Evolutionary Crystal Structure Prediction and USPEX

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Structure is the basis for understanding materials and their properties

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

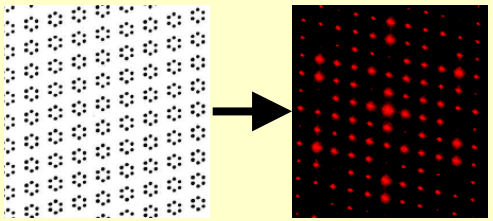
The Nobel Prize in Chemistry 1985

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

Herbert A. Hauptman

Jerome Karle

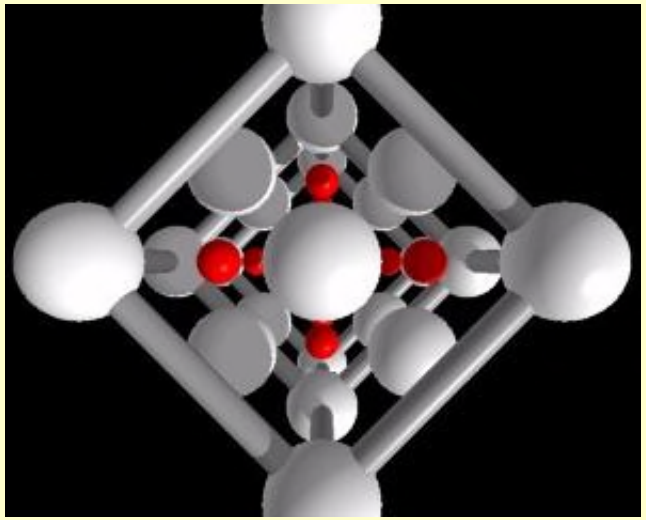
(from http://nobelprize.org)



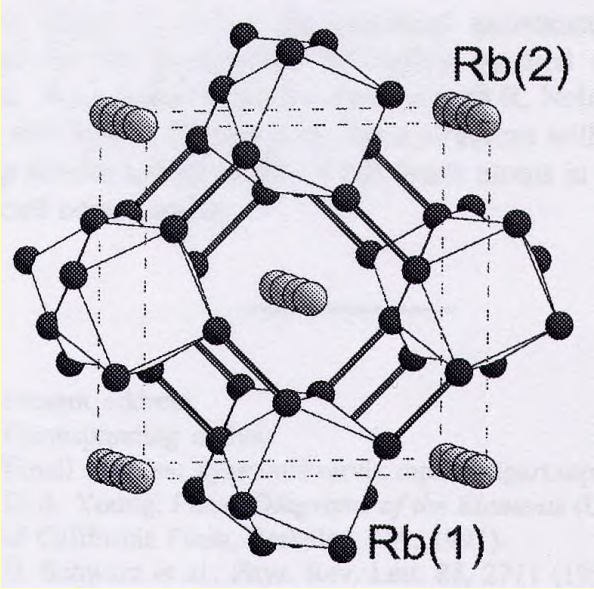
Structure Diffraction

Zincblende ZnS.

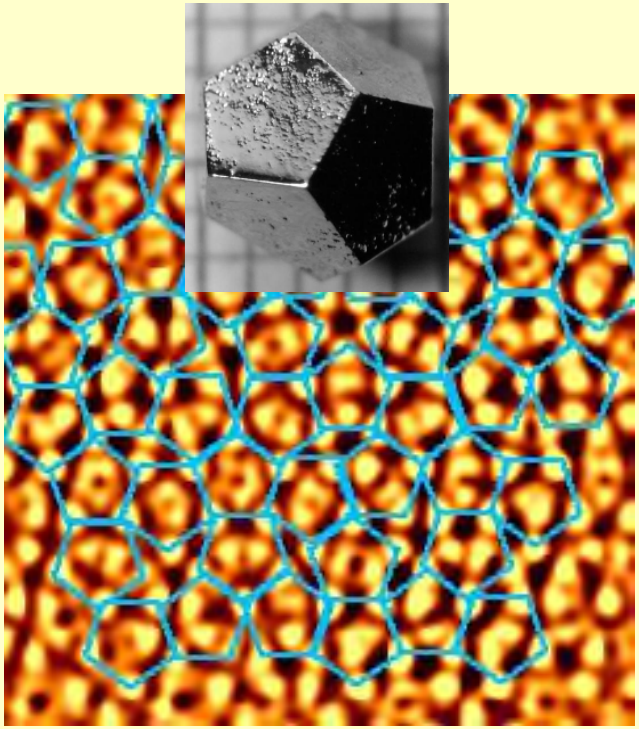
One of the first structures solved by Braggs in 1913.



With time, incredibly complex structures were discovered



Host-guest elements
(Rb-IV phase, U.Schwarz'99)



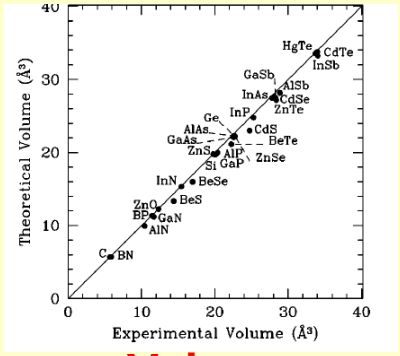
Quasicrystals

New state of matter discovered in lab in 1984. In nature found only in 2009!

Proteins

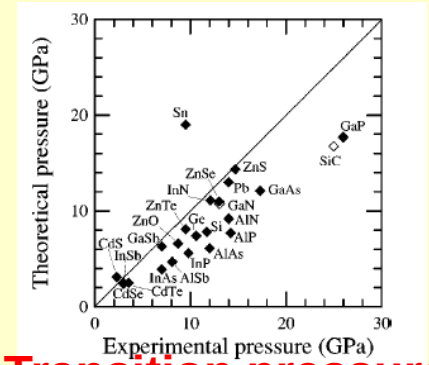
When the structure is known, many properties can be computed reliably

- State of art: DFT.
- Molar volumes: within 1-3% (LDA,GGA).
- Transition pressures: 10% underestimated (LDA), ± 5 GPa (GGA).
- Band gaps: ~30% underestimated (LDA, GGA), ±10% (GW).
- Unsatisfactory – for van der Waals crystals, systems with localised d- and f-electrons.



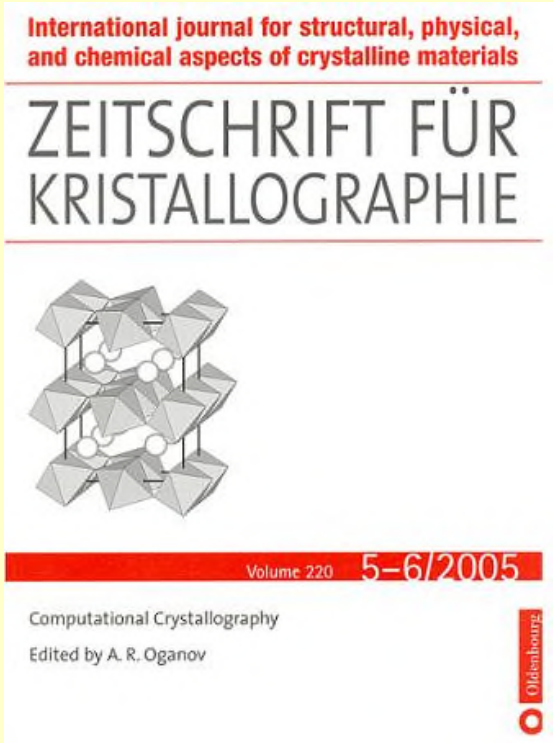
Volumes

LDA: Mujica‘03



Transition pressures

LDA: Mujica‘03



Experimentalists also like DFT

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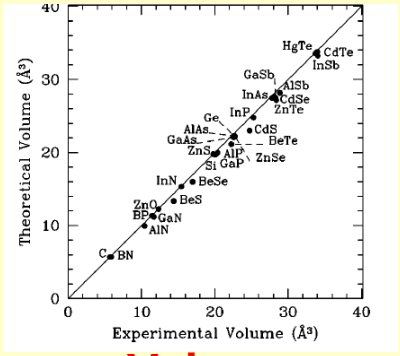
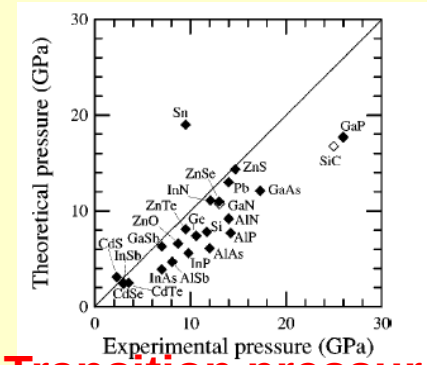


Volumes

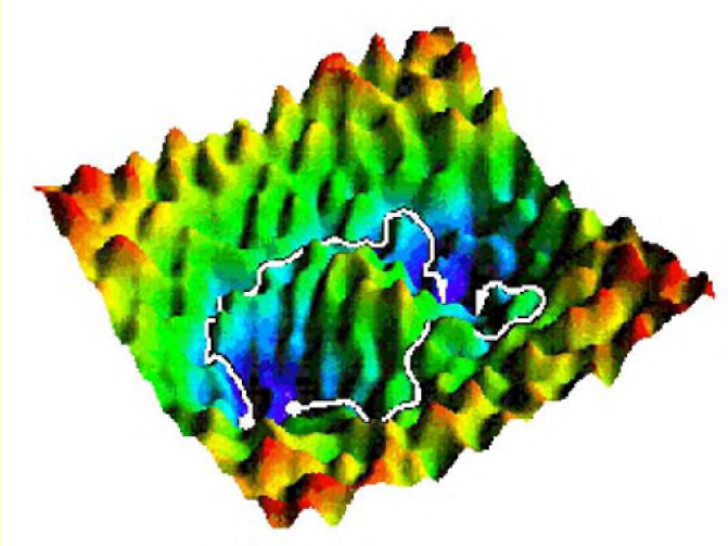
LDA: Mujica‘03



Transition pressures

LDA: Mujica‘03

(Free) energy landscape: key to thermodynamics and kinetics



E
H=E+PV
F=E-TS
G=E+PV-TS

Transition paths, rate constants etc.

J. Phys.: Condens. Matter **12** (2000) A147–A152. Printed in the UK

Transition path sampling: throwing ropes over mountains in the dark

Peter G Bolhuis†, Christoph Dellago‡, Phillip L Geissler‡ and David Chandler‡

† Department of Chemistry, Lensfield Rd, Cambridge CB2 1EW, UK
‡ Department of Chemistry, University of California, Berkeley, CA 94720, USA

Received 5 October 1999

Global minimum & low-energy local minima

THE JOURNAL OF CHEMICAL PHYSICS **124**, 244704 (2006)

Crystal structure prediction using *ab initio* evolutionary techniques: Principles and applications

Artem R. Oganov[a] and Colin W. Glass

Laboratory of Crystallography, Department of Materials, ETH Zurich, HCI G 515, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland

(Received 20 February 2006; accepted 12 May 2006; published online 28 June 2006)

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

Are Crystal Structures Predictable?

ANGELO GAVEZZOTTI*

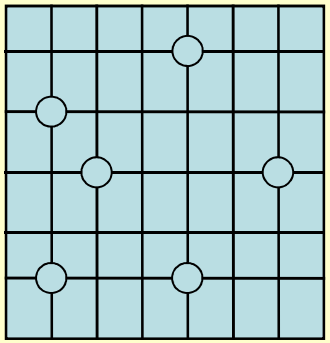
"No": by just writing down this concise statement, in what would be the first one-word paper in the chemical literature, one could safely summarize the present state of affairs

J. Maddox
(*Nature*, 1988)

Need to find GLOBAL energy minimum.

