# Evolutionary structure prediction: how does it work, and why

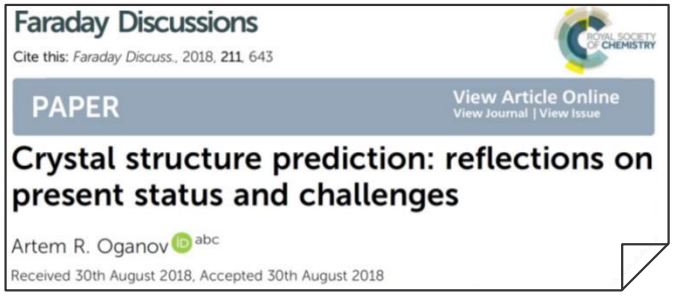

**Artem R. Oganov**

***Skolkovo Institute of Science and Technology, Russia***

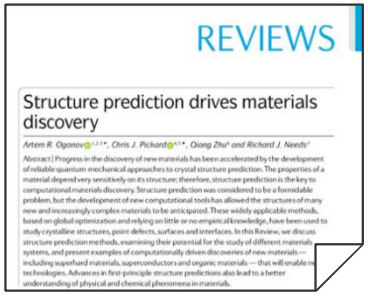
***Moscow Institute of Steel and Alloys, Moscow, Russia***

***Institute of Geochemistry and Analytical Chemistry, Moscow, Russia***

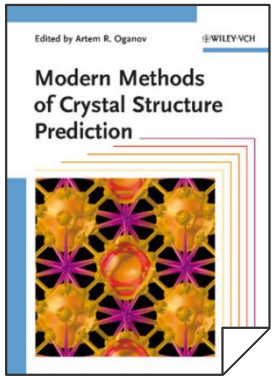
# Crystal Structure Prediction



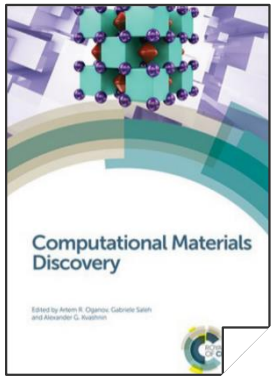

Faraday Discussions (2018)




Nature Reviews Materials (2019)




2011




2018

# Until recently, experiment was believed to be the only source of crystal structures

**The Nobel Prize in Physics 1914**

"for his discovery of the diffraction of X-rays by crystals"

Max von Laue

**The Nobel Prize in Physics 1915**

"for their services in the analysis of crystal structure by means of X-rays"

Sir William Henry Bragg

William Lawrence Bragg

**The Nobel Prize in Chemistry 1985**

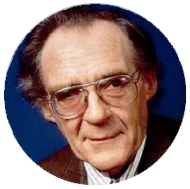
"for their outstanding achievements in the development of direct methods for the determination of crystal structures"

Herbert A. Hauptman

Jerome Karle

**(from http://nobelprize.org)**

Angelo Gavezzotti



John Maddox

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



## 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

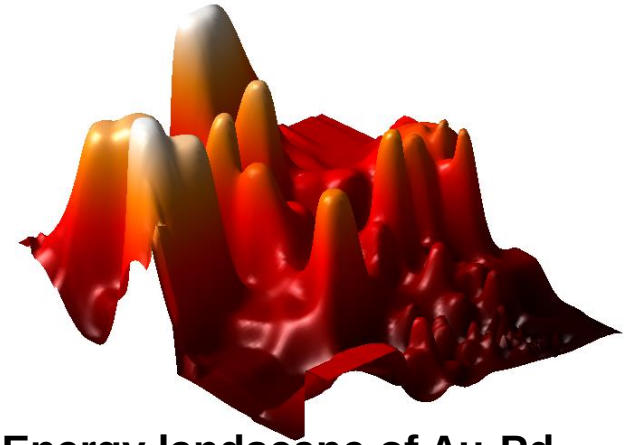
ONE of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition. Who, for example, would guess that graphite, not diamond, is the thermodynamically stable allotrope of carbon at ordinary temperature and pressure? Solids such as crystalline water (ice) are still thought to lie beyond mortals' ken.

$$C = \frac{1}{(V/\delta^3)} \frac{(V/\delta^3)!}{[(V/\delta^3) - N]!N!}$$

**- Astronomic number of possible structures!**

# 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

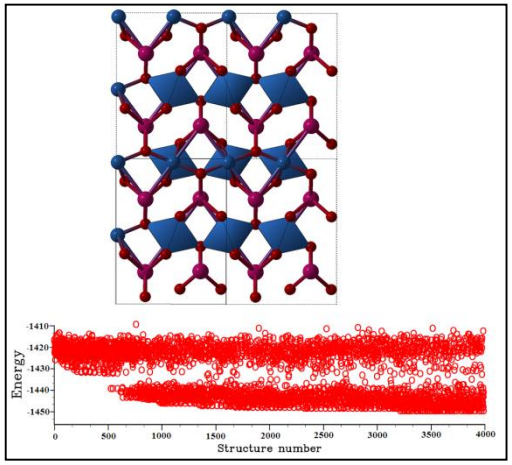
**Quantum-mechanical calculations (using density functional theory**

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

**W. Kohn**
**Nobel Prize in Chemistry 1998**

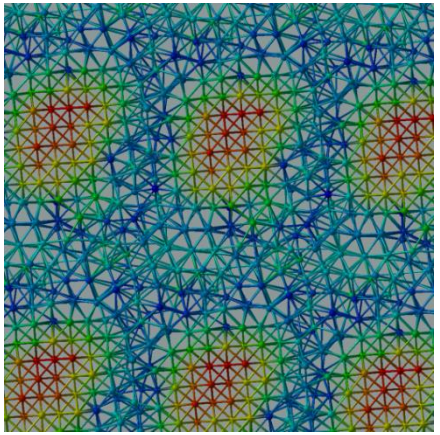
**E. Schroedinger**
**Nobel Prize in Physics 1933**

# Evolutionary approach is extremely powerful in computational materials science



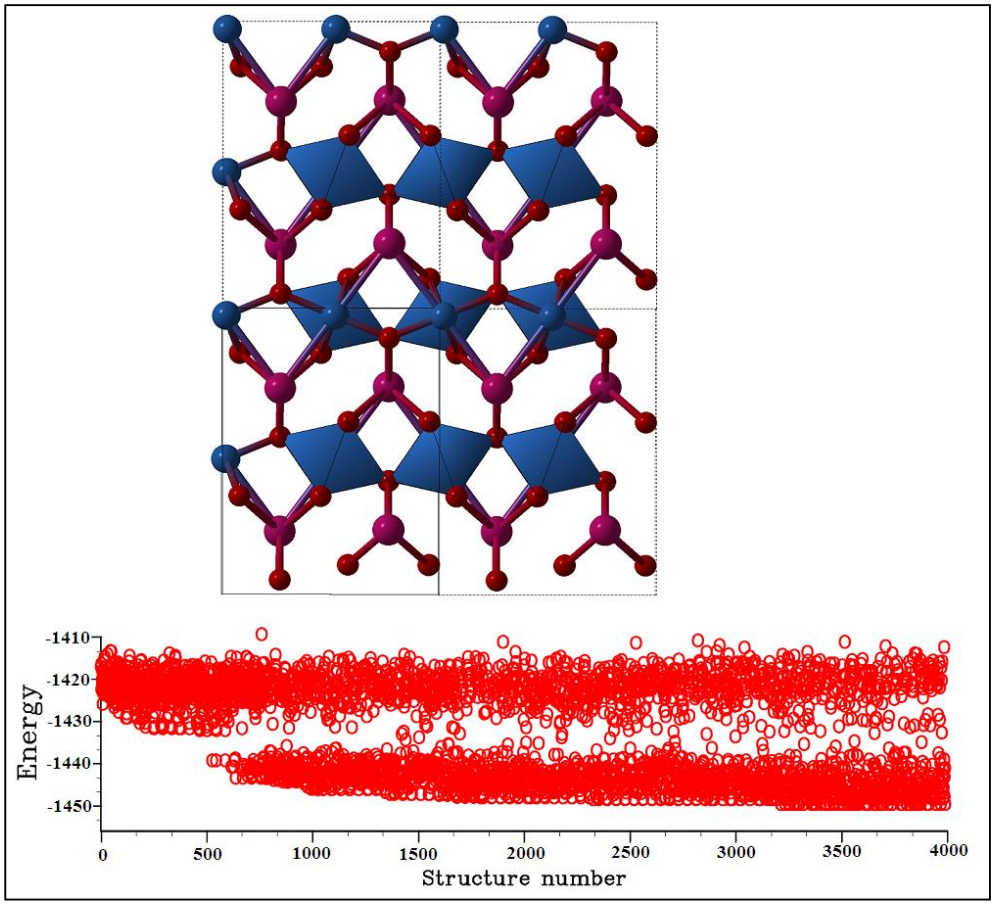

**1.Predicting structures by evolution**

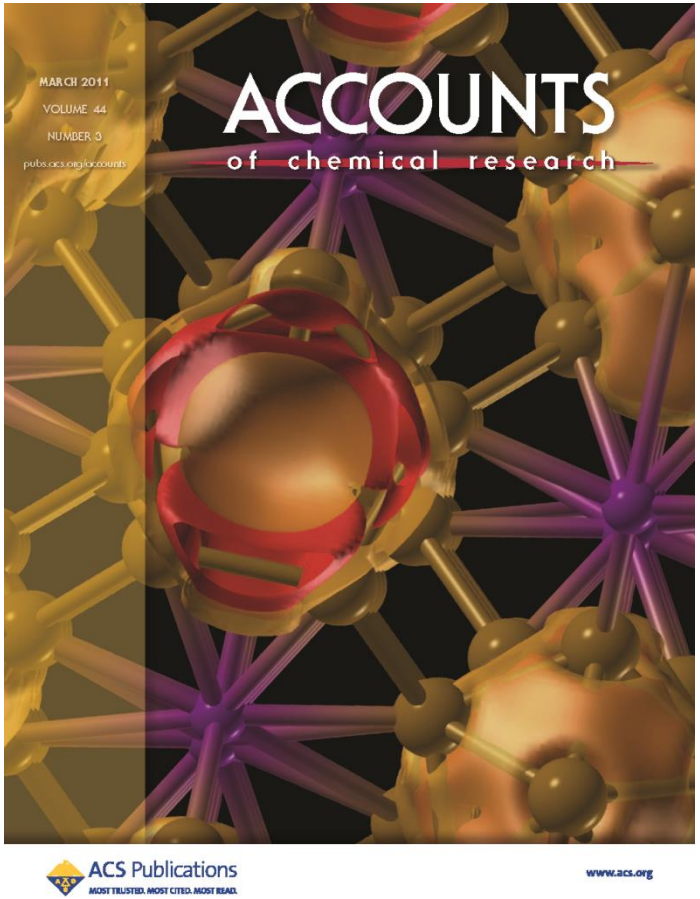
**2. When there's more than one solution**



