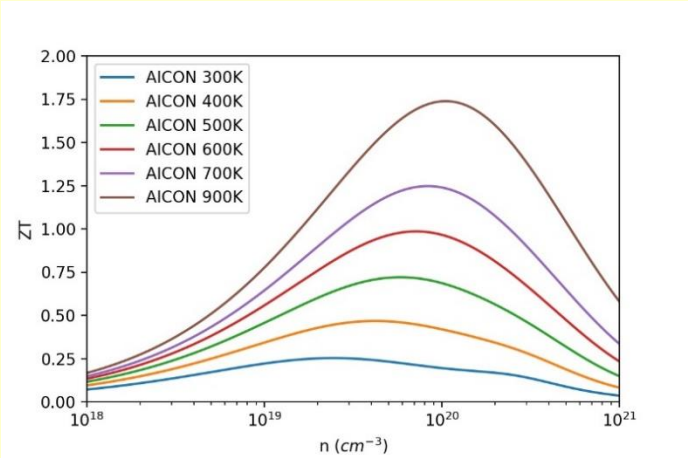
AICON: A program for calculating thermal conductivity quickly and accurately ☆, ☆☆

Tao Fan, Artem R. Oganov

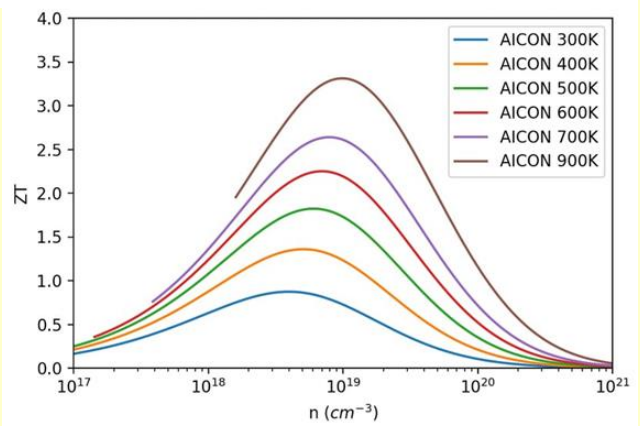
Computer Physics Communications
Volume 266, September 2021, 108027
ELSEVIER

AICON2: A program for calculating transport properties quickly and accurately ☆, ☆☆