Trying all structures is impossible:

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



N_{atoms}	Variants	CPU time
1	**1**	**1 sec.**
10	**10^{11}**	**10^{3} yrs.**
20	**10^{25}**	**10^{17} yrs.**
30	**10^{39}**	**10^{31} yrs.**

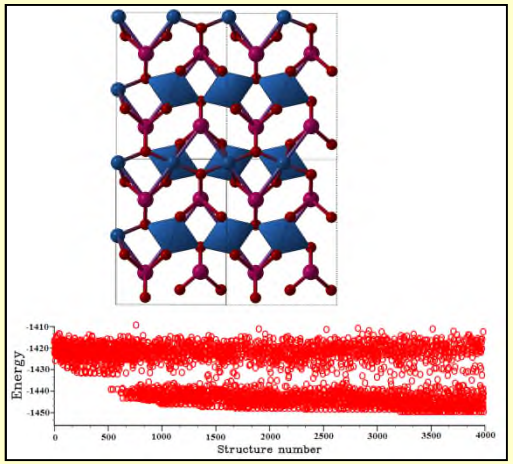
RESEARCH NEWS

Crystal structure prediction – evolutionary or revolutionary crystallography?

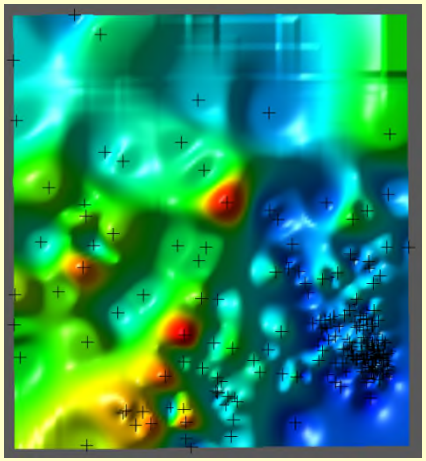
S. L. Chaplot and K. R. Rao CURRENT SCIENCE, VOL. 91, NO. 11, 10 DECEMBER 2006

Overview of USPEX (Oganov & Glass, *J.Chem.Phys.* 2006)

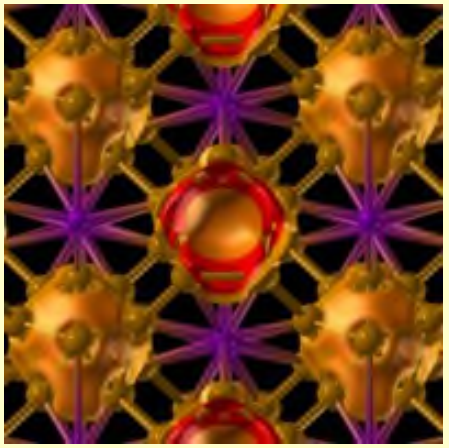
New developments in crystal structure prediction extend the range of problems that can be solved



1. Predicting crystal structures by evolution

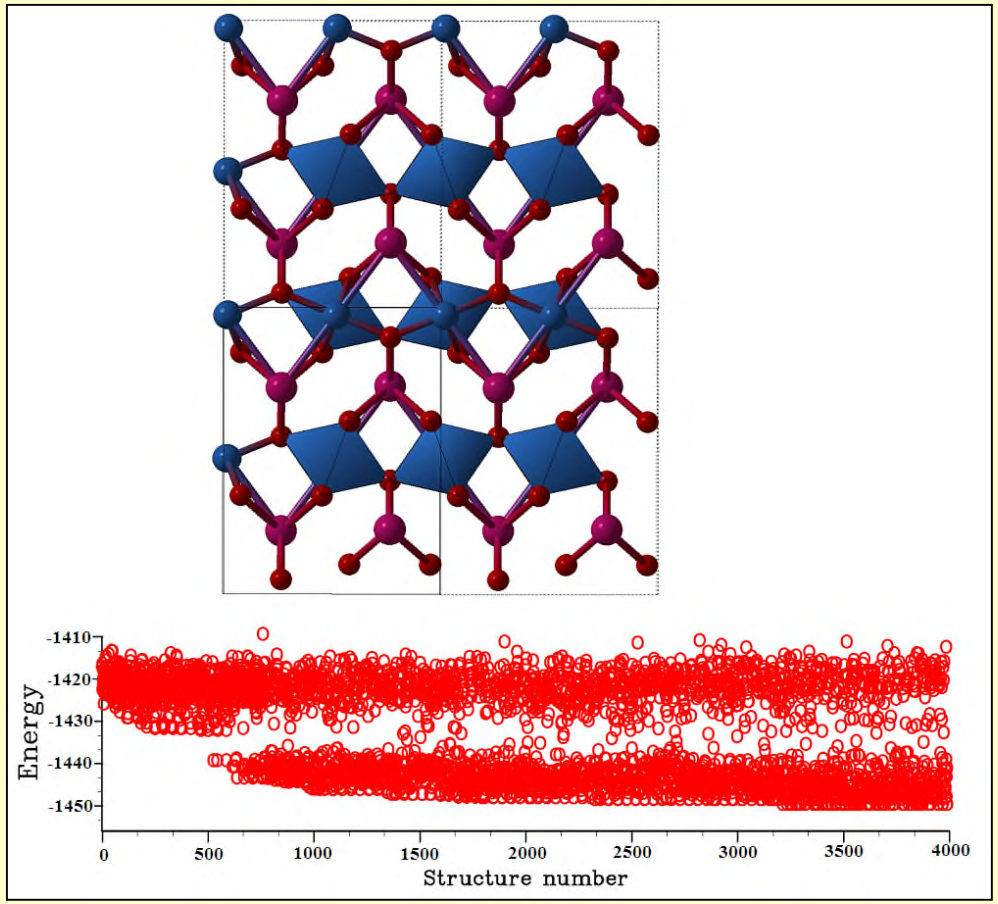


2. Why does it work?



3. Predicting new materials

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.**

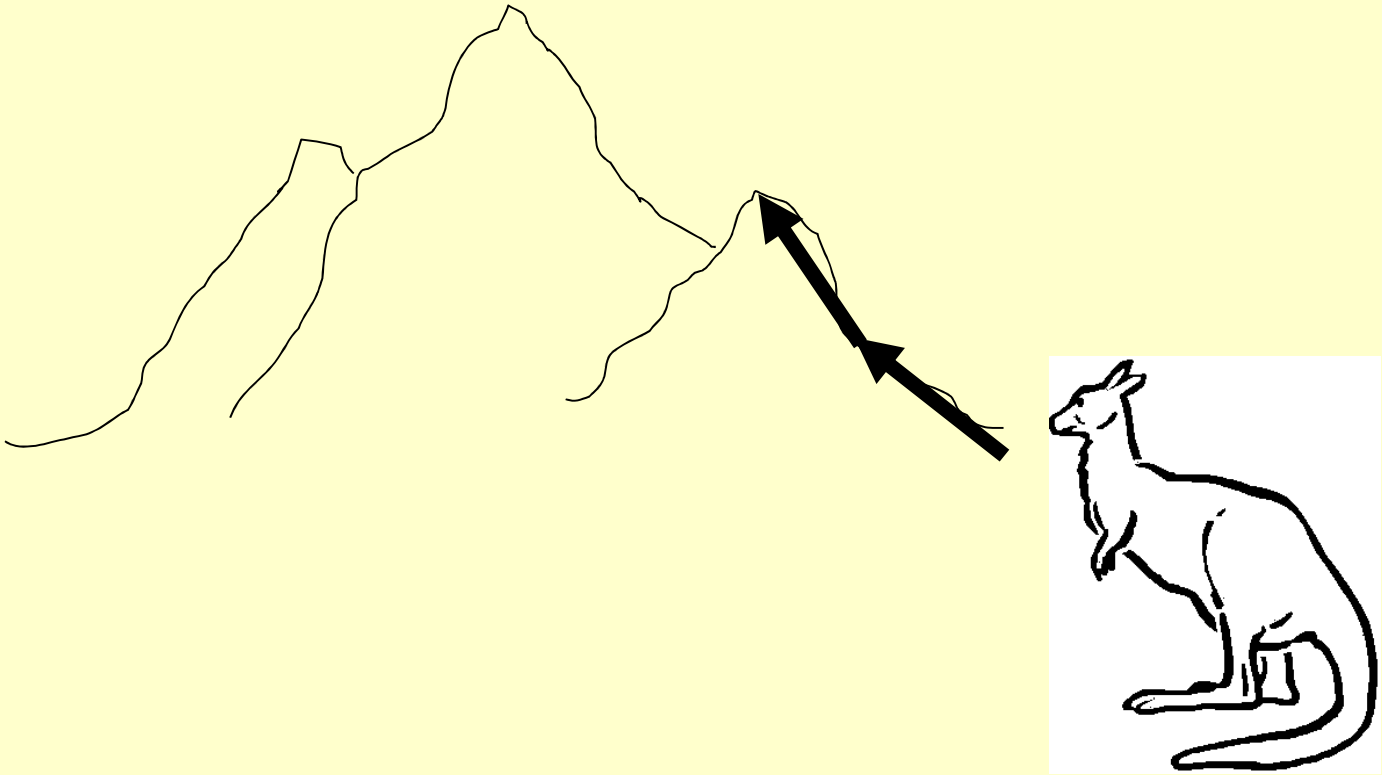
Crystal structure prediction methods

1. **Random sampling** (Freeman & Catlow, 1992)
2. **Simulated annealing** (Pannetier, 1990)
3. **Molecular dynamics and metadynamics** (Martonak, 2003)
4. **Data mining** (Curtarolo, 2003)
5. **Minima hopping** (Goedecker, 2004)