**3. Looking into the genome**

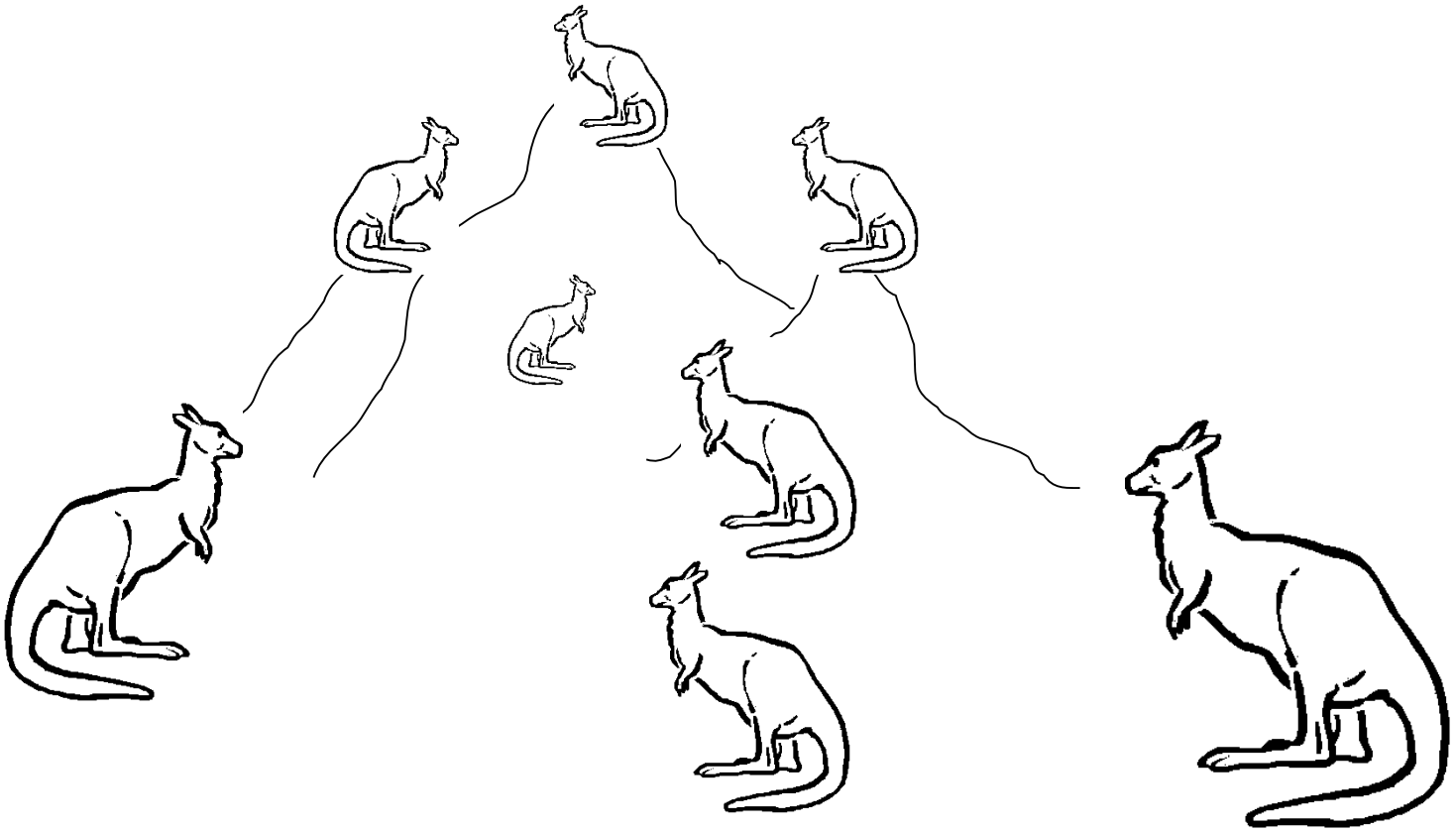
# 1. Predicting structures by evolution



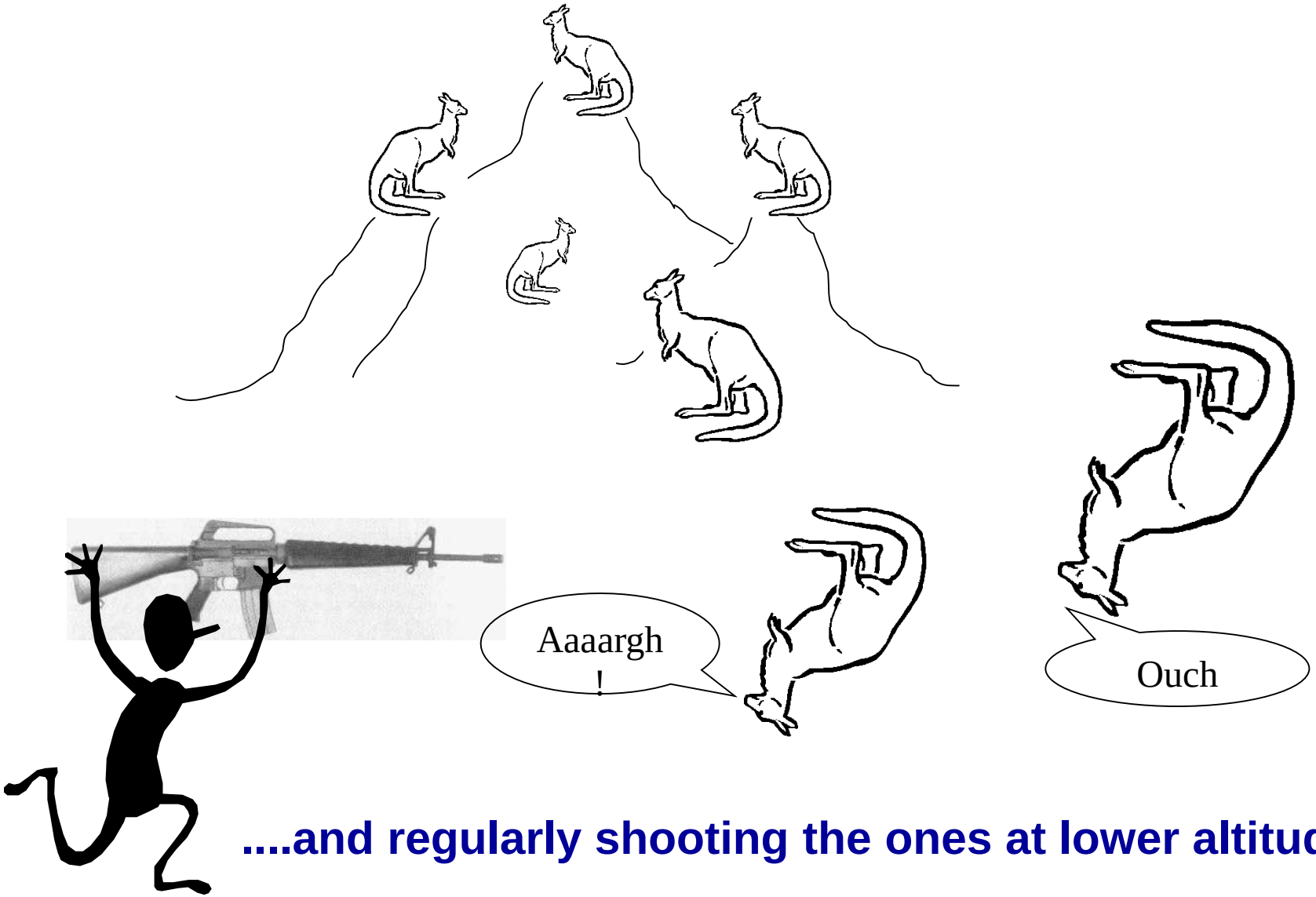

**Oganov A.R., Lyakhov A.O., Valle M. (2011).**
**How evolutionary crystal structure prediction works - and why.**
***Acc. Chem. Res.* 44, 227-237.**

# Global optimisation methods: Kangaroo's climb to Mt. Everest



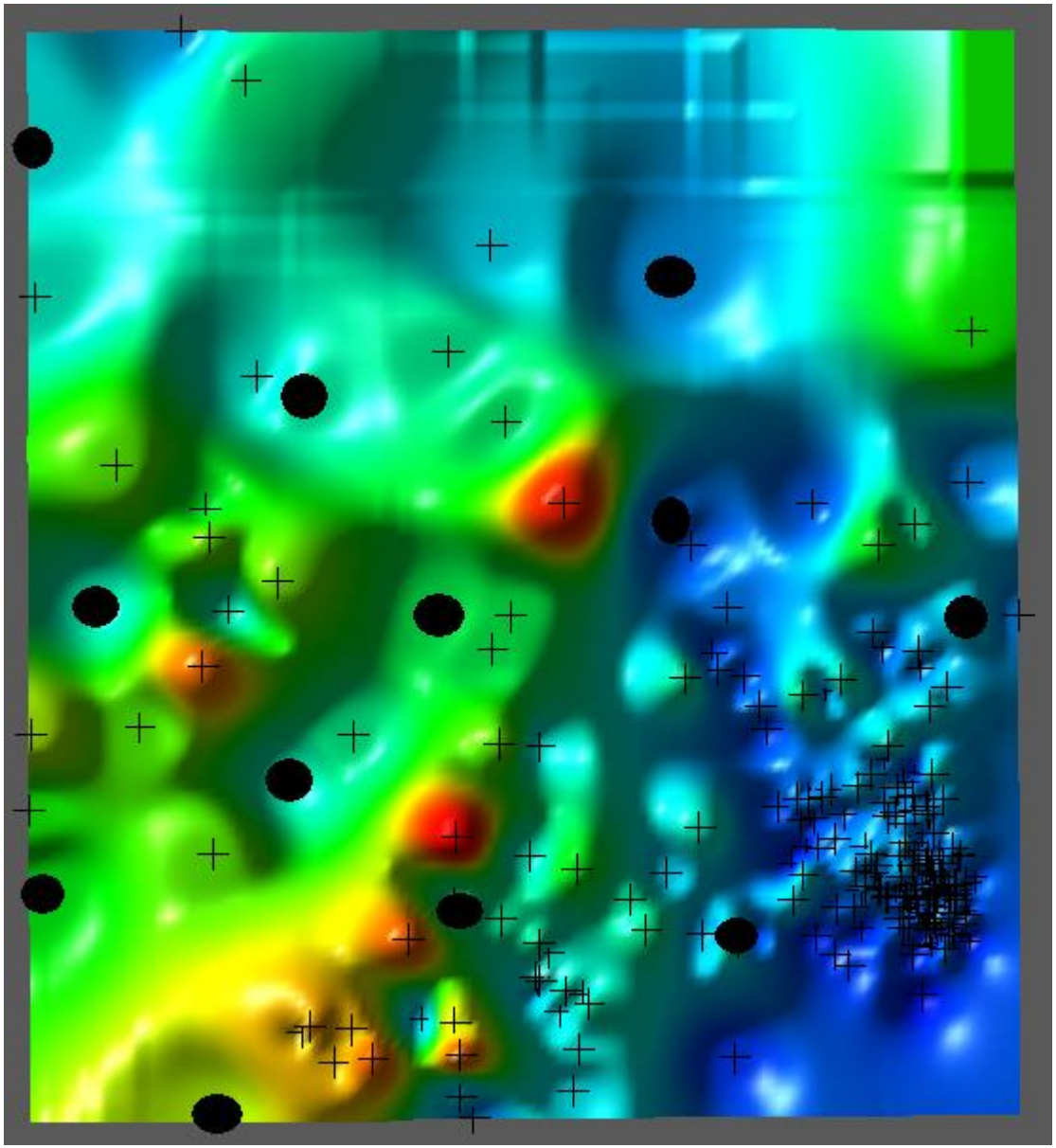
**Evolutionary Algorithms are like taking a whole plane load of kangaroo's and letting them reproduce freely (not pictured).....**

# Global optimisation methods: Kangaroo's climb to Mt. Everest




**....and regularly shooting the ones at lower altitudes.**

# Evolutionary simulations learn & explore the most promising regions of search space



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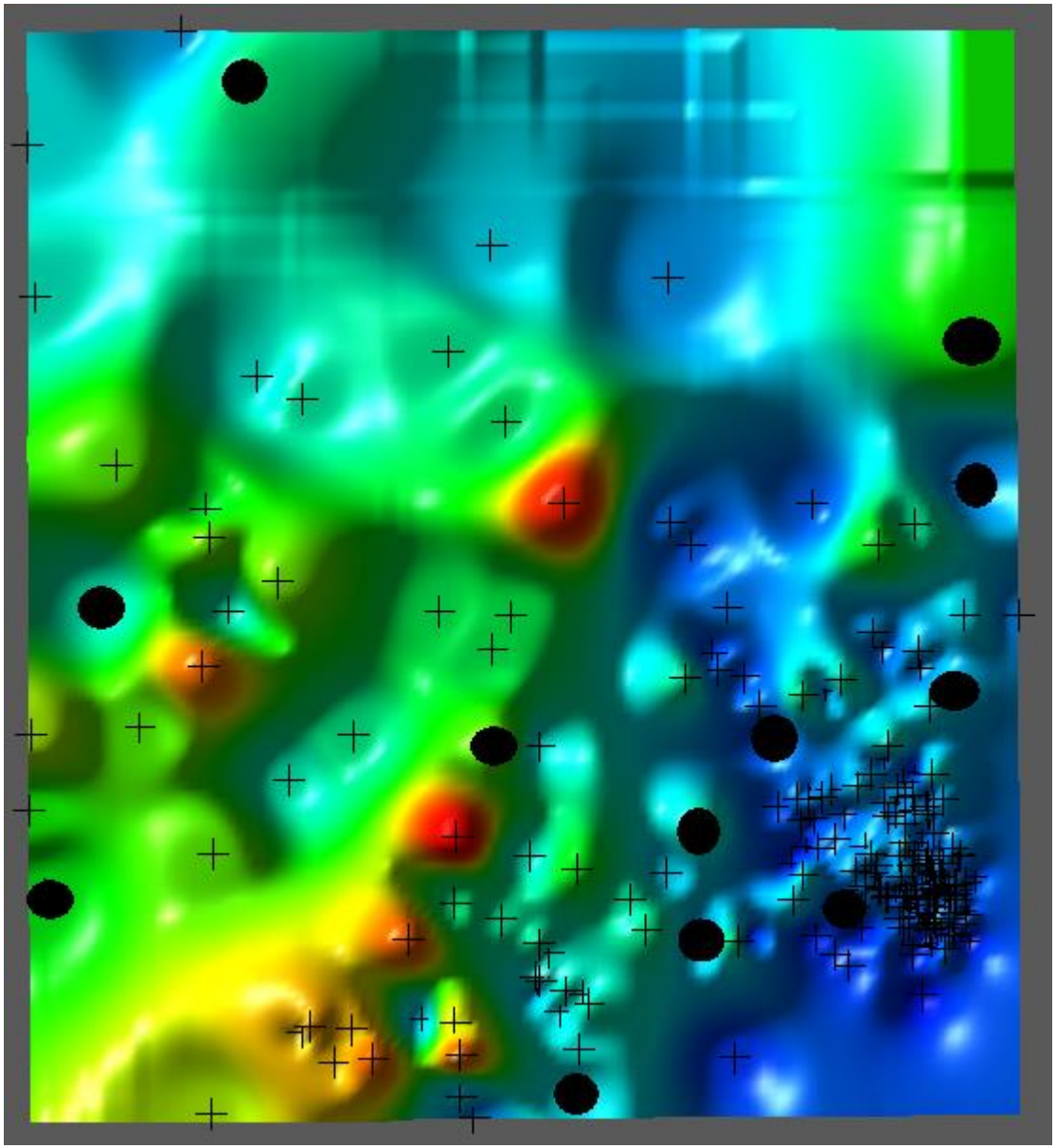

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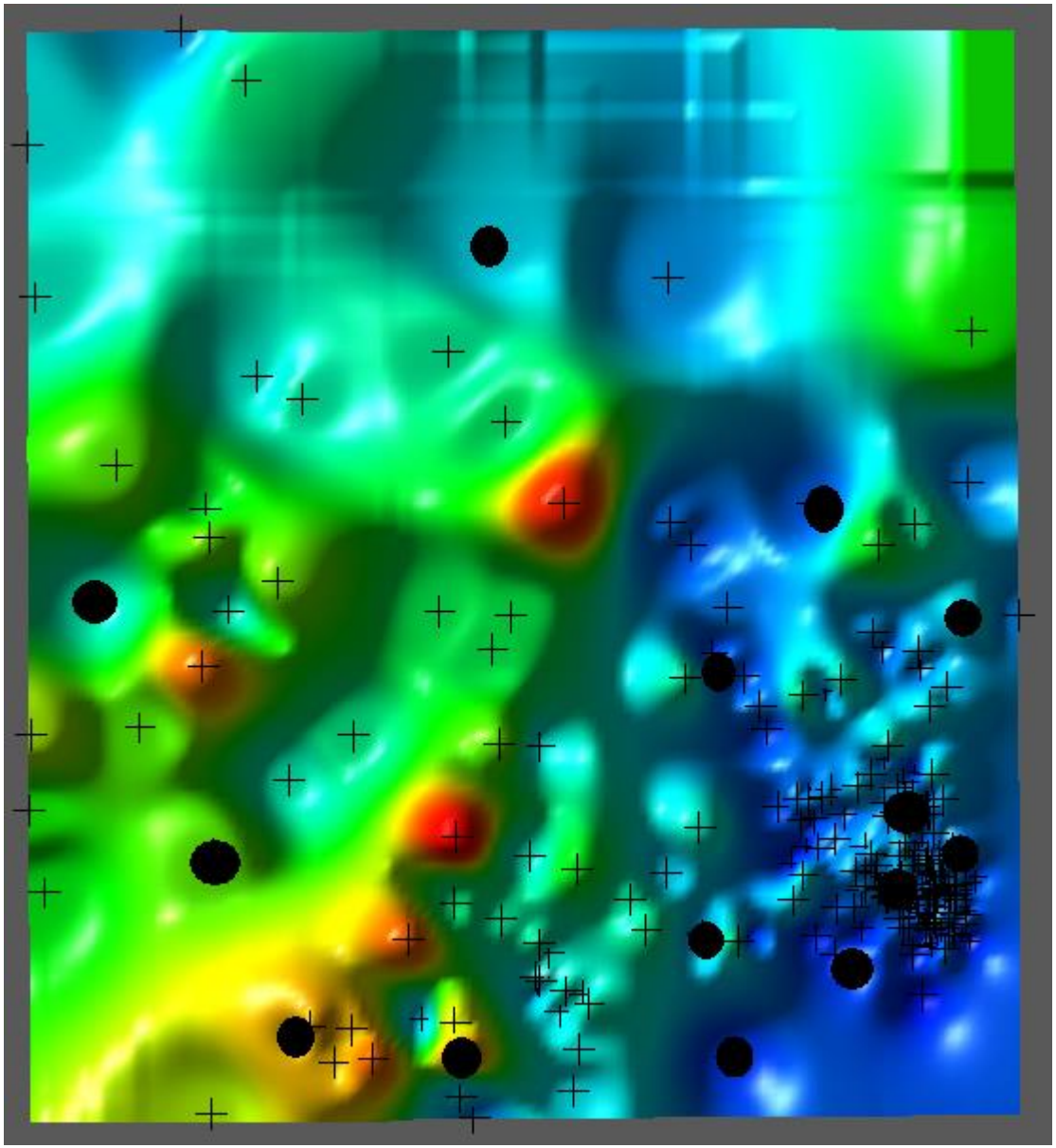