Tao Fan, Artem R. Oganov

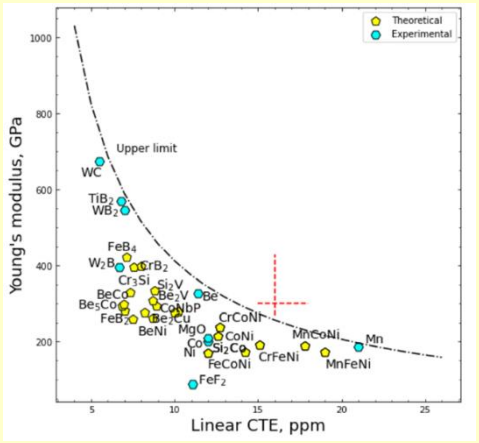


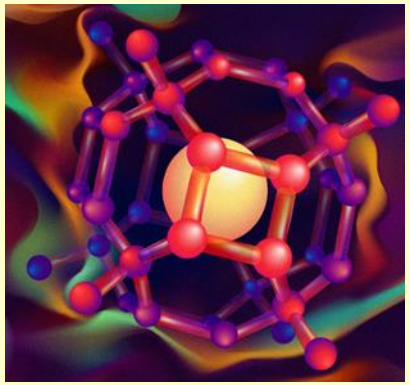

**AlTe, n-type**



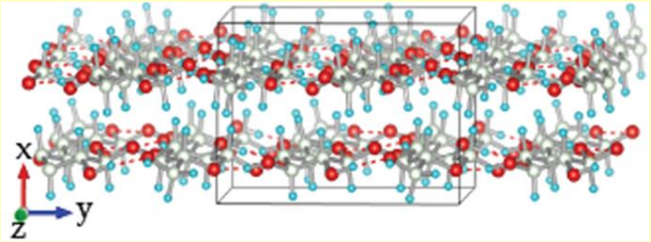

**Predicted material with ZT~3.4. If confirmed, will be transformative.**

# Advanced algorithms predict new supermaterials



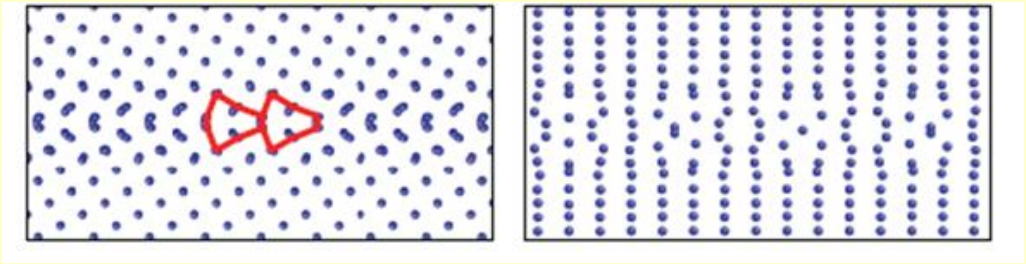



**Machine learning + Structure prediction**

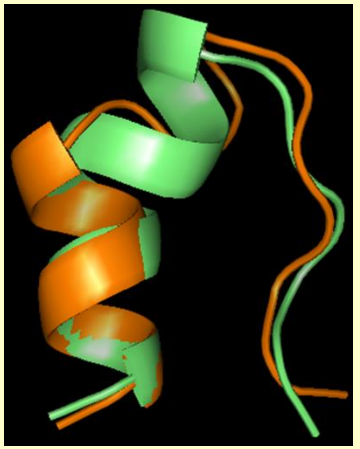



**Polymers for capacitors**
**Room-temperature superconductivity**
**Thermoelectrics with ZT~3.4**
New nanoparticles (catalysis etc)
Electrides
**Diamond is the hardest material**

**<u>Challenges:</u>**
Very large systems
Disordered systems



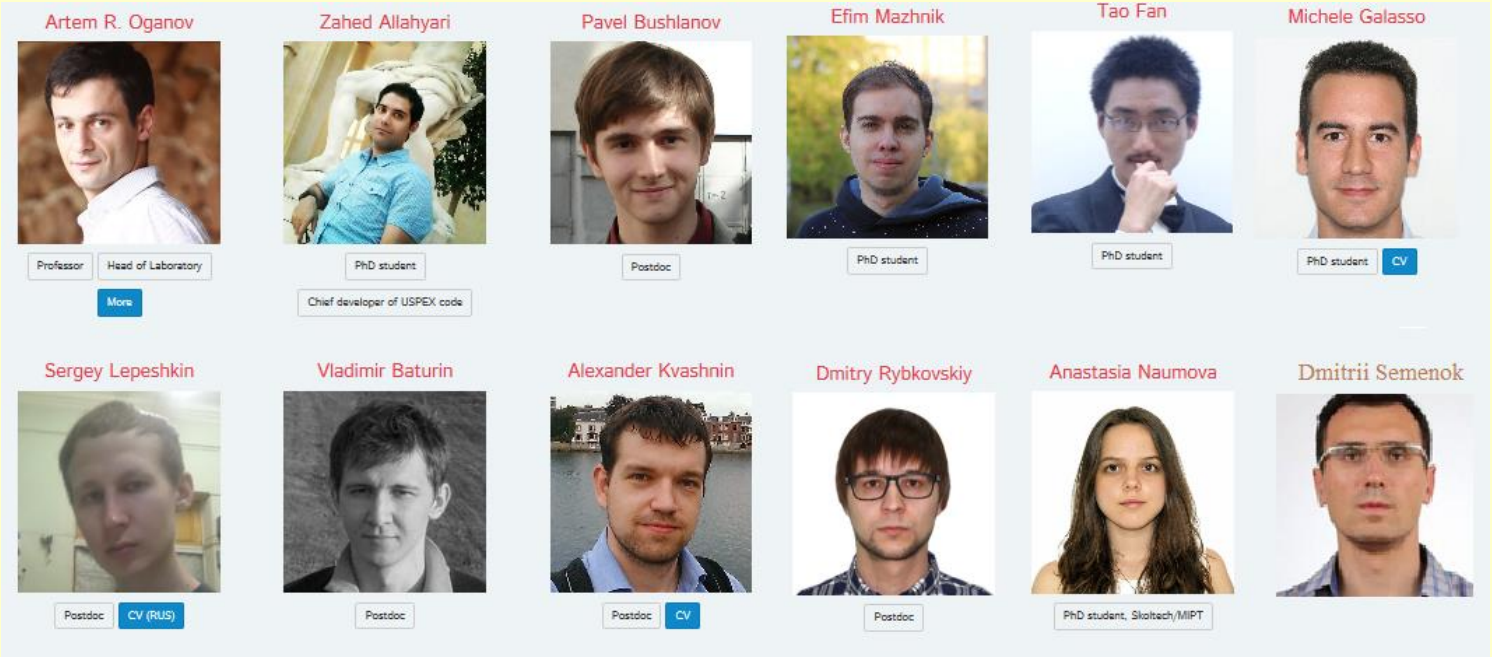
**Prediction of grain boundary structures**



**Protein structure prediction**

# Our team. Where great minds do NOT think alike

USPEX Computational Materials Discovery





A.Lyakhov


Q. Zhu


X.F.Zhou


W. Zhang


X. Dong


G.R.Qian


H.Niu


J. Zhang


S.Y. Yu


M.Davari


A. Goncharov


V. Blatov


I. Troyan