6. **Evolutionary algorithms / PSO**

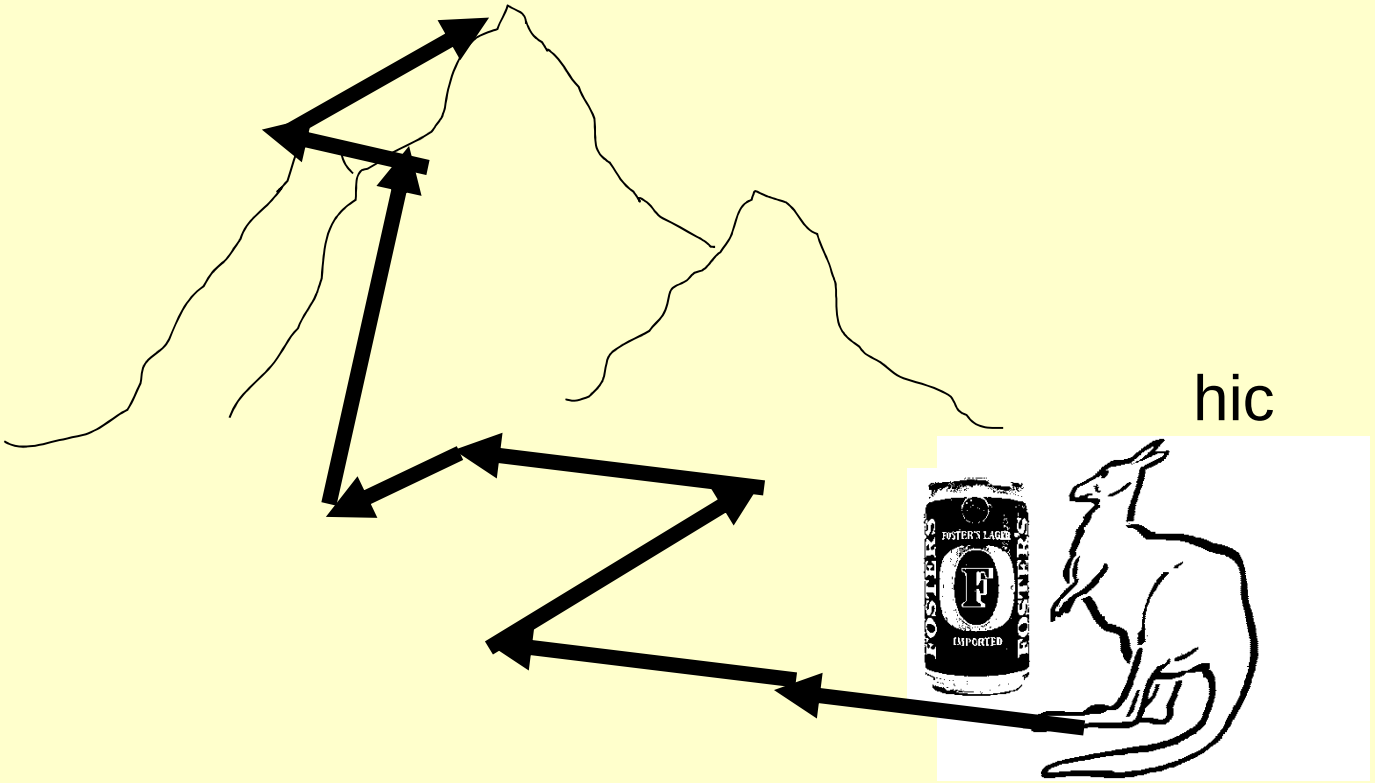
All of them rely on local optimization methods!

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



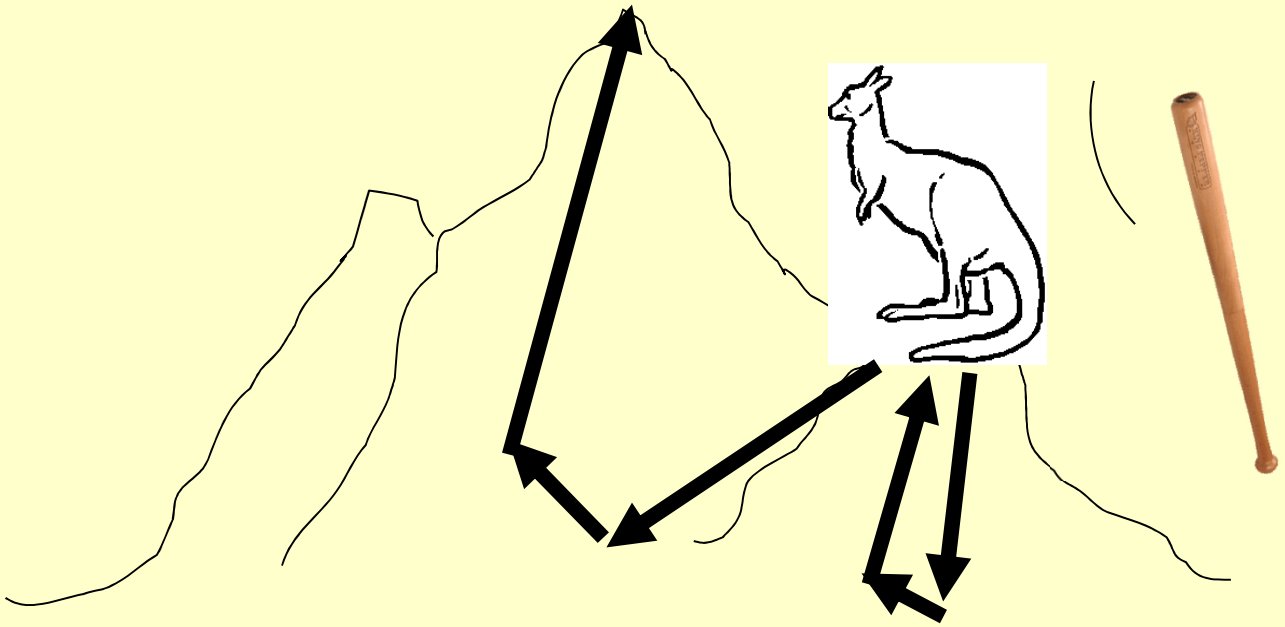
Random sampling is like dropping a kangaroo somewhere on the surface of the earth, telling it to only hop uphill and hoping it will get to the top of mount Everest.

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



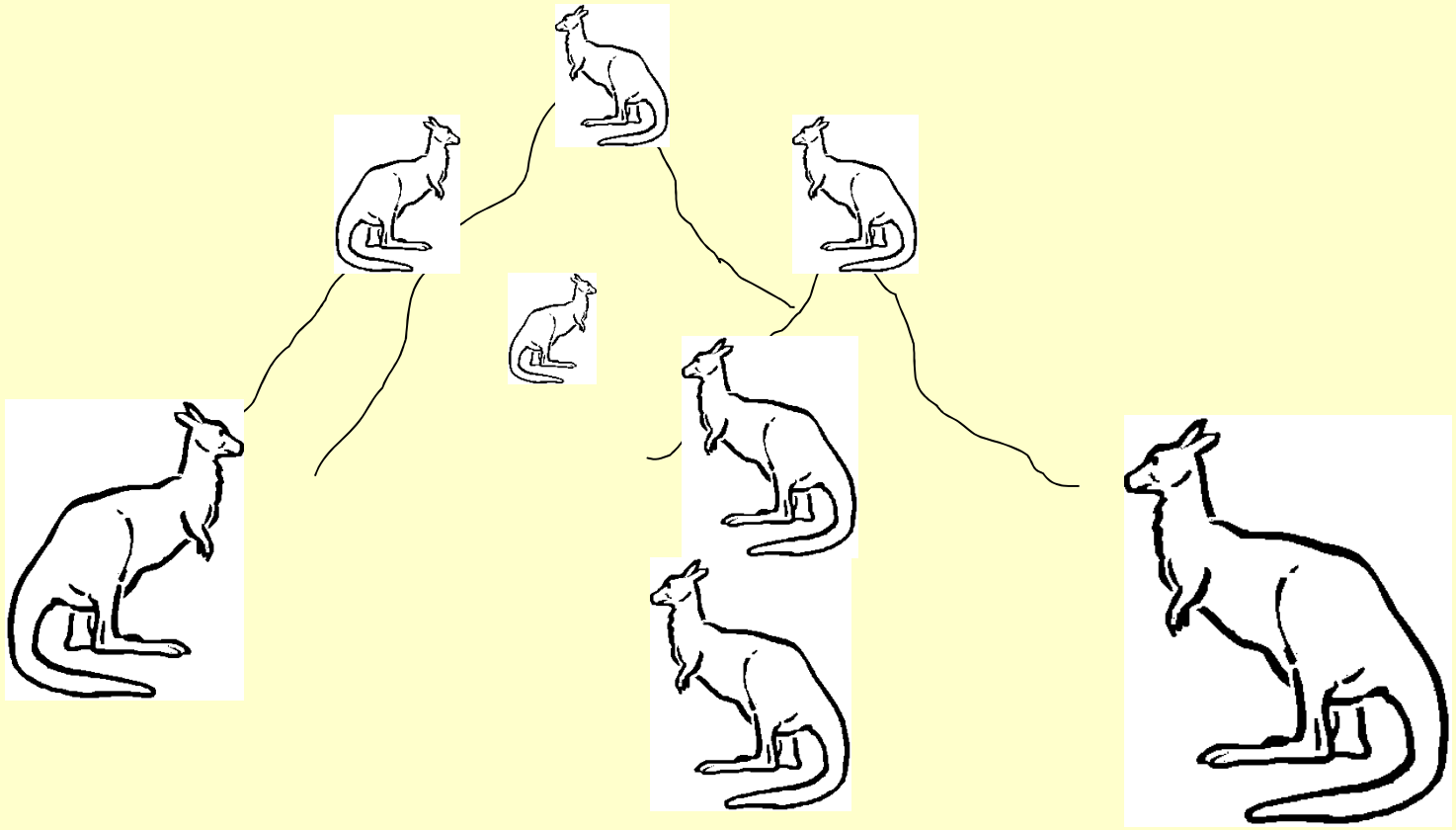
Simulated Annealing is like doing the same but getting the kangaroo very very drunk first.

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



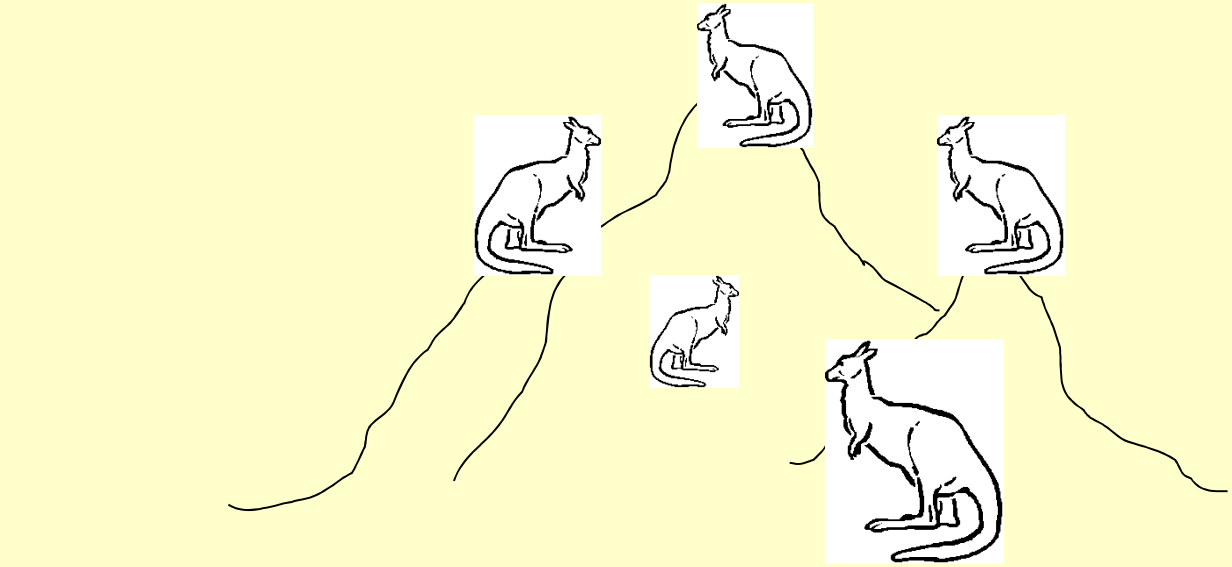
Minima Hopping is like knocking the kangaroo off the smaller hill with a bat harder and harder till it is close enough to another hill to climb it.