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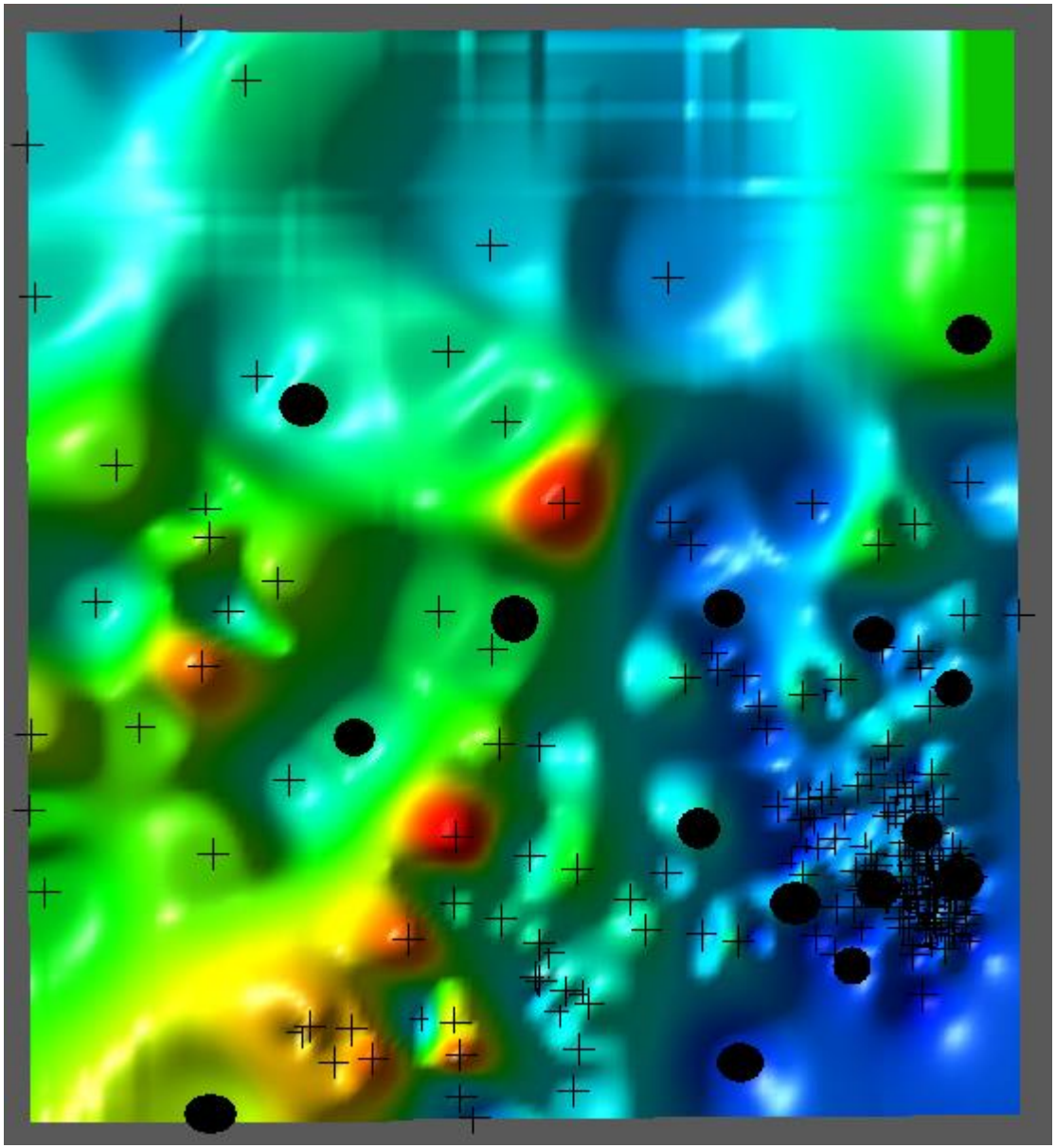
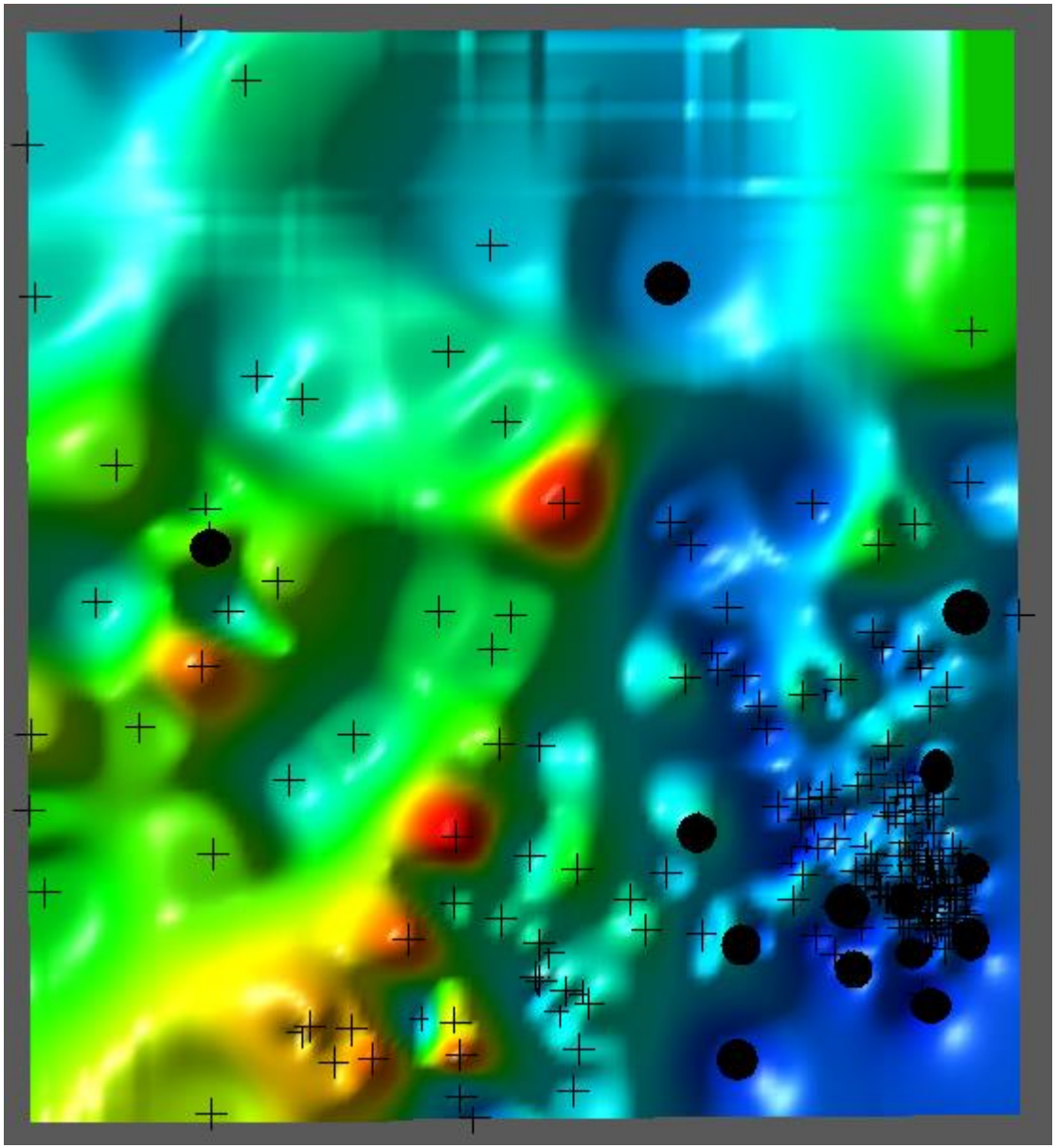
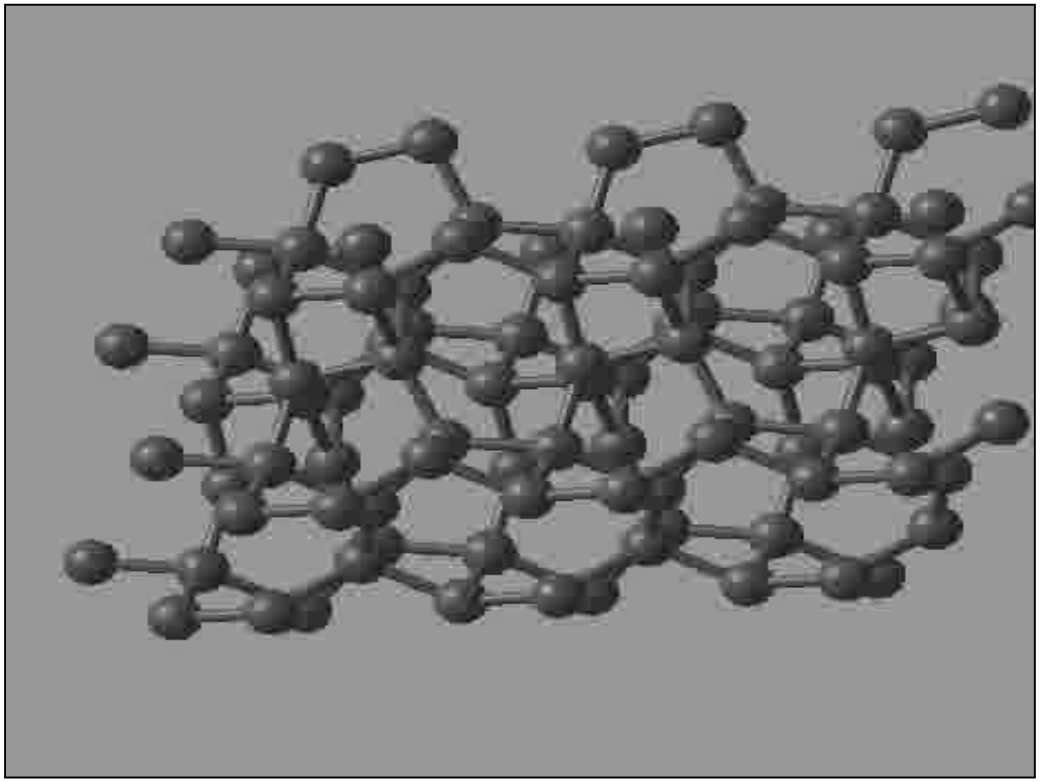


# Evolutionary simulations learn & explore the most promising regions of search space



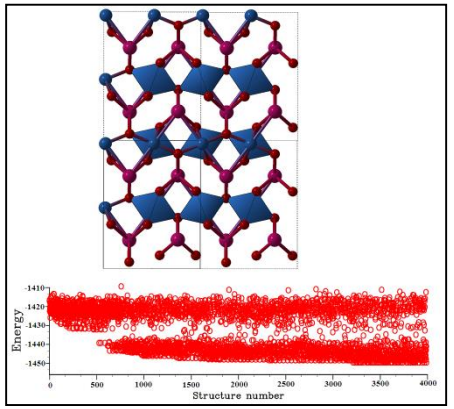
# Without any empirical information, method reliably predicts materials

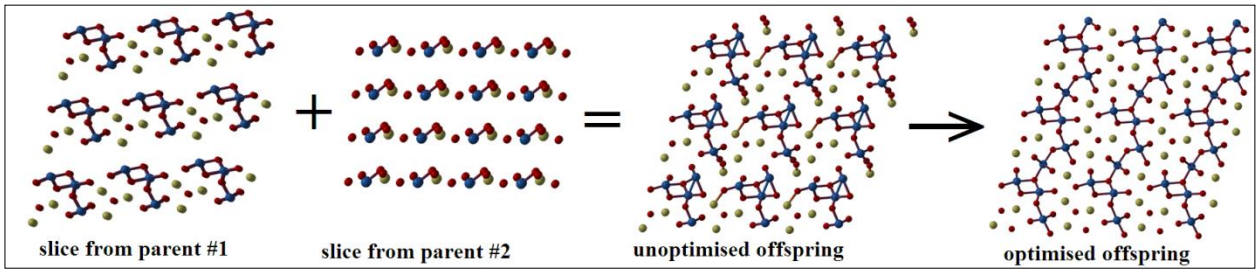


**Carbon at 100 GPa – diamond structure is stable**

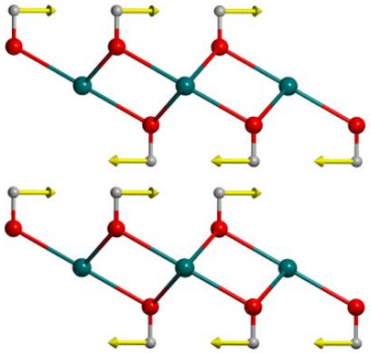
# USPEX
# (Universal Structure Predictor: Evolutionary Xtallography)

- (Random) initial population
- Evaluate structures by relaxed (free) energy
- Select lowest-energy structures as parents for new generation
- Standard variation operators:

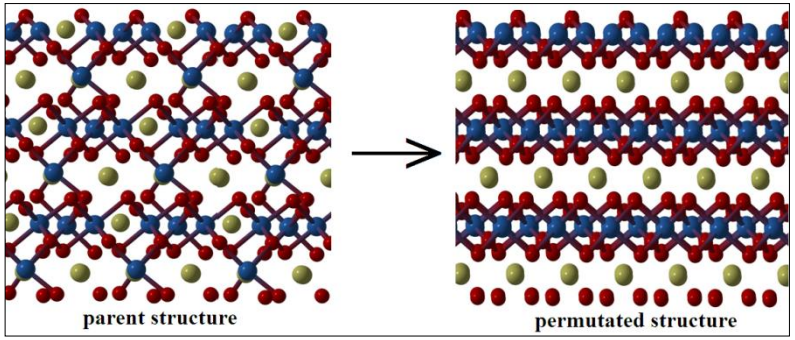



**(1) Heredity (crossover)**



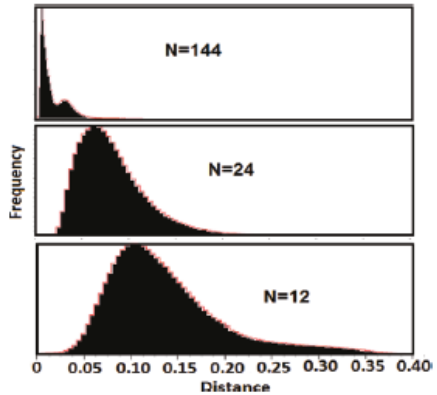
**(2) Soft mode mutation**




**(3) Permutation**

**+(4) Transmutation, +(5) Rotational mutation, +(6) Soft-mode mutation, +...**

# Why does USPEX work so well? A few tips and tricks




Distribution of distances between randomly sampled local minima in a binary Lennard-Jones system $AB_2$.

formal dimensionality of full energy landscape: $d = 3N+3$

intrinsic dimensionality of reduced landscape: $d^* = 3N+3-k$

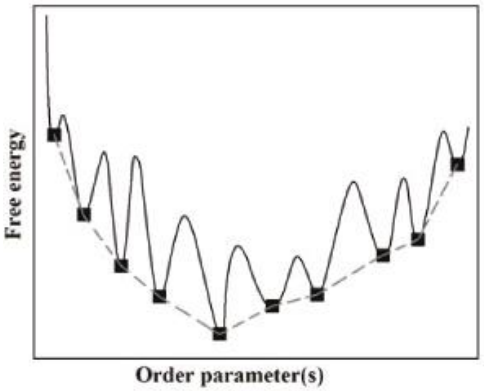
number of distinct structures: $C^* \sim \exp(\beta d^*)$

$d^* = 10.9$ ($d = 39$) for $Au_8Pd_4$

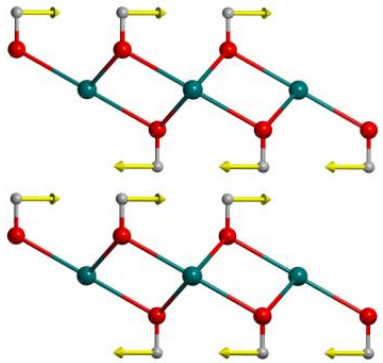
$d^* = 11.6$ ($d = 99$) for $Mg_{16}O_{16}$

$d^* = 32.5$ ($d = 39$) for $Mg_4N_4H_4$

**I. Reduction of dimensionality through unbiased symmetric initialization.**




**II. Reduction of effective dimensionality of problem by structure relaxation (also reduces "noise" and transforms energy landscape to a convenient shape).**



**III. Variation operators are defined in subspaces of reduced dimensionality and involve cooperative transformations.**

# First lessons

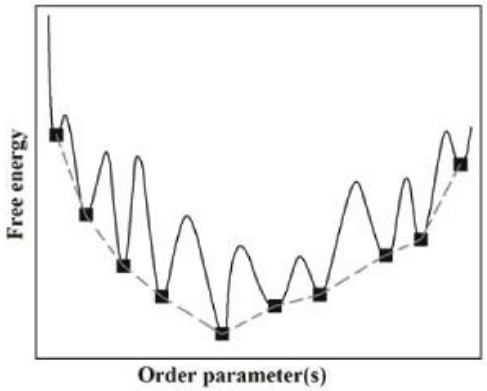
I. Local optimization (as part of global) is essential.