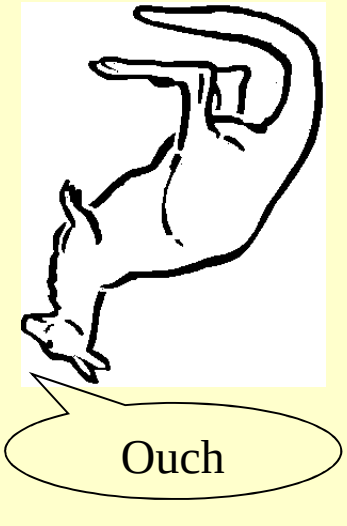
Global optimisation methods:
Kangaroo's climb to Mt. Everest



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

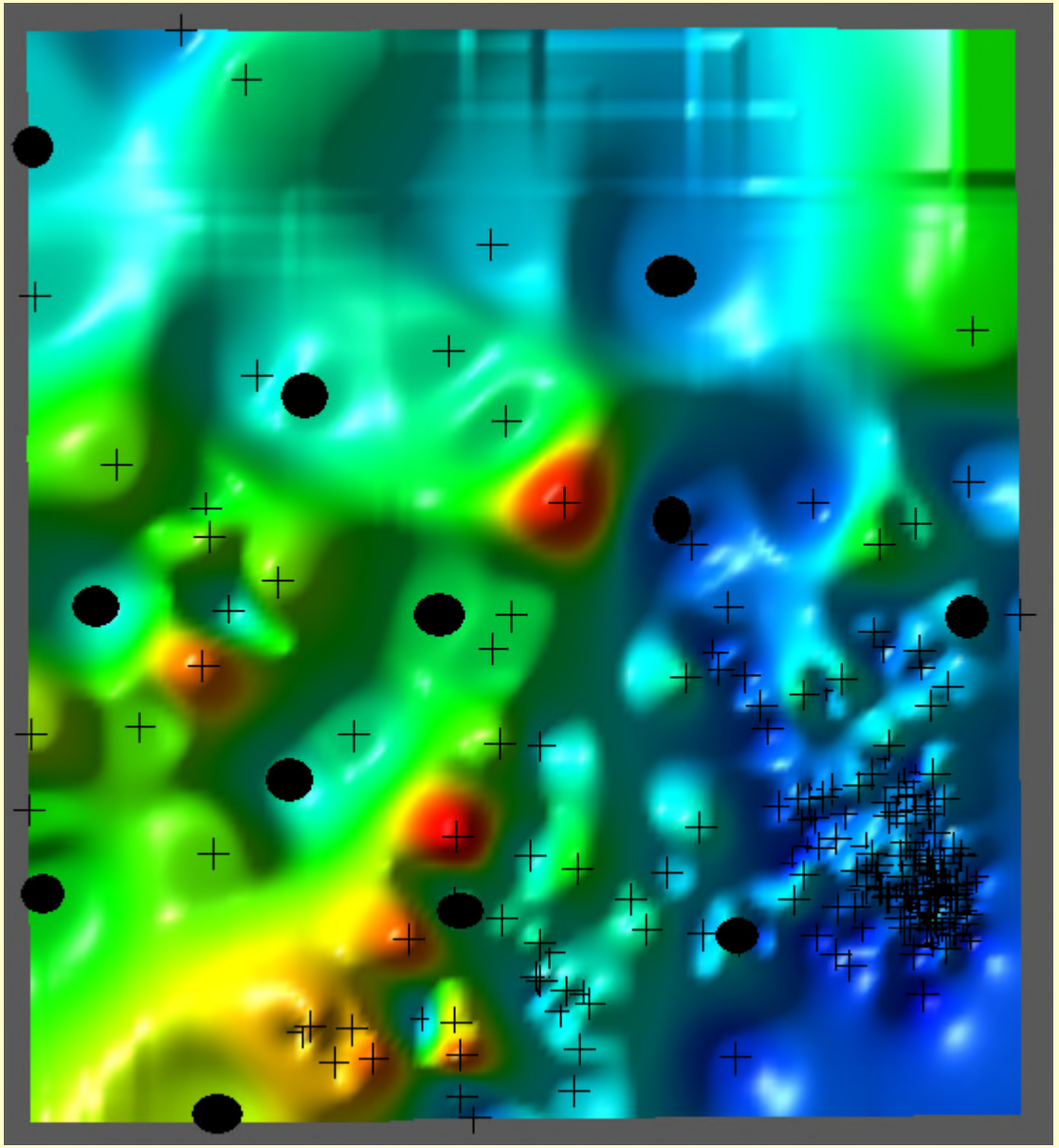
Global optimisation methods:
Kangaroo's climb to Mt. Everest



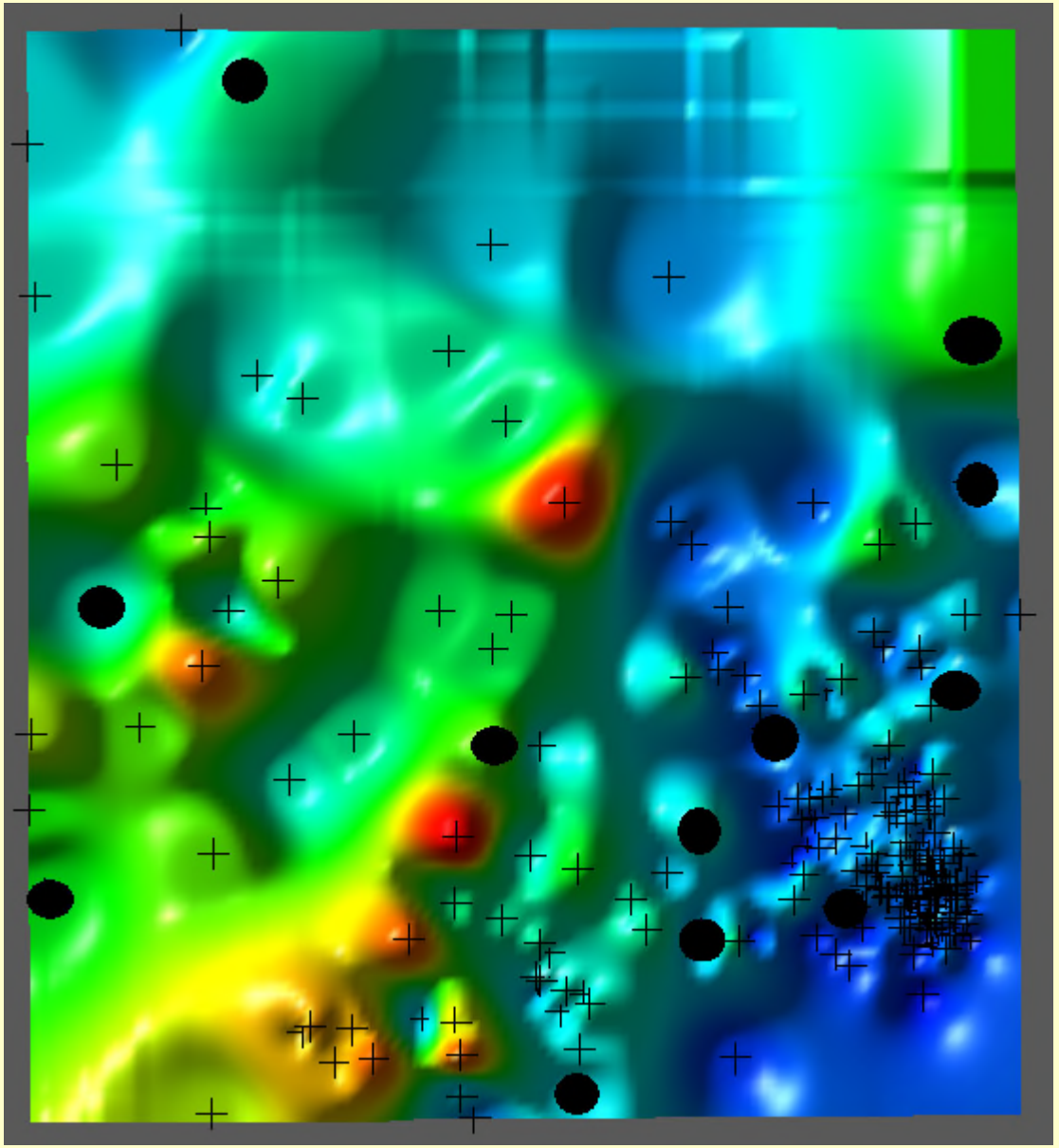


....and regularly shooting the ones at lower altitudes.

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



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



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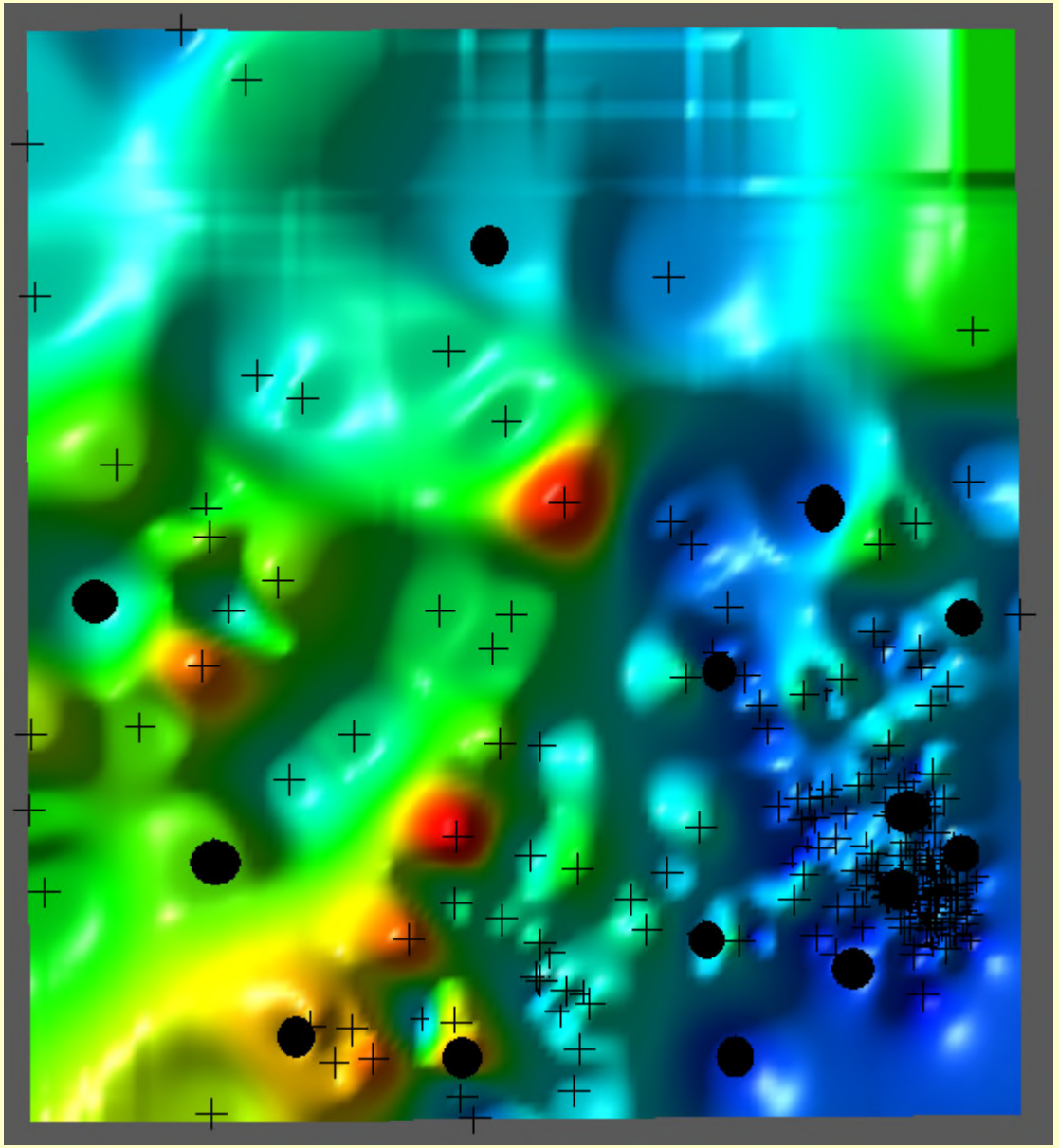
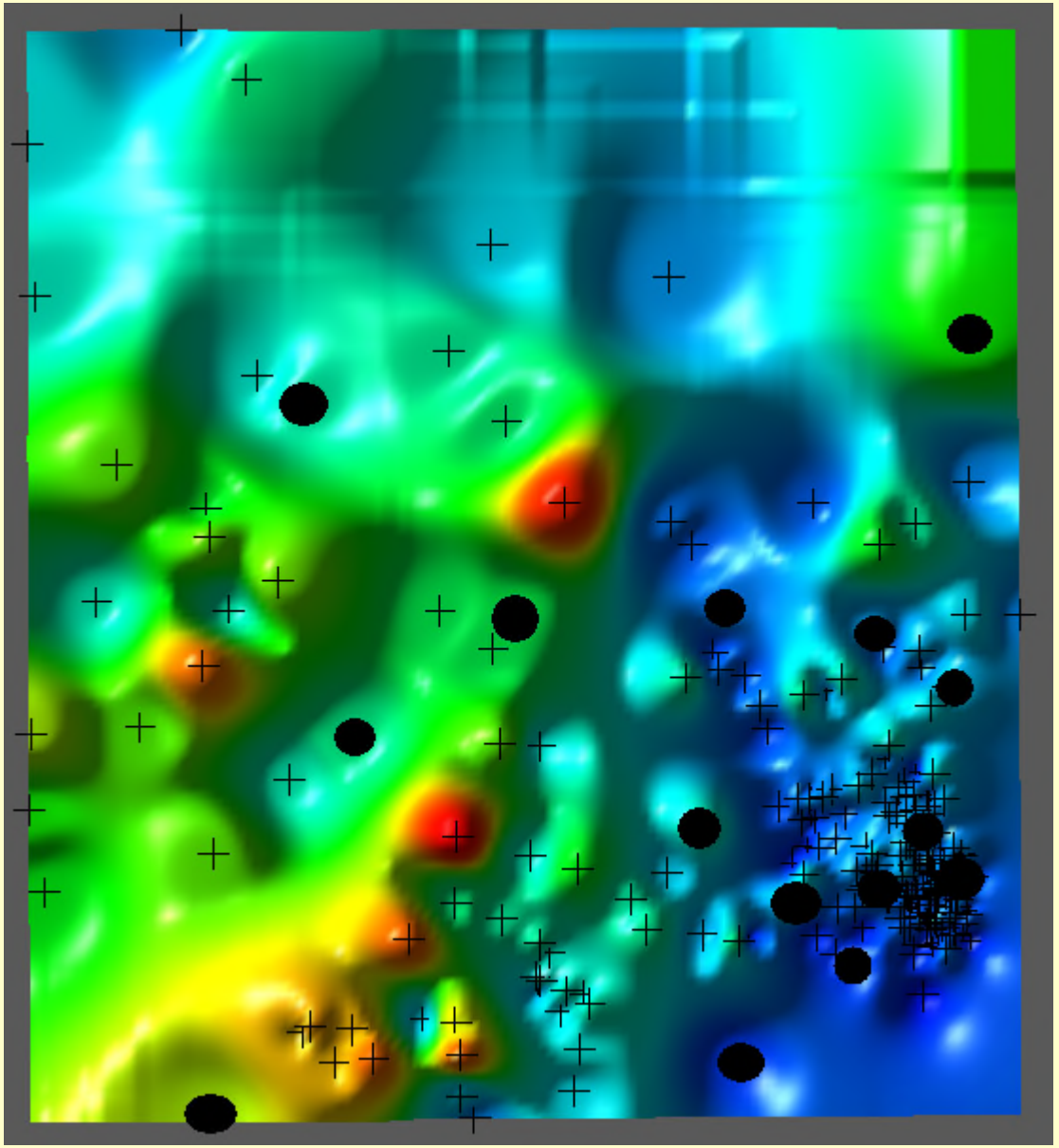
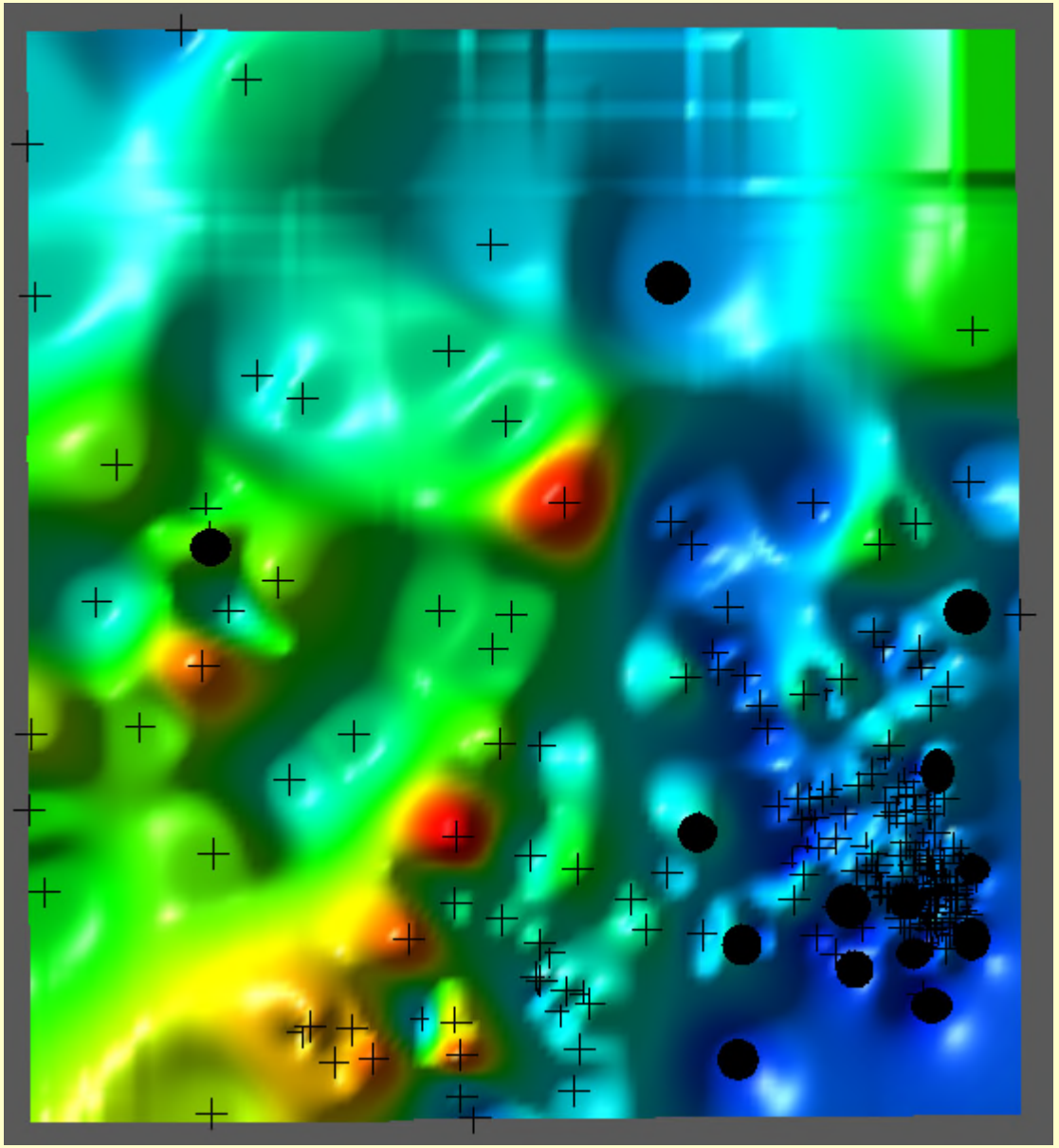


Evolutionary simulations learn & explore the most promising regions of search space

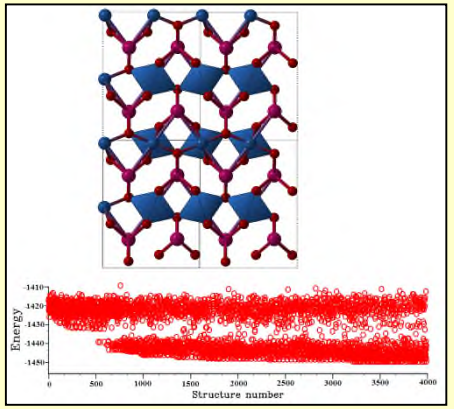


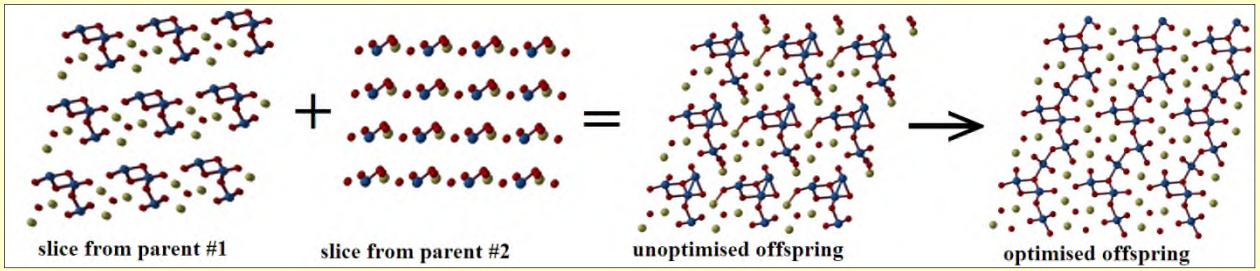
Evolutionary simulations learn & explore the most promising regions of search space



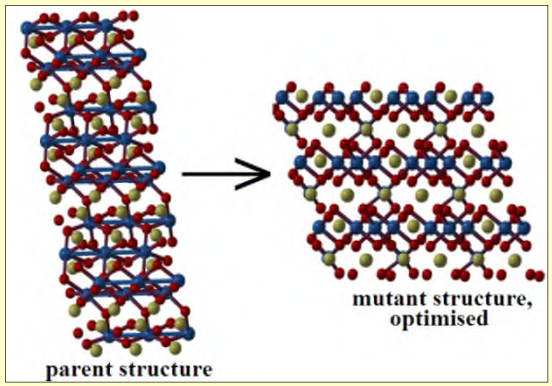
USPEX
(Universal Structure Predictor: Evolutionary Xtallography)

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

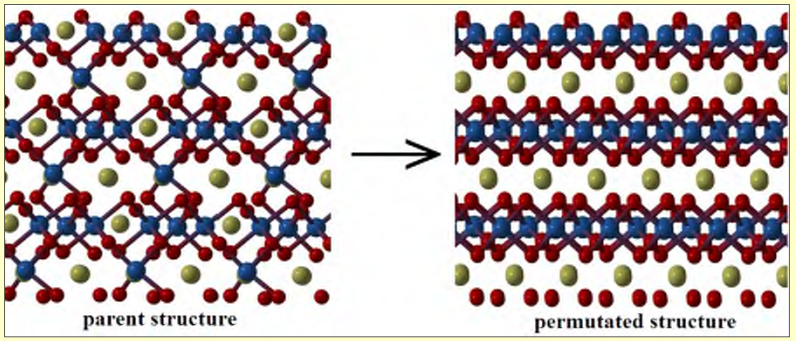




(1) Heredity (crossover)