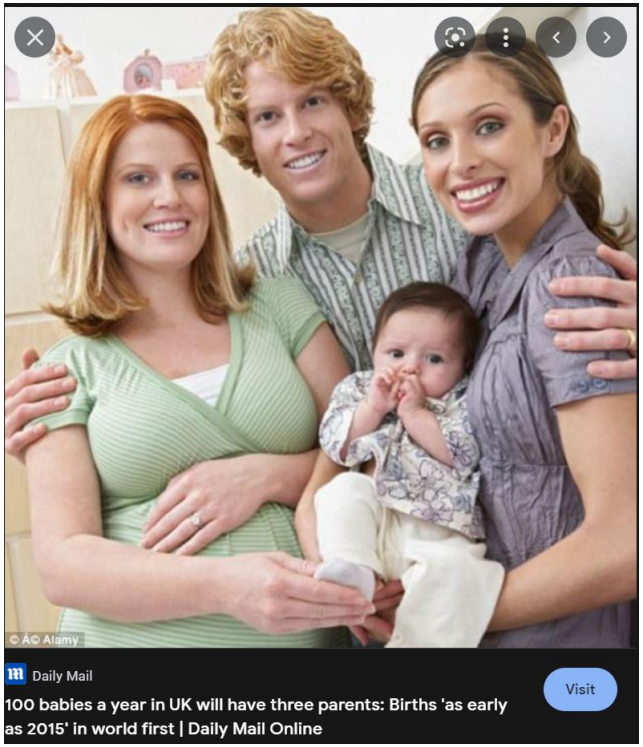
II. Initialization: must have diverse initial population.

III. Selection of potential parents: non-greedy.

IV. Variation operators: low-dimensional (alter a few degrees of freedom at a time).

V. Variation operators: 1-parent (mutations) or 2-parent (crossover). 3-parent crossover creates defective children.



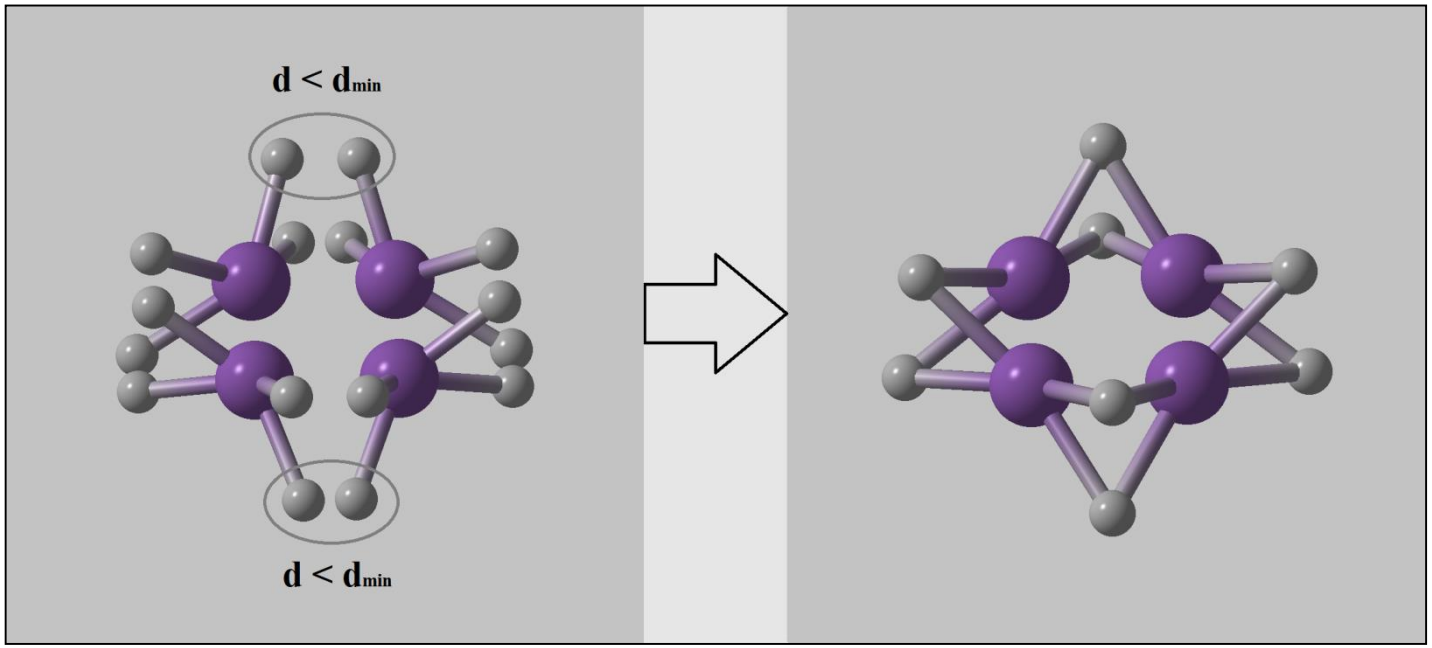



# Ways to initialize a diverse population:

## 1. Random symmetric structure generator

**(Lyakhov & Oganov, Comp. Phys. Comm., 2013)**

**Crystals: 230 space groups**
**Nanoparticles: point groups**



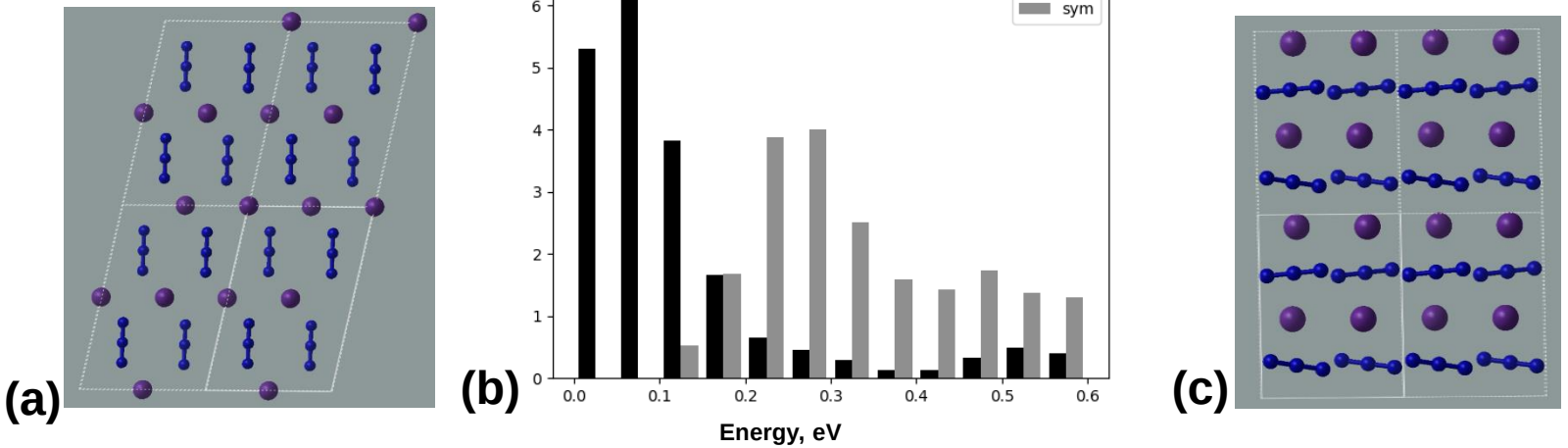

**Enables moderately efficient random sampling as one of possible USPEX regimes**

Zhu, Oganov, et al, Acta. Cryst. B, 68, 215-226 (2012)

# Ways to initialize a diverse population: 2. Random topological structure generator

**(Bushlanov, Blatov, Oganov, Comp. Phys. Comm. 2019)**

**Speedup ~3 times**

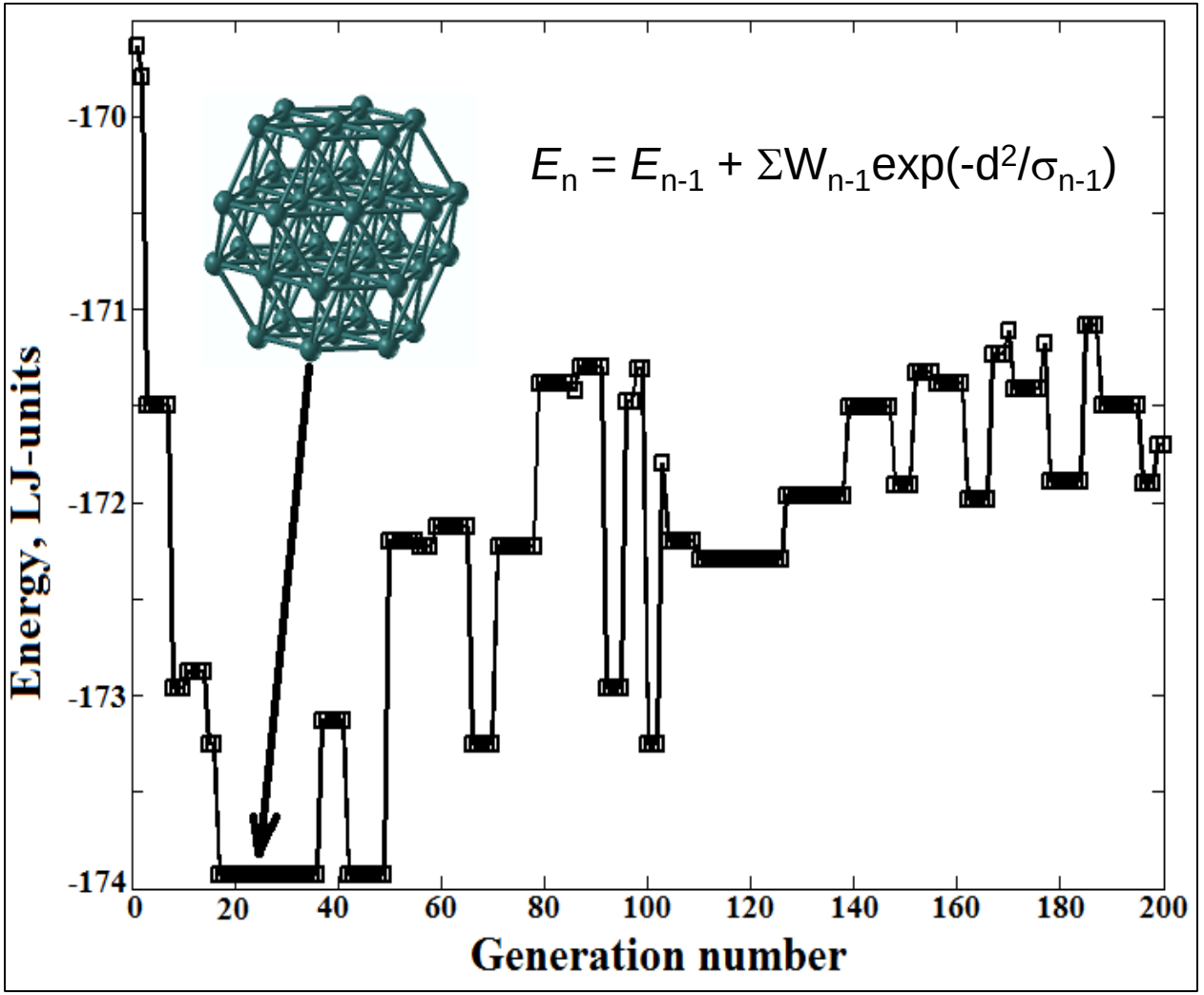



**Example of $KN_3$: (a) topological structure, (c) random symmetric structure, (c) energy distribution of topological (TR) and random symmetric structures**

**Statistics (100 runs) of USPEX performance on $MgAl_2O_4$ (28 atoms/cell) at 100 GPa**

| | Original | On-the-fly adaptation | On-the-fly adaptation AND topology |
|---|---|---|---|
| <No. of structures> | 1307 | 1069 | 368 |
| Success rate | 100% | 100% | 100% |

# One more lesson: ‘aging’ technique to prevent “genetic drift”




**A metastable state is found first and the ground state is found shortly after**

**[Lyakhov, ARO, et al. (2013)]**

# 2. When there is more than one optimal solution

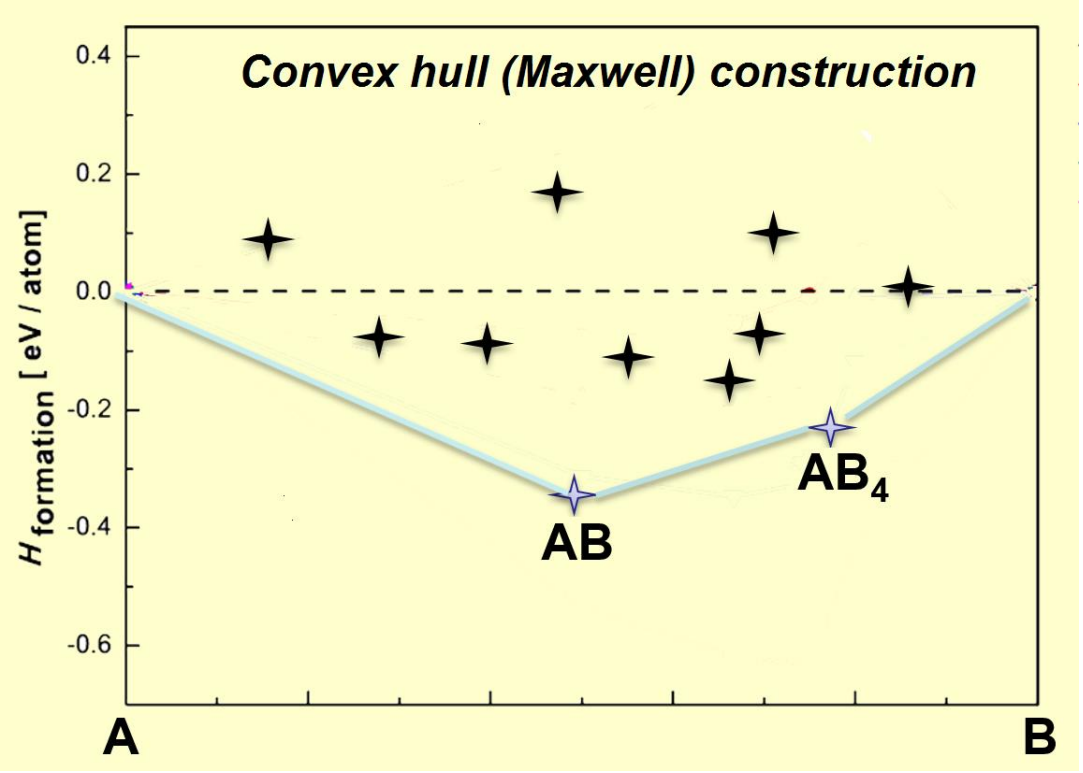
**-Pareto optimization**
**-Variable-composition systems**
**-Coevolution**

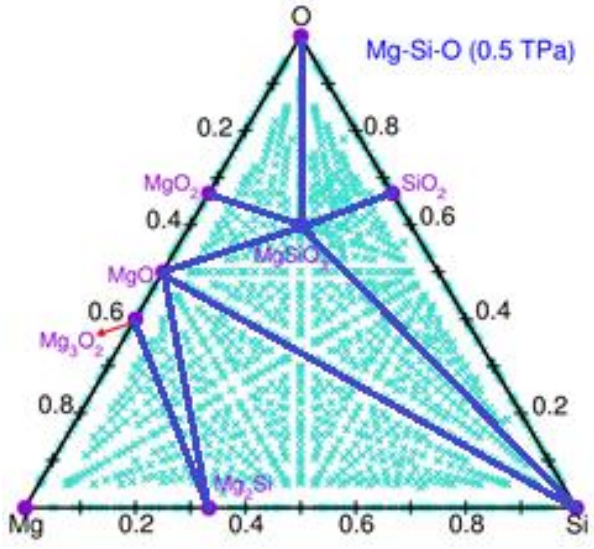
Which compounds of elements A and B are stable?