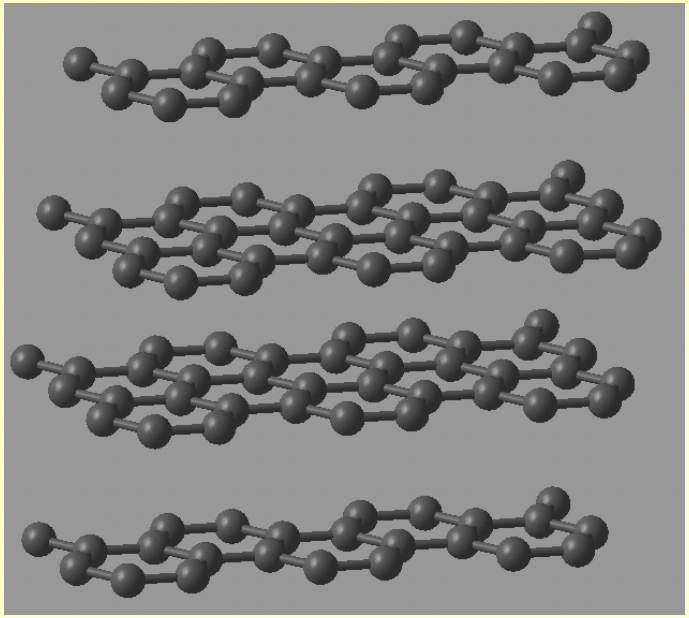


(2) Lattice mutation

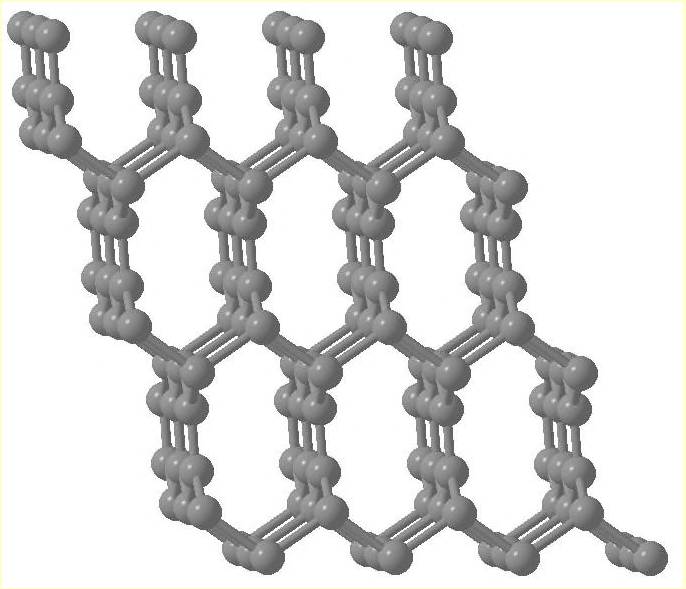


(3) Permutation

Test: „Who would guess that graphite is the stable allotrope of carbon at ordinary pressure?“ (Maddox, 1988)

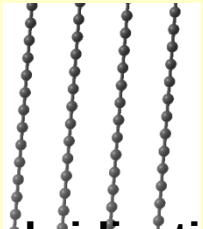


Graphite, correctly predicted to be the stable phase at 1 atm

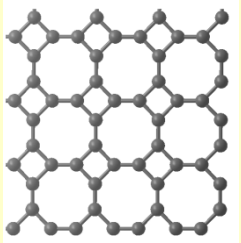


Metastable superhard sp^2-forms with 3D-topology. First proposed by R.Hoffmann (1983)

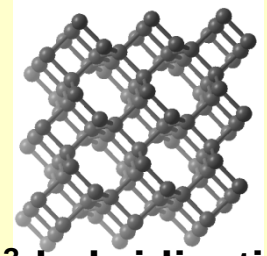
Low-energy structures reveal chemistry



sp-hybridisation (carbyne)



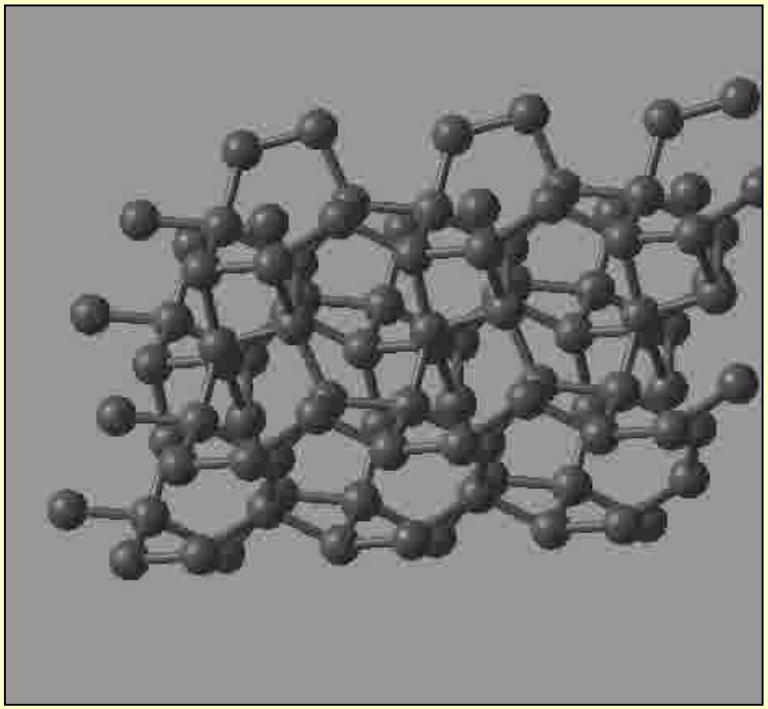
sp^2-hybridisation



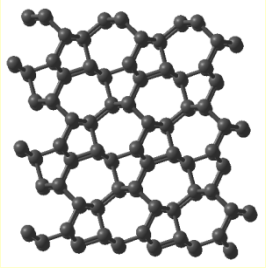
sp^3-hybridisation

[ARO & Glass, J.Chem.Phys. (2006)]

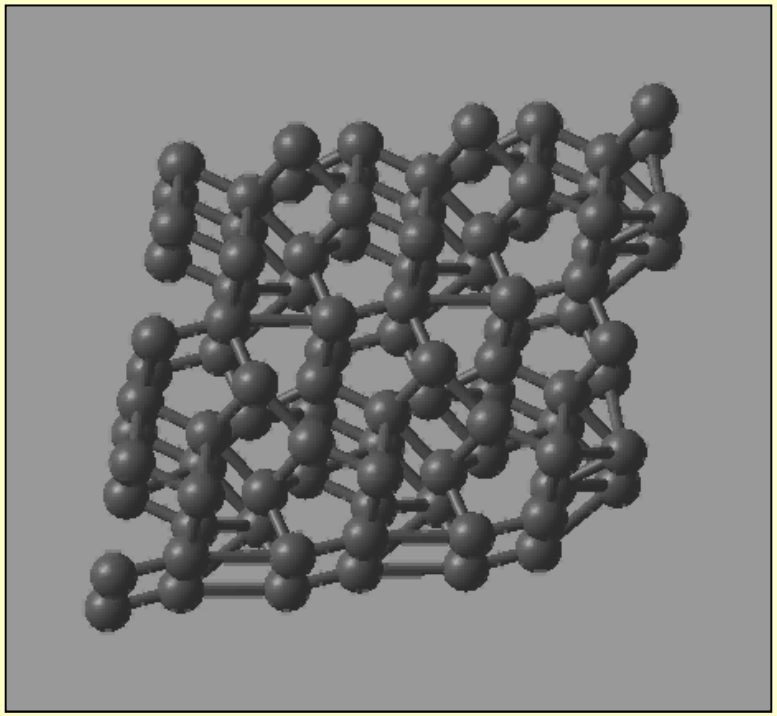
Test: High-pressure phases of carbon are also successfully reproduced



100 GPa: diamond is stable



+found metastable form
that matches
„superhard graphite“ of W.Mao
(Li, ARO, Ma, et al., PRL 2009)



2000 GPa: bc8 phase, potentially important in astrophysics

Metastable bc8 form of Si
Is known (Kasper, 1964)

[ARO & Glass, J.Chem.Phys. (2006)]

Alternative methods:

Random sampling

(Freeman & Catlow, 1993; Schmidt et al., 1996; van Eijck & Kroon, 2000; Pickard & Needs, 2006)

- No „learning“. Works well only for small problems (<30 degrees of freedom – e.g. 10 atoms).

Simulated annealing (Pannetier 1990; Schön & Jansen 1996)

- Random walk. Ever decreasing probability to accept step to worse solution
- Difficult to control parameters.
- No „learning“ - only current position as source of information!

Metadynamics (Martonak, Laio, Parrinello 2003)

- Taboo search with reduced dimensionality.

$$G^t(\mathbf{h}) = G(\mathbf{h}) + \sum_{t'<t} We^{\frac{|h-h^{t'}|^2}{2\delta h^2}}$$

$$\mathbf{h}^{t+1} = \mathbf{h}^t + \delta h \frac{\phi^t}{|\phi^t|}$$

Minima hopping (Gödecker 2004)

- Keep history of visited minima. Escape minima with MD, using feedback to control temperature

Genetic and evolutionary algorithms

- Bush (1995), Woodley (1999) – works only for small systems, inefficient.
- Deaven & Ho (1995) – developed only for clusters. Efficient.
- ARO& Glass (2006), Abraham (2006), Fadda (2010), Wang (2010), Lunie (2011)

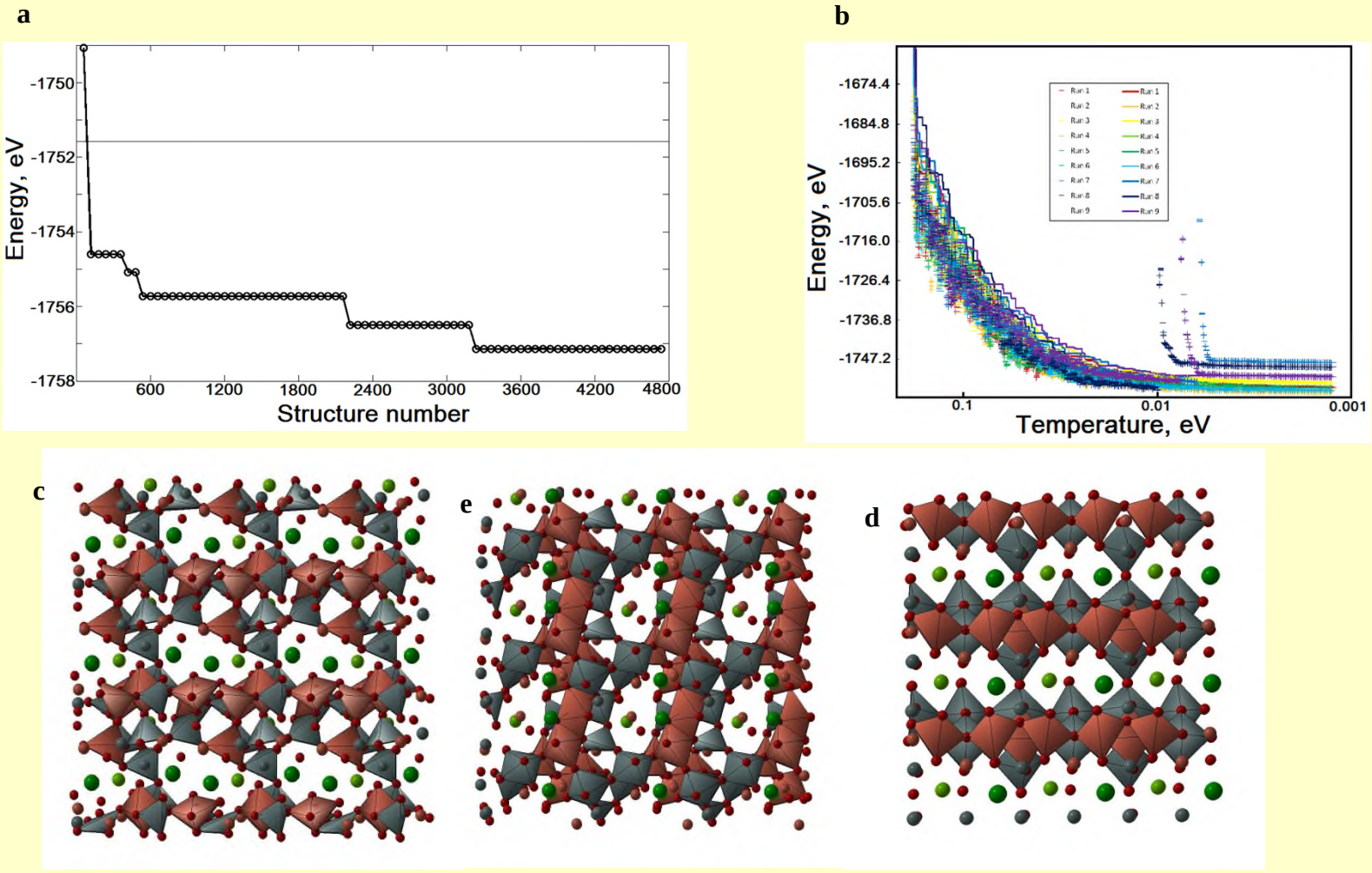
Blind test (2010): USPEX is superior to random sampling and simulated annealing