(*cf* a class of related species?)

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

## Thermodynamic stability in variable-composition systems

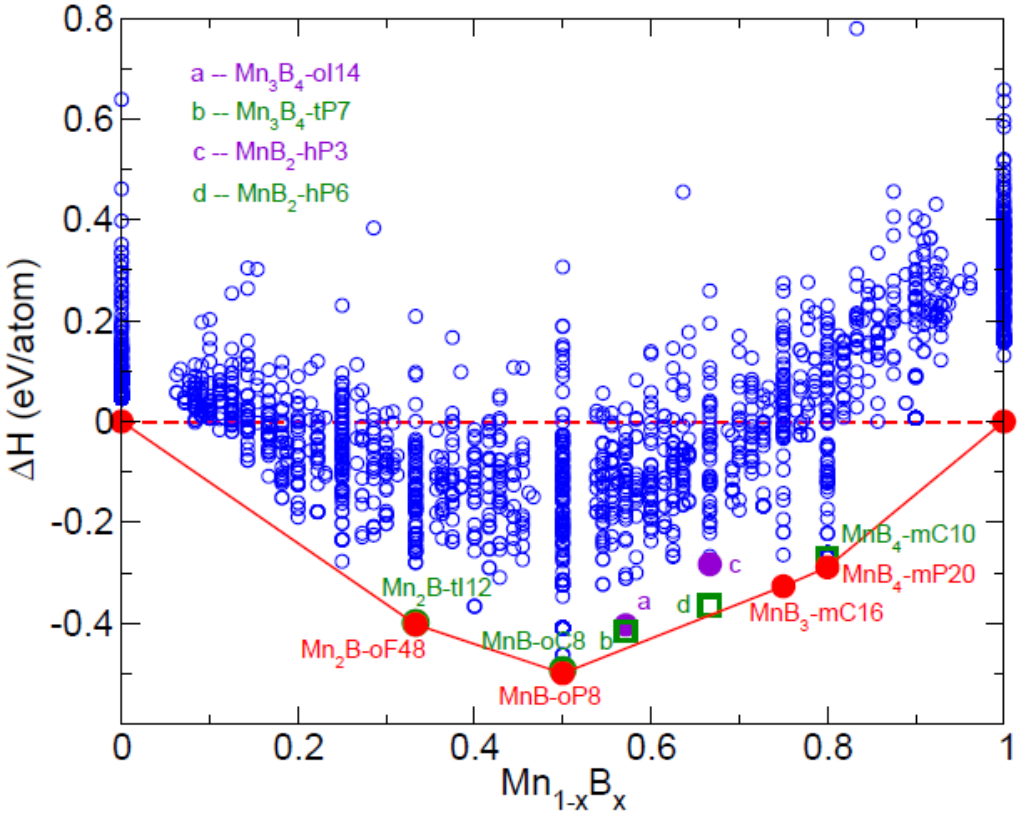


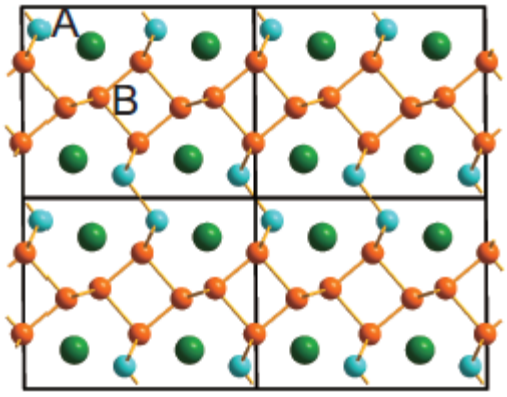




**3-component convex hull: Mg-Si-O system at 500 GPa (Niu & Oganov, *Sci. Rep.* 2015)**

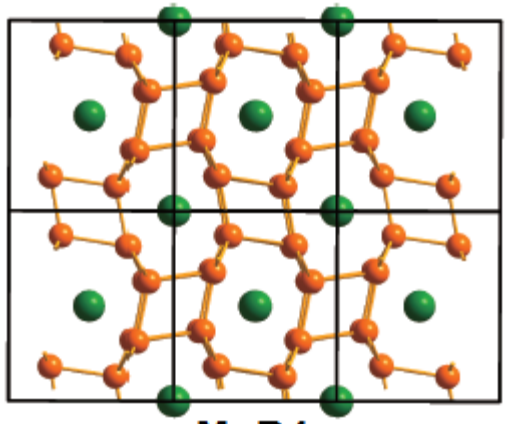
**Stable structure must be below all the possible decomposition lines !!**

# Predicting new compounds: example of “well-known” system Mn-B




MnB3



MnB4

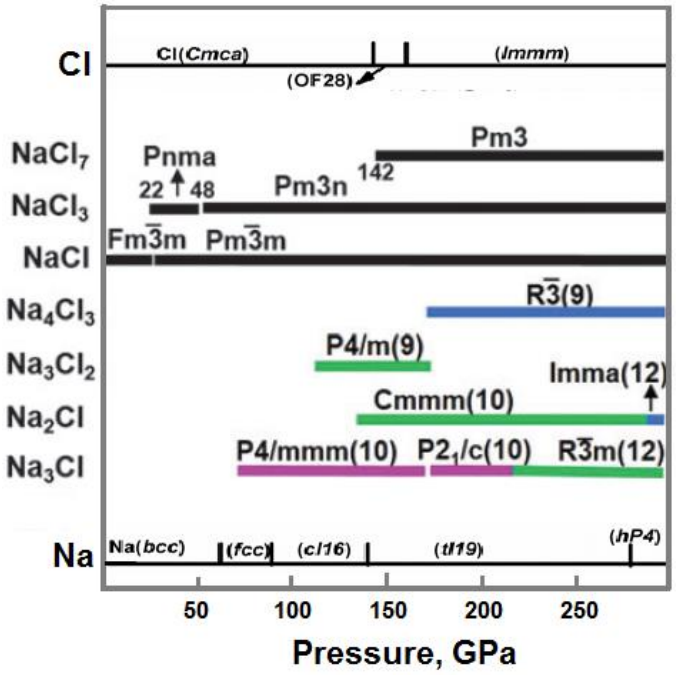
**MnB3 was predicted and then synthesized (Niu et al., PCCP, 2014)**

1. **New compound discovered – MnB3.**
2. **For MnB4, reported experimental structure was wrong – new experiments confirm our structure.**

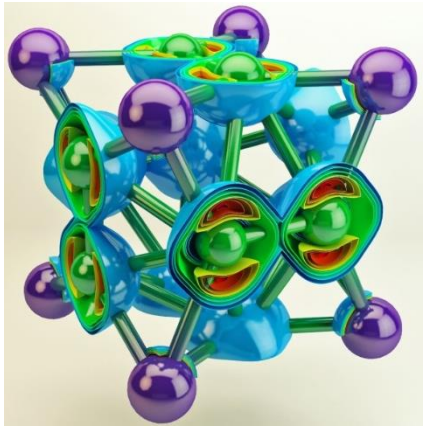
# Predictive power of modern methods:

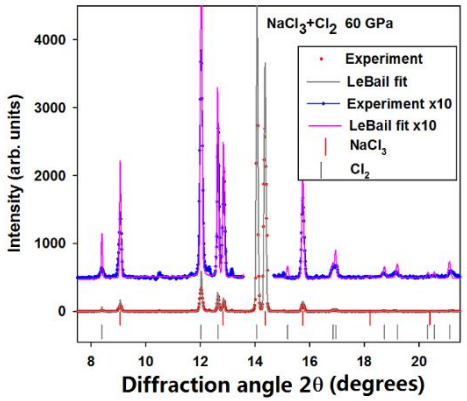
**Na-Cl**

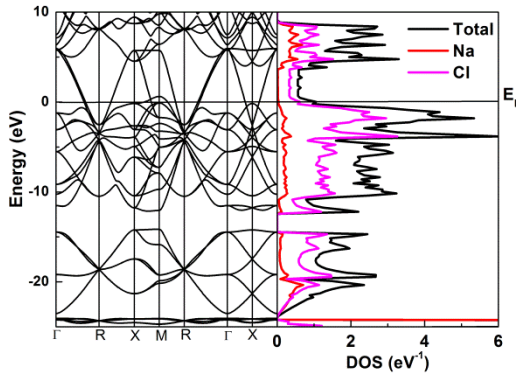
**$Na_3Cl$, $Na_2Cl$, $Na_3Cl_2$, NaCl, $NaCl_3$, $NaCl_7$ are stable under pressure [Zhang, Oganov, et al. *Science*, 2013].**

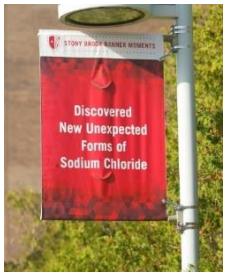



**Stability fields of sodium chlorides**





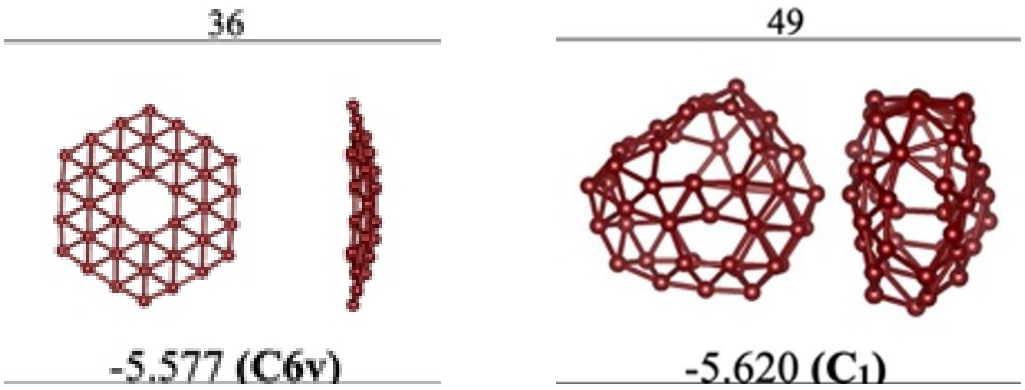

**$NaCl_3$: atomic and electronic structure, and experimental XRD pattern**

## Chemical anomalies:

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

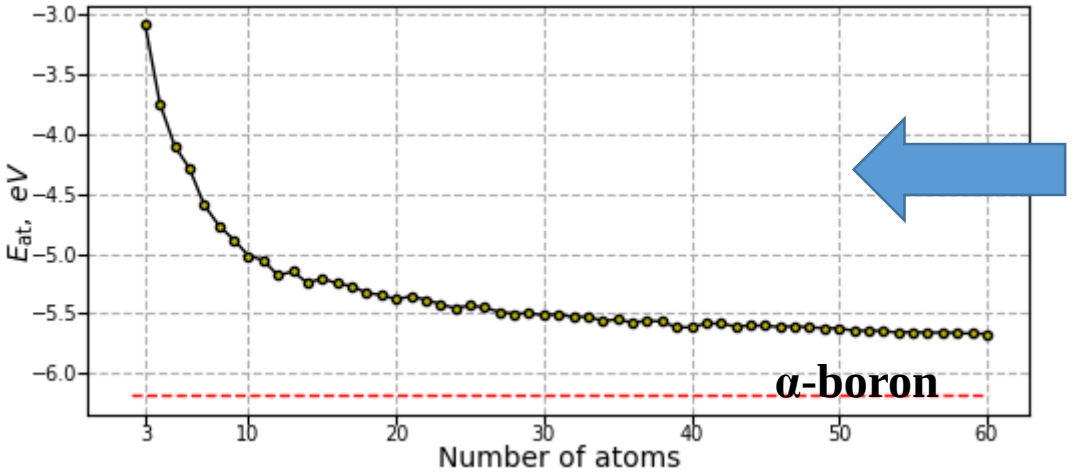
**[Zhang, Oganov, et al., *Science* (2013)]**
**[Saleh & Oganov, *PCCP* (2015)]**

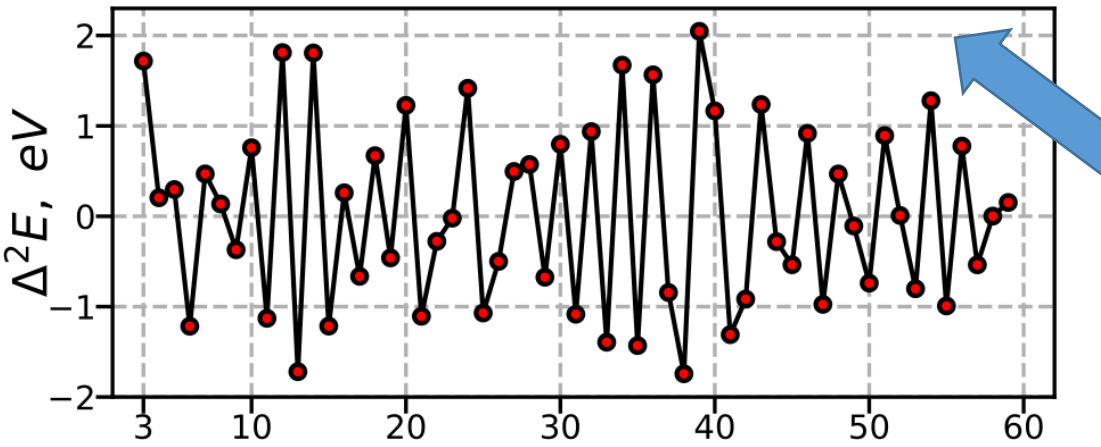
**For molecules we should not discuss absolute stability**



# Stability of molecules does not follow from straight comparison of energies

**Example of boron clusters (Tantardini & Oganov, in prep.)**



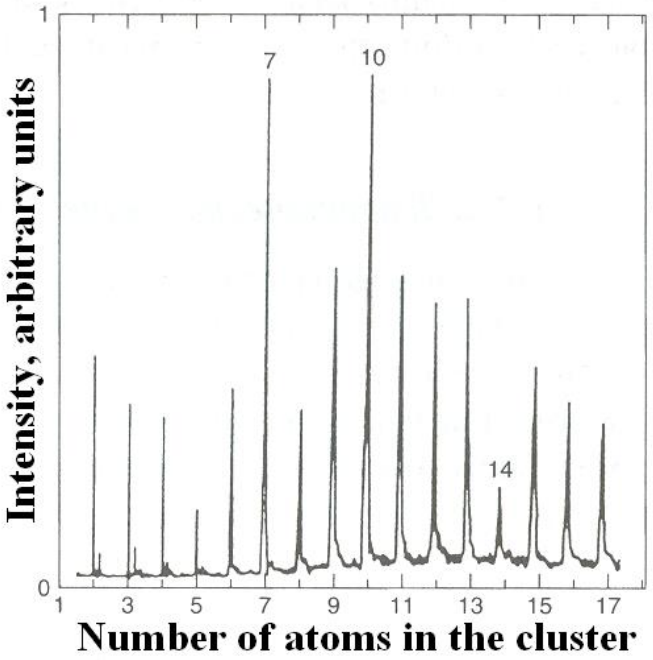

**1. Energy falls almost monotonically with number of atoms.**

**2. Infinite crystal always wins by energy.**

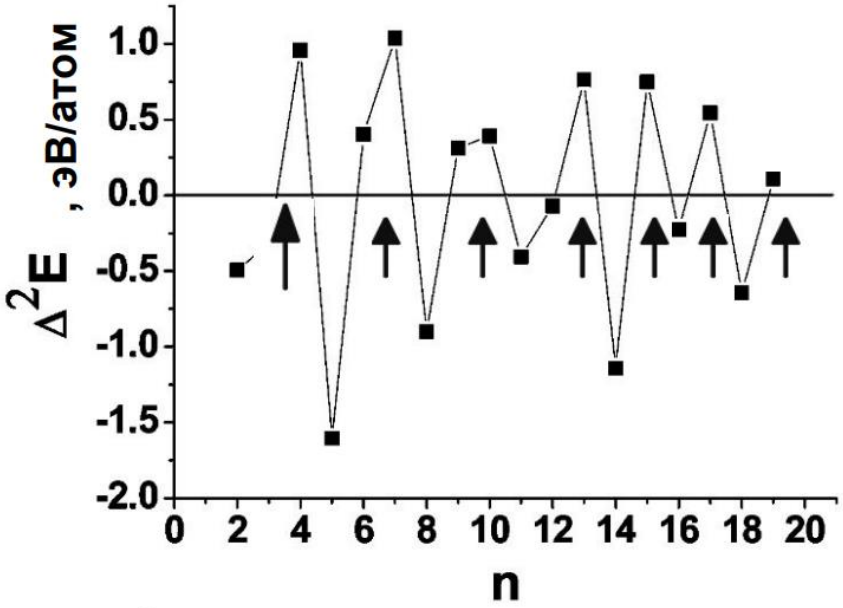
**3. Correct comparison of energies – only with neighbor compositions.**

**4. $\Delta^2$E 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)**

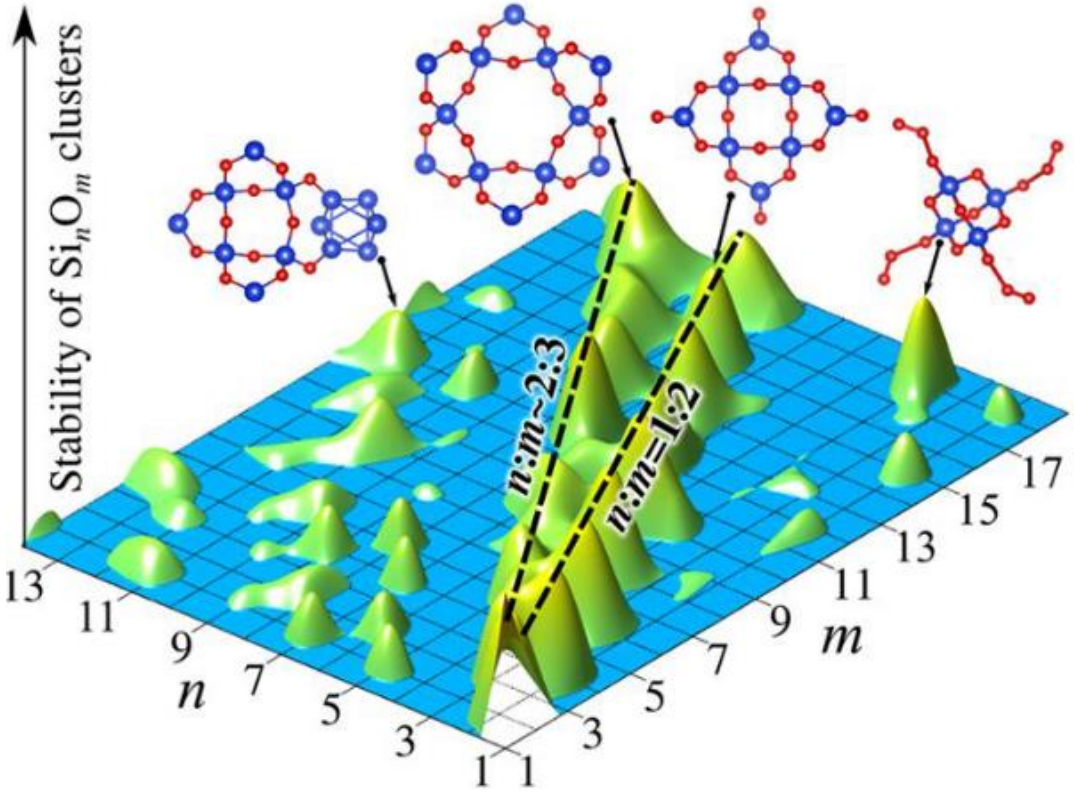
↑ – "magic" cluster

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

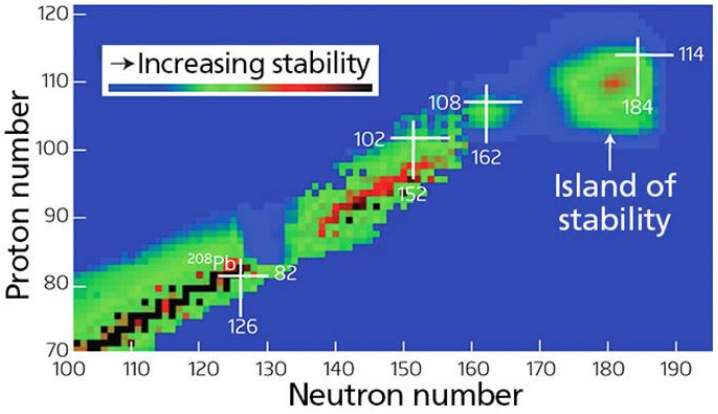
# Map of stability of Si-O clusters

[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)

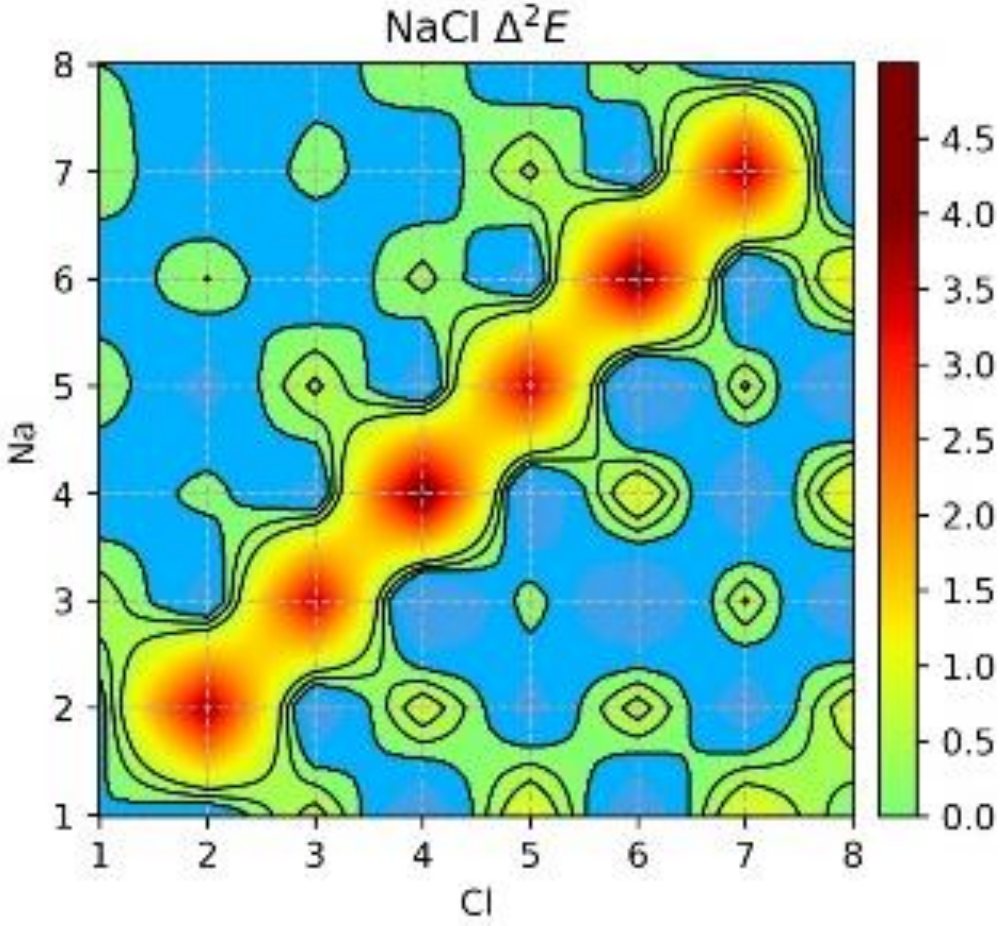
**Analogy with magic atomic nuclei**

**Na-Cl**

# How to predict stability of NaCl molecules

**$(NaCl)_n$ ridge of stability.**

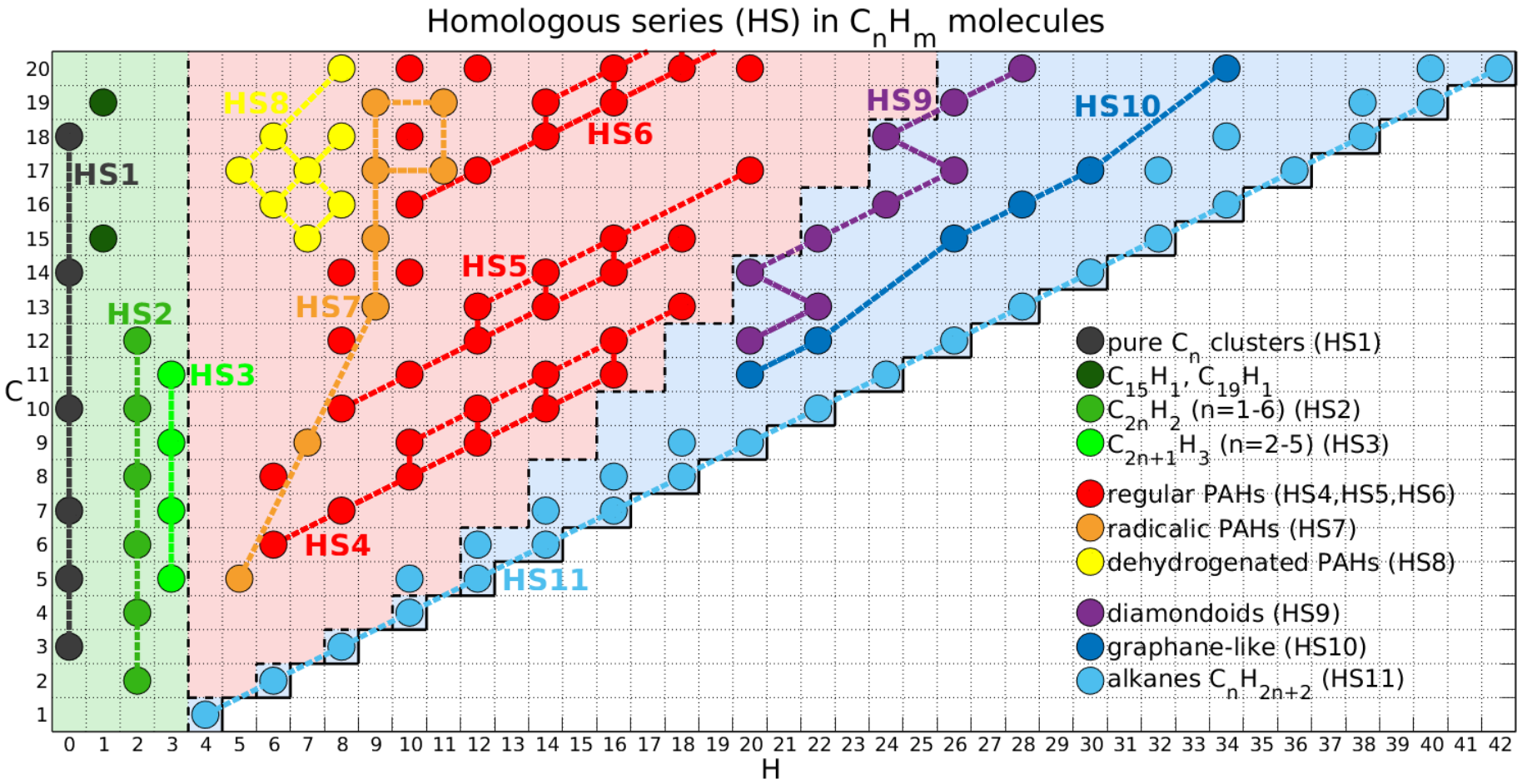
**Numerous islands of stability.**




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

# Which C-H molecules are stable?
## [Lepeshki & Oganov, 2022]

**-Huge diversity, explaining the richness of organic chemistry.**



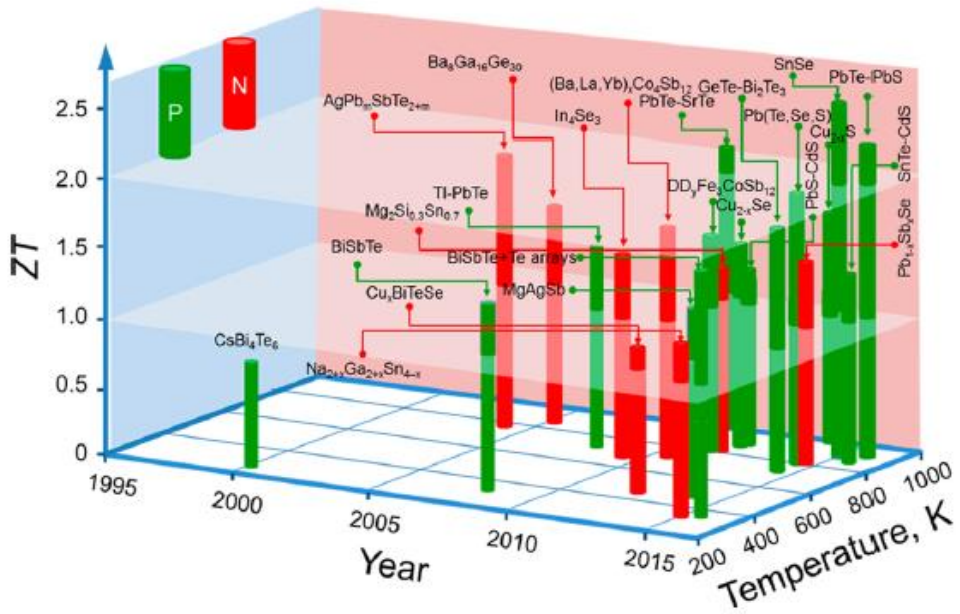
Which compounds have an optimal combination of several properties?

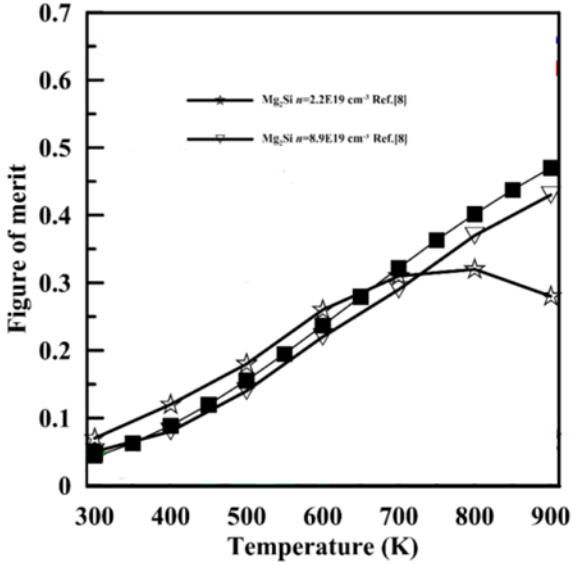
(Pareto optimization – *cf* ecological niches)

# How to improve efficiency of thermoelectric devices?

"One shouldn't work on semiconductors, that is a filthy mess; who knows whether any semiconductors exist"

*-W. Pauli, letter to R. Peierls (1931)*




**[Fan & Oganov (2018)]**

$$ZT = \frac{\sigma S^2 T}{\kappa}$$

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3}$$

$$\eta = \frac{\Delta T}{T_H} \frac{\sqrt{1+zT}-1}{\sqrt{1+zT}+\frac{T_C}{T_H}}$$

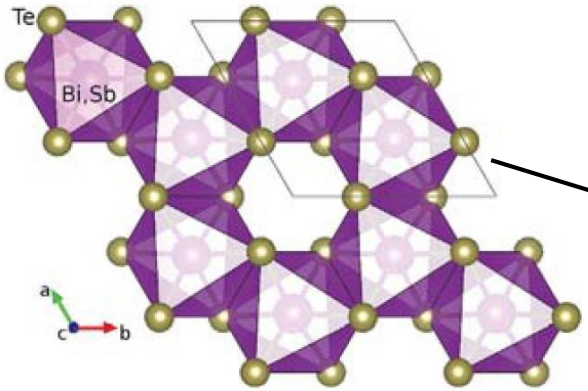
**- efficiency**

# Multiobjective (Pareto) optimization finds a new thermoelectric polymorph of $Bi_2Te_3$

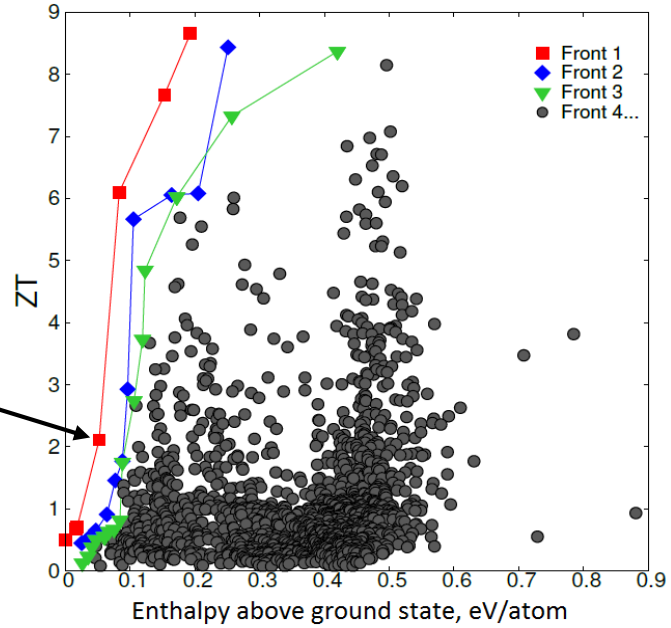
Computer Physics Communications 222 (2018) 152–157

## Efficient technique for computational design of thermoelectric materials

Maribel Núñez-Valdez , Zahed Allahyari , Tao Fan , Artem R. Oganov

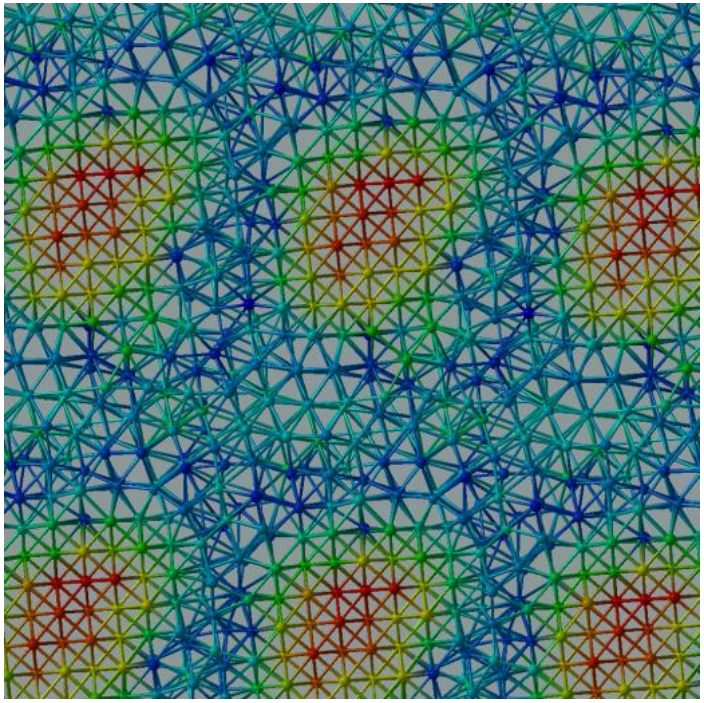



**Predicted *P*6$_3$*cm* structure of $Bi_2Te_3$**



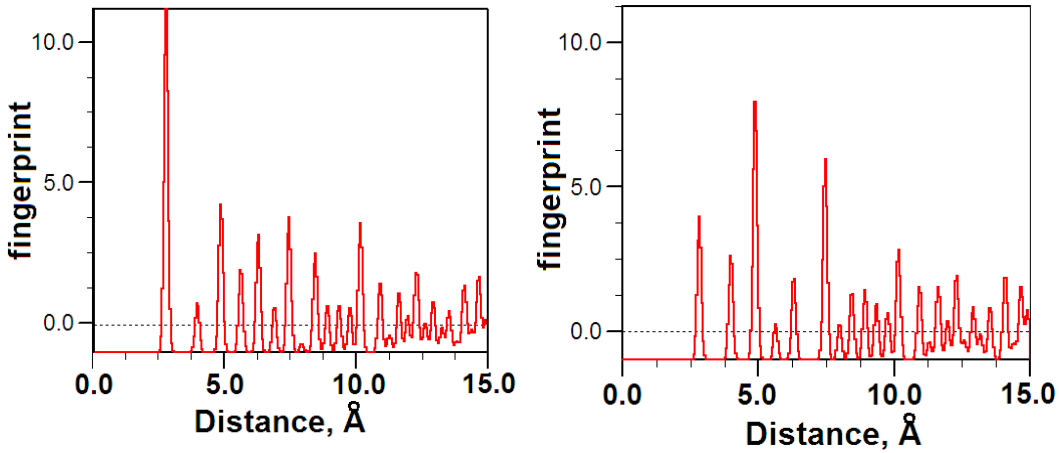

**Pareto optimization of ZT and stability in the Bi-Te system**

# 3. Looking into the genome



# Fingerprint theory is the basis of our analysis

**Fingerprint function is a 1D-descriptor of the structure: diffraction spectrum, PCF, ...**




**Fingerprint is related to the pair correlation function**

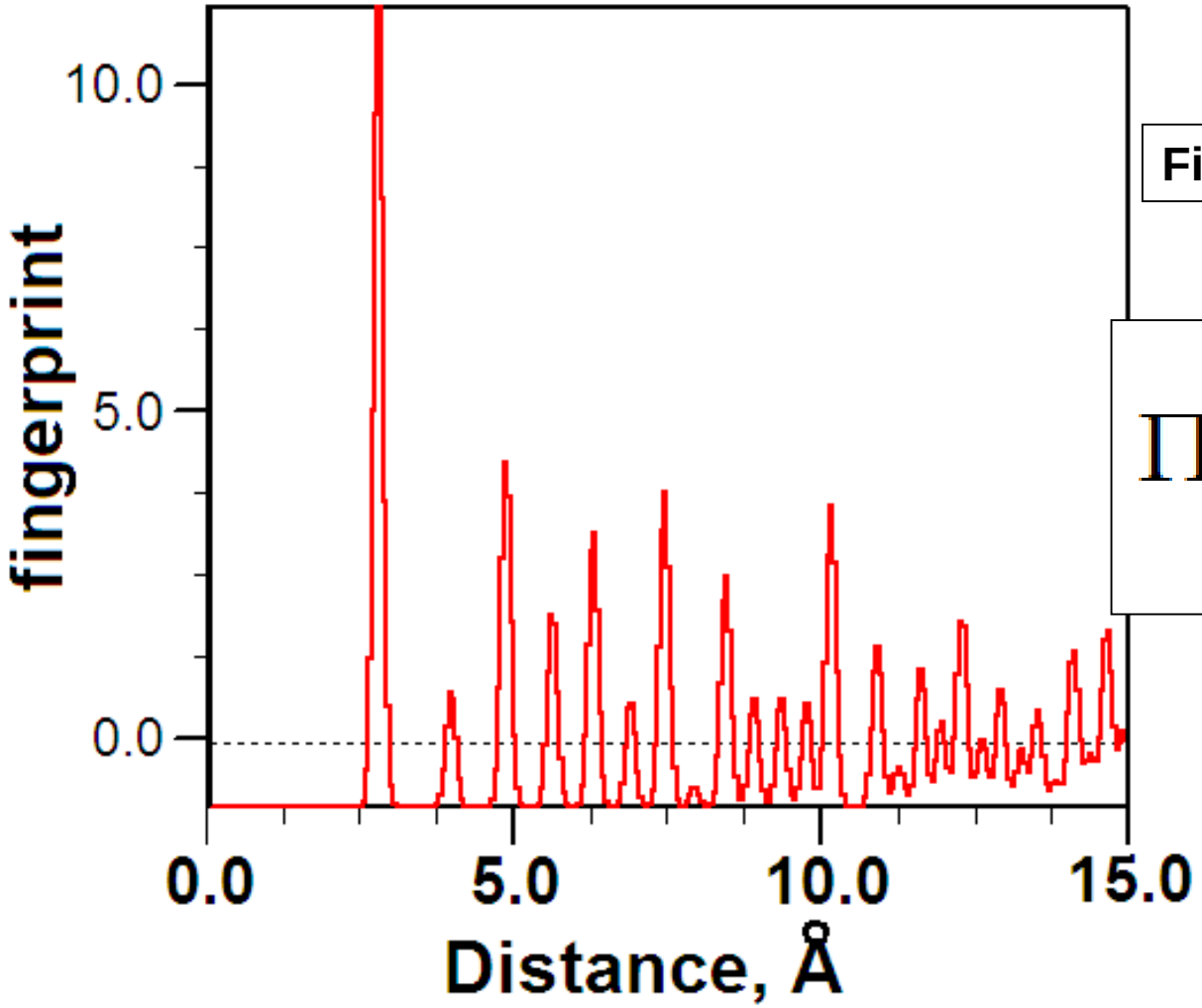
$$F_{AB}(R) = \sum_{A_i,\text{cell}} \sum_{B_j} \frac{\delta(R - R_{ij})}{4\pi R_{ij}^2 \frac{N_A N_B}{V} \Delta} - 1 = g_{AB}(R) - 1$$

***Difference between 2 structures is given by „distance“, e.g.:*** $D = \int (f_1 - f_2)^2 dR$

**“Cosine distance”** $D = \frac{1}{2}\left(1 - \frac{f_1 f_2}{|f_1||f_2|}\right)$**, always in the range [0;1]**

[ARO & Valle, J. Chem. Phys. 130, 104504 (2009)]

# Structure fingerprints




**Fingerprint f=0 for ideal gas**

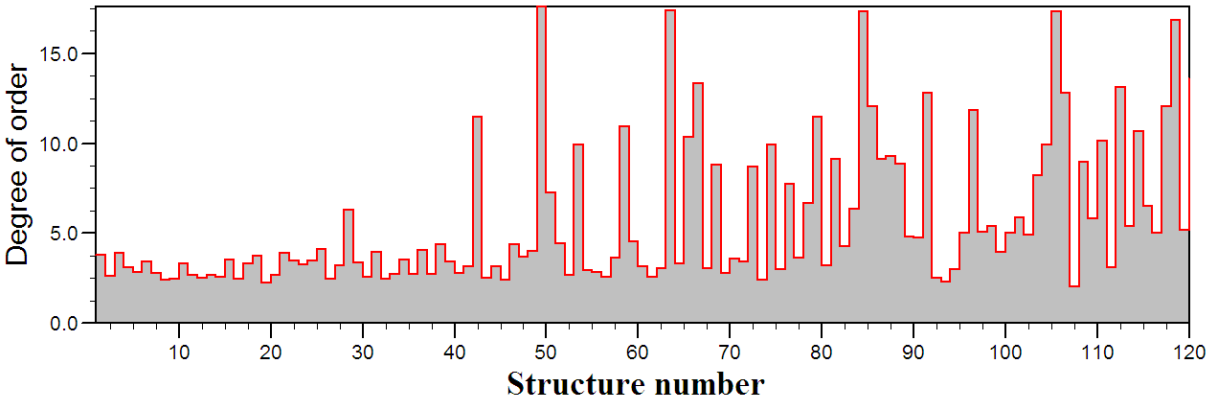
**Degree of order :**

$$\Pi = \frac{1}{V^{1/3}} \int_0^{\infty} f^2 \, dR$$

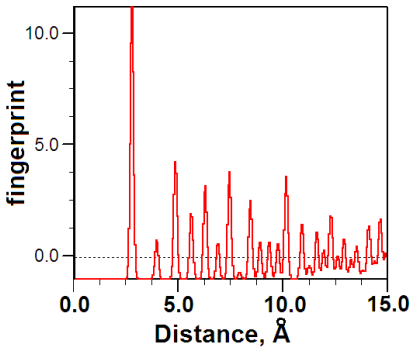
[ARO & Valle, J. Chem. Phys. 130, 104504 (2009)]

# Evolution leads to the loss of entropy

$$\Pi = \frac{1}{V^{1/3}} \int_0^{\infty} f^2 dR$$ - Degree of order

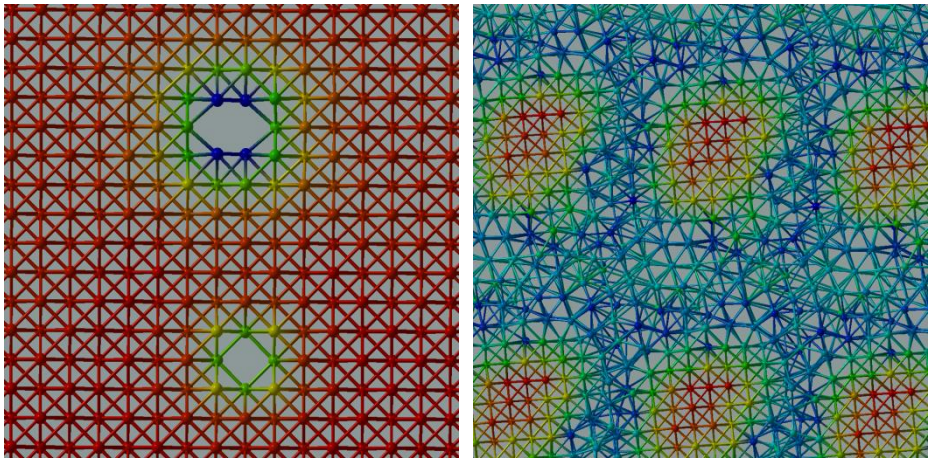



Emergence of order from chaos during evolutionary simulation




Fingerprint: can be computed for whole structure or for each atomic site

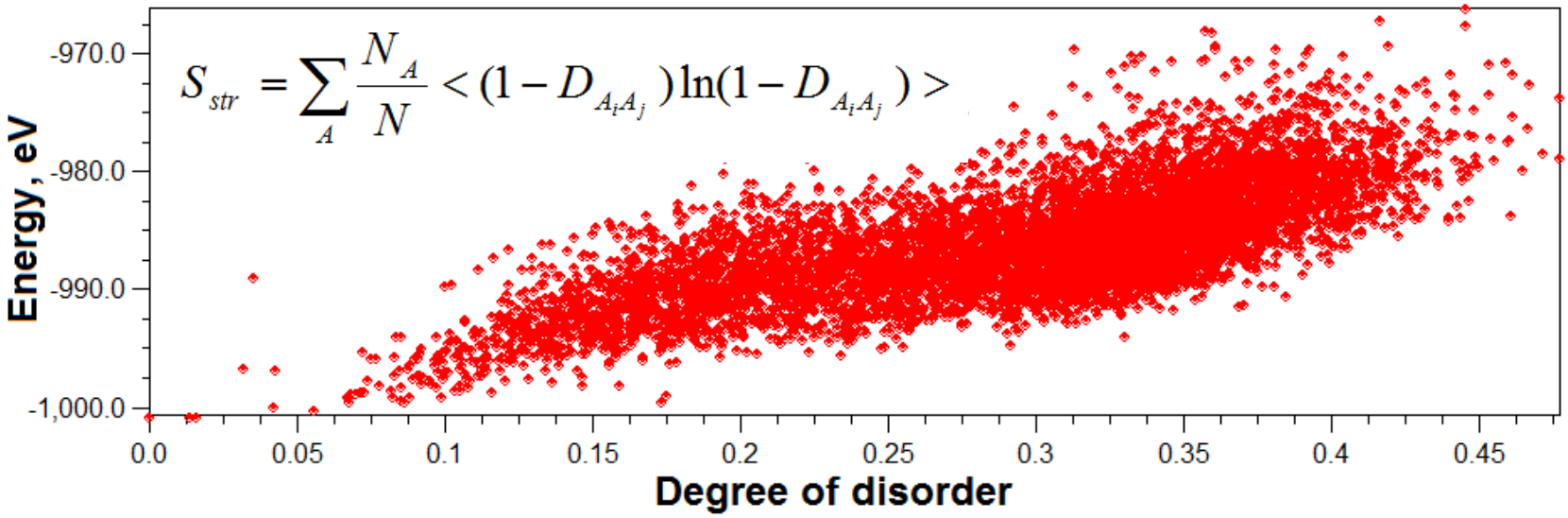
Local degree of order – indicates defects and low-symmetry sites



[ARO & Valle (2009), Lyakhov et al. (2010)]

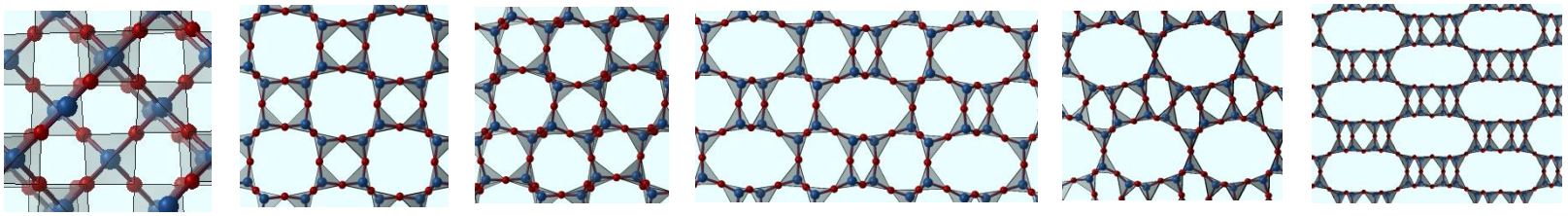
# Stability vs complexity.
# Pauling‘s 5th rule:

**„The number of essential structural elements of stable structures tends to be small“**



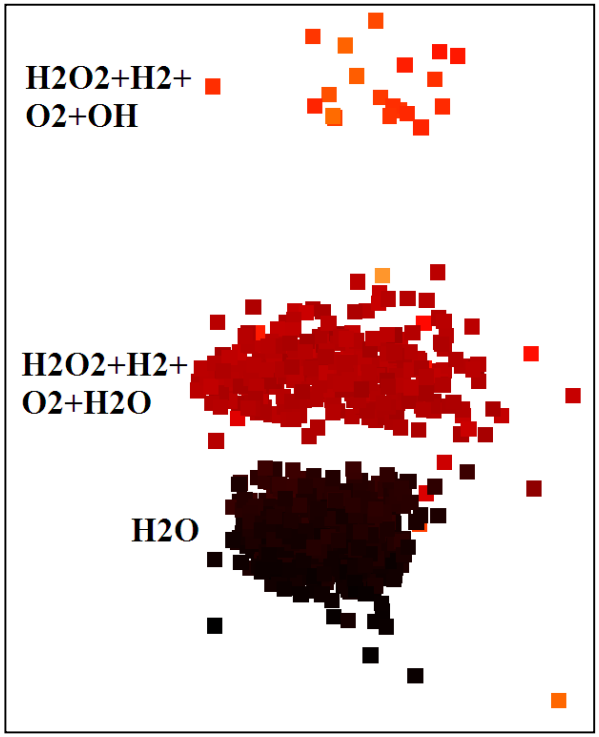

**Correlation plot for 6900 structures of $SiO_2$ with 24 atoms/cell**

**Some of the (many) remarkable silicate frameworks:**

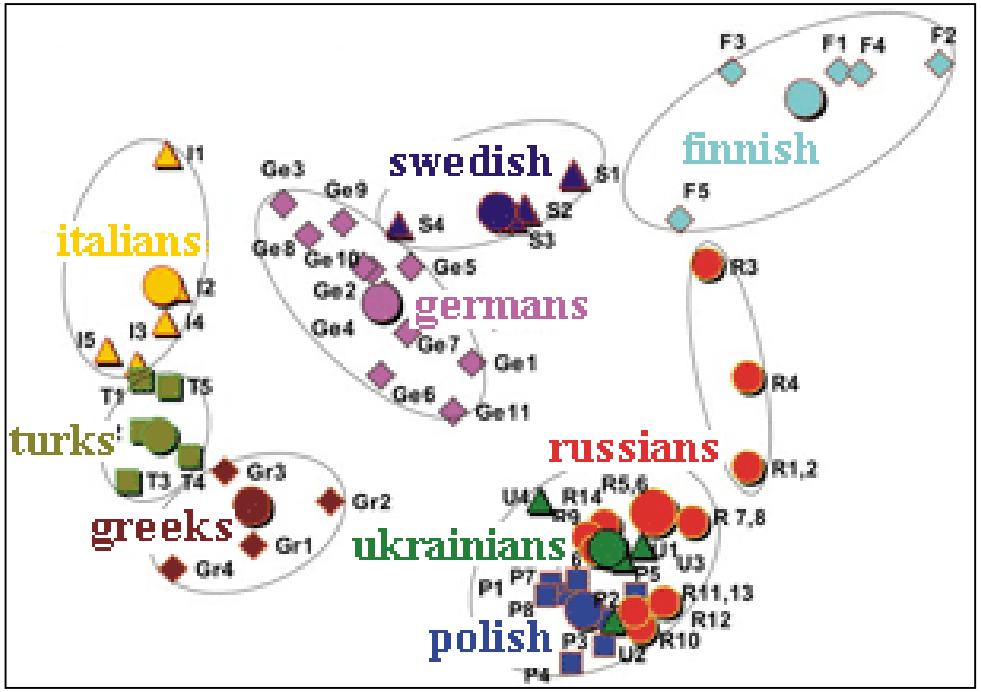


Increasing energy

# Grouping structures into similarity classes: quest for more insight in complex systems



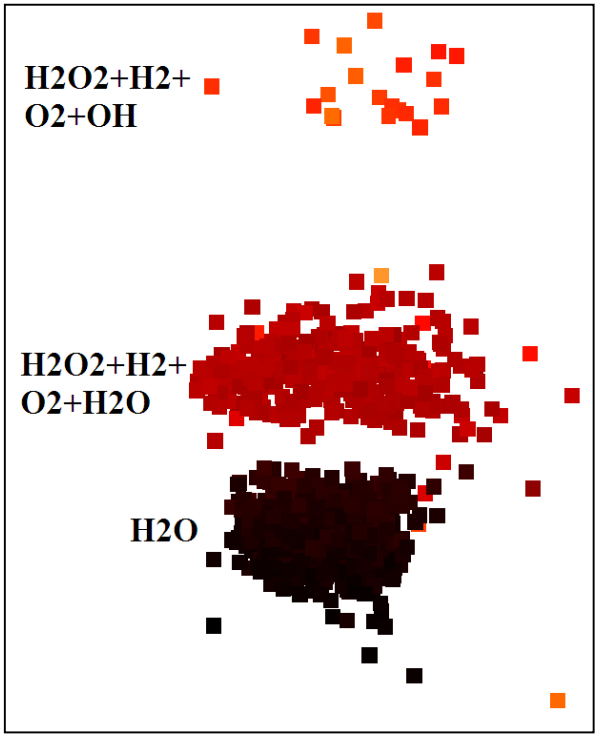

Distance-preserving mapping of crystal structures of $H_2O$ (*darker* – lowest E, *lighter* – higher E).




DNA grouping in Europe

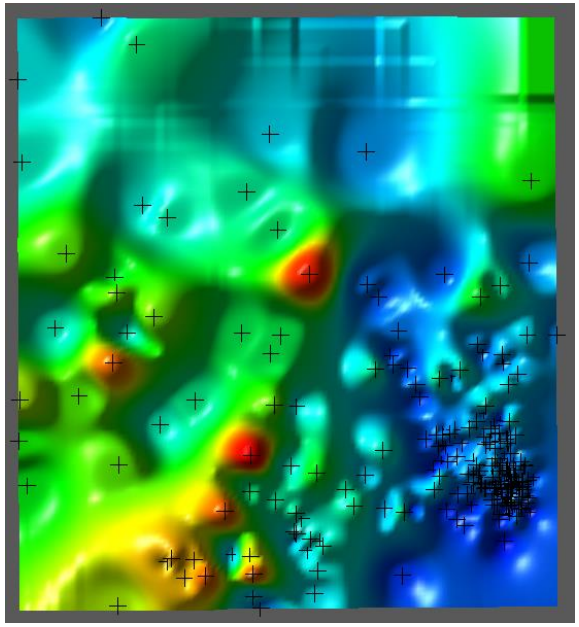
[ARO & Valle, J. Chem. Phys. 130, 104504 (2009)]

# Grouping structures into similarity classes: quest for more insight in complex systems

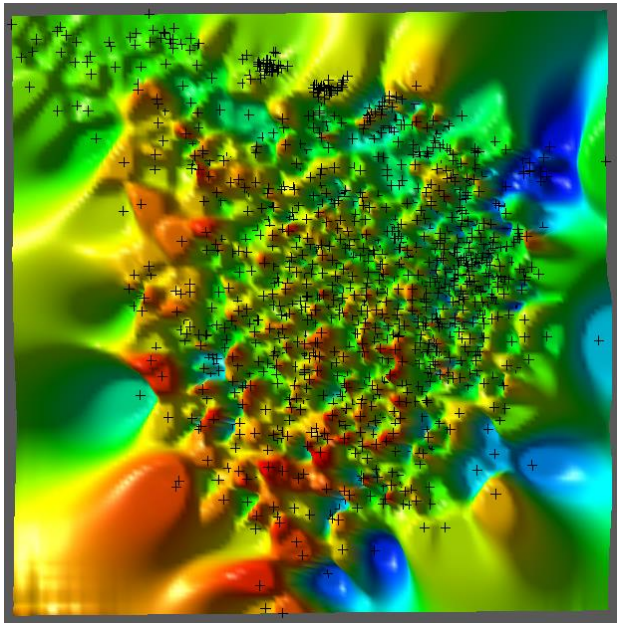


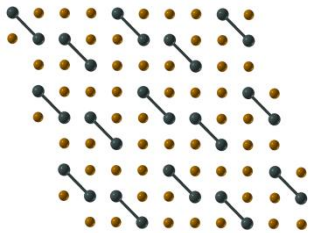

Distance-preserving mapping of crystal structures of $H_2O$ (*darker* – lower E, *lighter* – higher E)

$Au_8Pd_4$ - simple

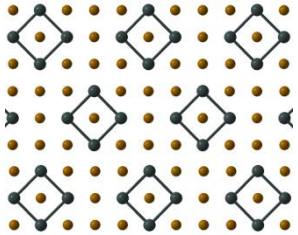


$L_4J_8$ - complex

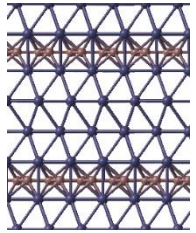




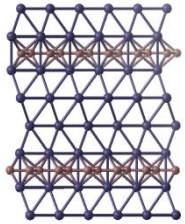
-61.960 eV



-61.957 eV



-99.12$\varepsilon$



-99.05$\varepsilon$

[ARO & Valle, J. Chem. Phys. 130, 104504 (2009)]

**Evolution is nature's preferred way of solving complex problems**

**The analogy between biological and computational evolution is limited and profound at the same time**

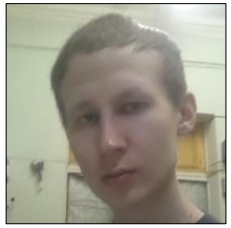
USPEX Computational Materials Discovery

# Our team. Where great minds do NOT think alike.

**Artem R. Oganov**
Professor, head of laboratory

**Zahed Allahyari**
Postdoc

**Pavel Bushlanov**
Postdoc



**Sergey Lepeshkin**
Postdoc

**Vladimir Baturin**
Postdoc

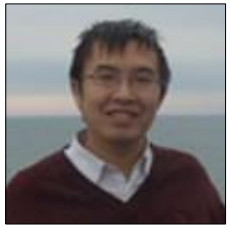
**A. Goncharov**
Experimental confirmation

**Dmitrii Semenok**
PhD student

**Efim Mazhnik**
PhD student

**Tao Fan**
PhD student

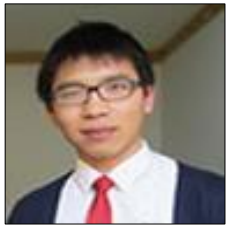
**V. Blatov**



**X. Dong**

**Q. Zhu**

**X. F. Zhou**



**H. Niu**

**A. Kvashnin**

**I. Troyan**
Experimental confirmation