- **Blind test (ARO, Schon, Hennig, 2010) – on extremely difficult cases:**

	Random sampling	Sim. annealing	USPEX
Test #1, $BaMgAl_4Si_4O_{16}$ with fixed cubic cell (with forcefields)			
Number of runs (runs producing lowest E)	1 (1)	10 (1)	2 (2)
Minimum energy, eV	-876.94	**-877.99**	-877.71
# of structure relaxations before ground state	14794	7330	1465
Test #2, $Ba_2Mg_2Al_8Si_8O_{32}$ with fixed cubic cell (with forcefields)			
Number of runs (runs producing lowest E)	1 (1)	9 (1)	2 (1)
Minimum energy, eV	-1751.57	-1756.03	**-1757.14**
# of structure relaxations before ground state	14102	2435	3210
Test #3, $Mg_{10}Al_4Ge_2Si_8O_{36}$ with variable cell (with forcefields)			
Number of runs (runs producing lowest E)	1 (1)	9 (1)	1 (1)
Minimum energy, eV	-1943.46	-1949.10	**-1950.53**
# of structure relaxations before ground state	13029	685	4610
Test #4, $Mg_{13}Al_8P_3$ with variable cell (*ab initio*)			
Number of runs (runs producing lowest E)	1 (1)	-	1 (1)
Minimum energy, eV	-68.82	-	**-70.37**
# of structure relaxations before ground state	978	-	4071

Random sampling failed to give lowest-enthalpy structures for 2 phases (out of 3 predicted) of SiH_4 (Pickard, PRL 2006), 1 for Nitrogen (Pickard PRL 2009), 1 for SnH_4 (Pickard, 2010)

Benchmarking the power of the method



Test #2 (Ba2Mg2Al8Si8O32, with fixed cell): (a) Variation of the lowest energy during the evolutionary USPEX run, (b) Summary of simulated annealing runs, (c-e) Lowest-energy structures obtained by random sampling, simulated annealing and USPEX, respectively. Thin horizontal line in (a) shows the lowest energy found in 14102 random sampling attempts.

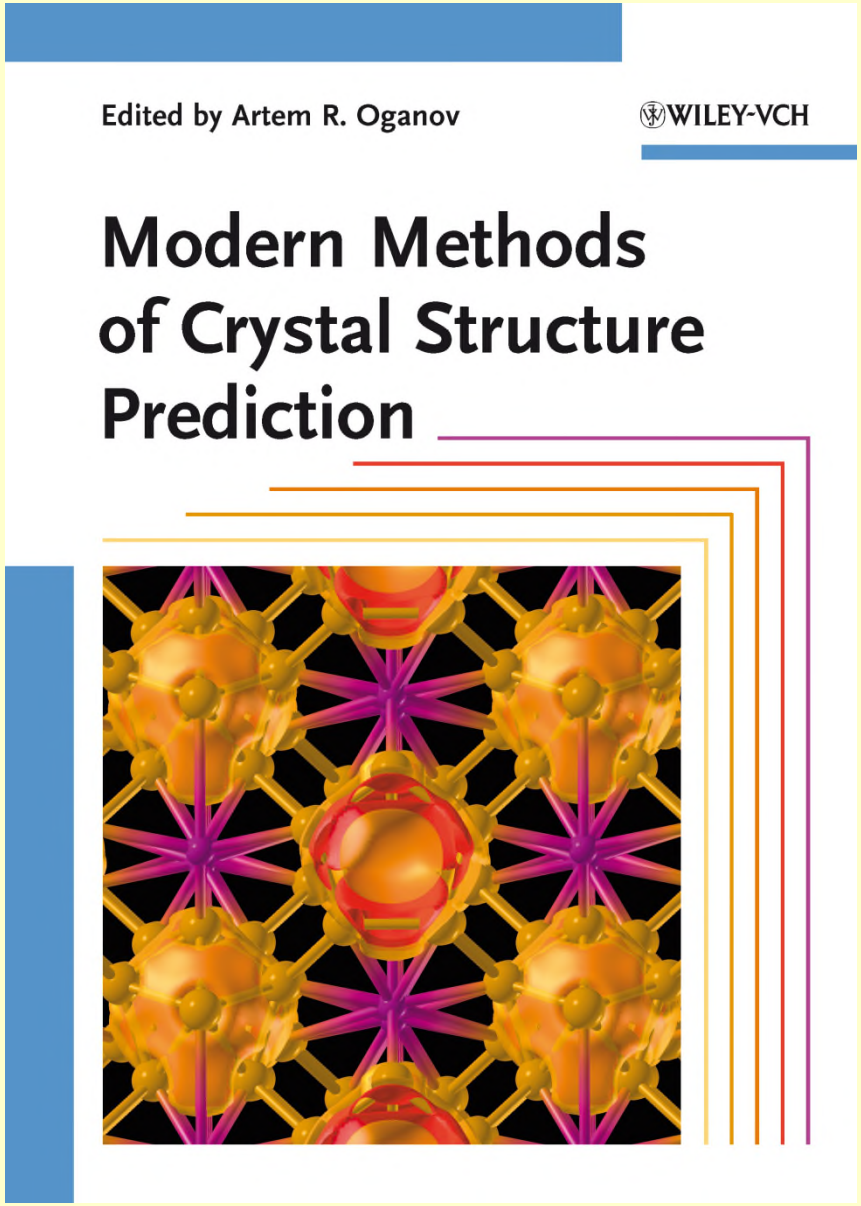
Crystal structure prediction methods

1. Random sampling (Freeman & Catlow, 1992)
2. Simulated annealing (Pannetier, 1990)
3. Molecular dynamics and metadynamics (Martonak, 2003)
4. Data mining (Curtarolo, 2003)
5. Minima hopping (Goedecker, 2004)
6. Evolutionary algorithms / PSO

Test on TiO_2: USPEX *vs* PSO
(data from Wang et al., 2012; Lyakhov et al., 2013)

Method	Success rate	<#relaxations>
USPEX, cell splitting	100%	41
USPEX, no symmetry	100%	80
USPEX, with symmetry	100%	77
CALYPSO with symmetry	100%	168 - 400
CALYPSO no symmetry	90%	508

For more information…



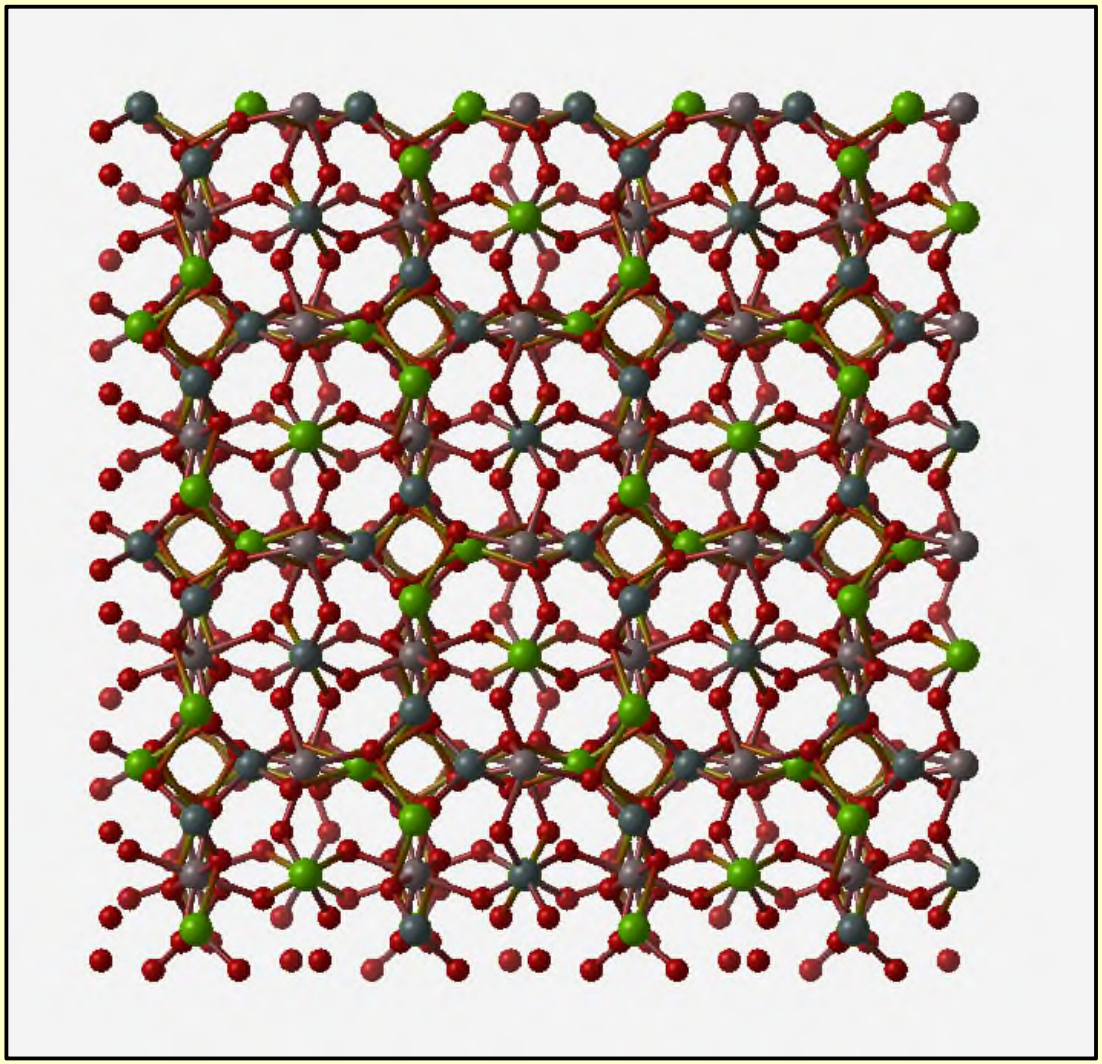
USPEX

New developments:

• improved efficiency

- **nanoparticles**
- **surfaces and interfaces**
- **properties optimization**
- **molecular crystals**
- **variable composition**
- **TPS and vcNEB modules**
- **evolutionary metadynamics**

Power of the new method



Garnet, 160 atoms/cell, $Mg_{24}Al_{16}Si_{24}O_{96}$:

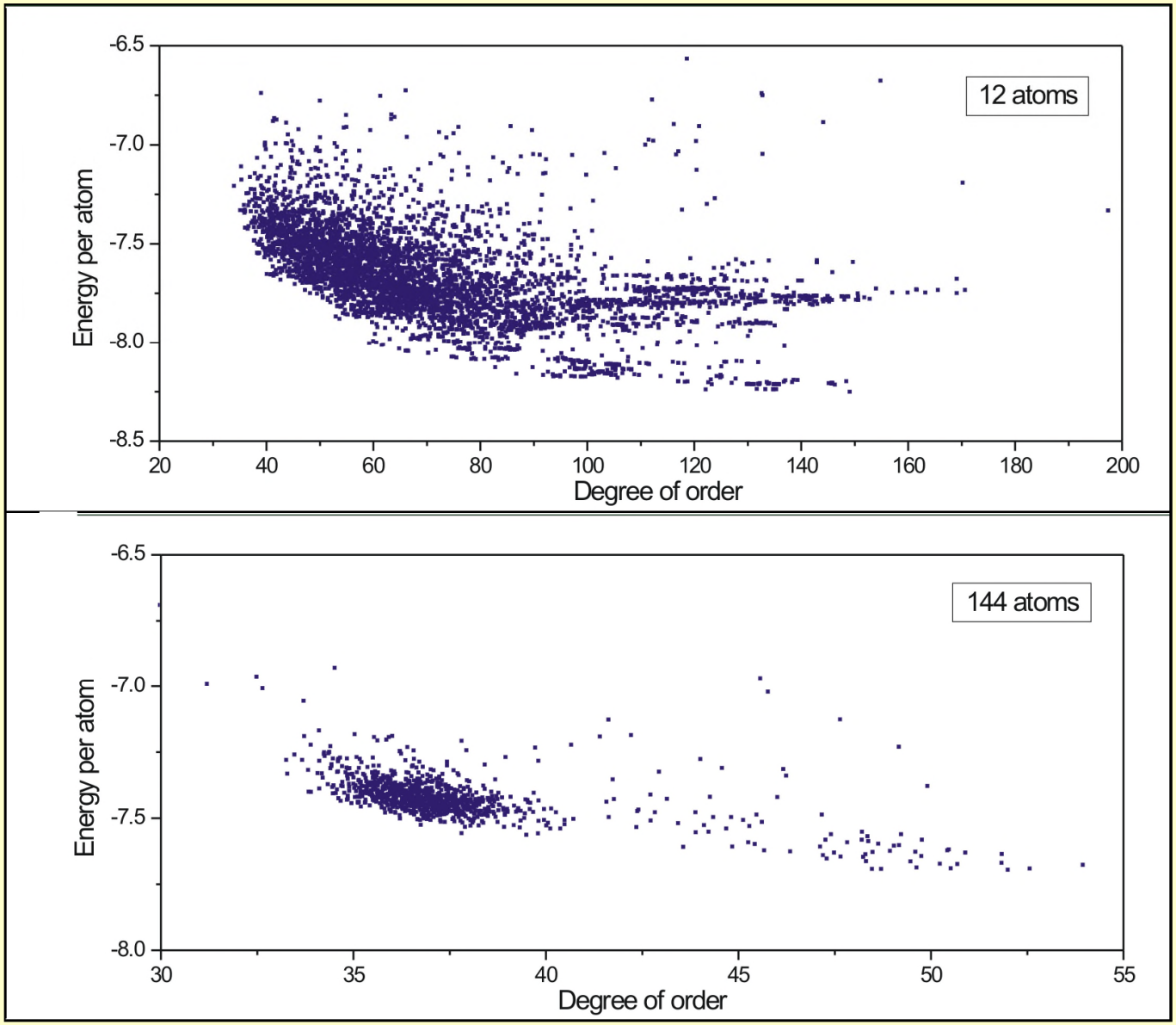
100% success rate; <N> = 294; 35 calculations so far

Key improvements

- **Symmetrical initialization**
- **Aging technique**
- **Smart mutation**

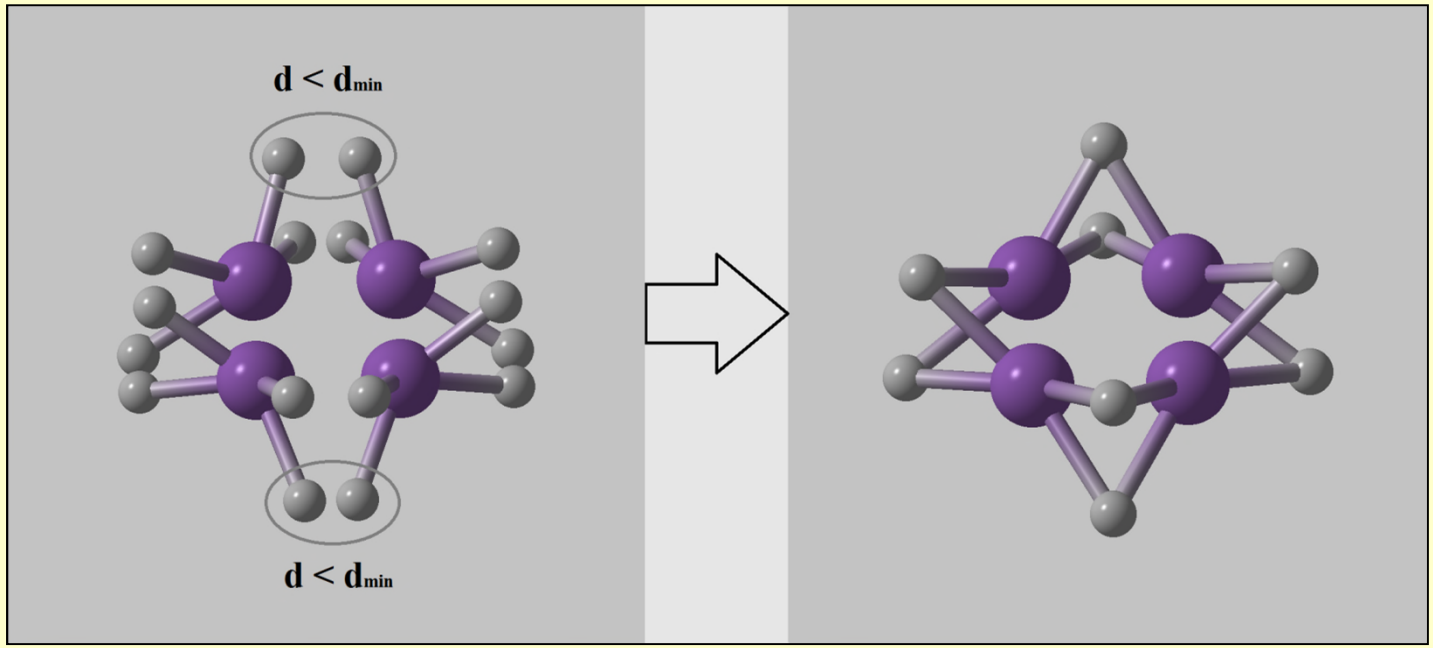
(plus plethora of methodological developments published in 2010-2011)

Symmetrical initialization



Symmetrical initialization

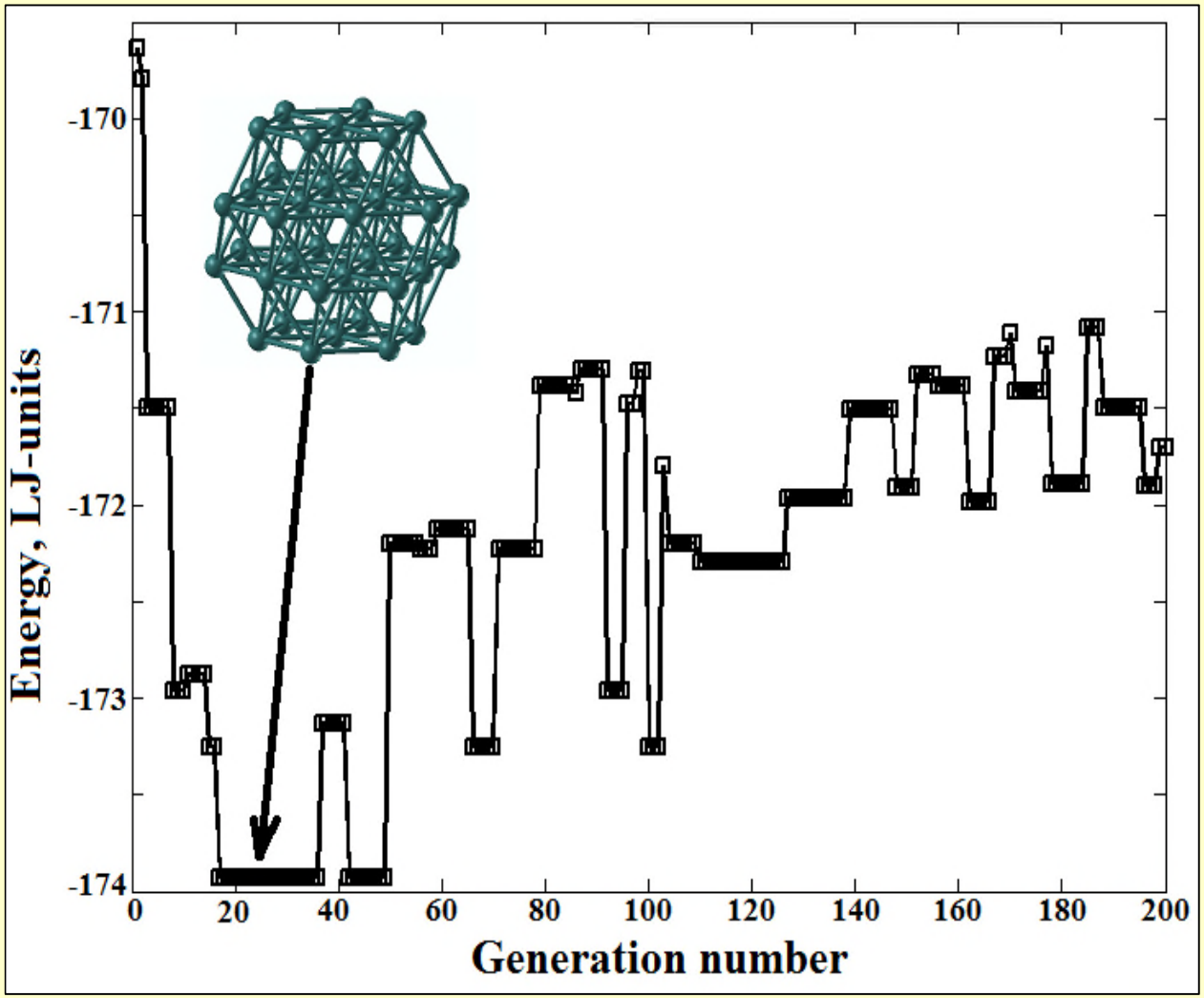
Crystals: 230 space groups
Nanoparticles: point groups



Enables moderately efficient random sampling as one of possible USPEX regimes

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

‘Aging’ technique (antiseeds)

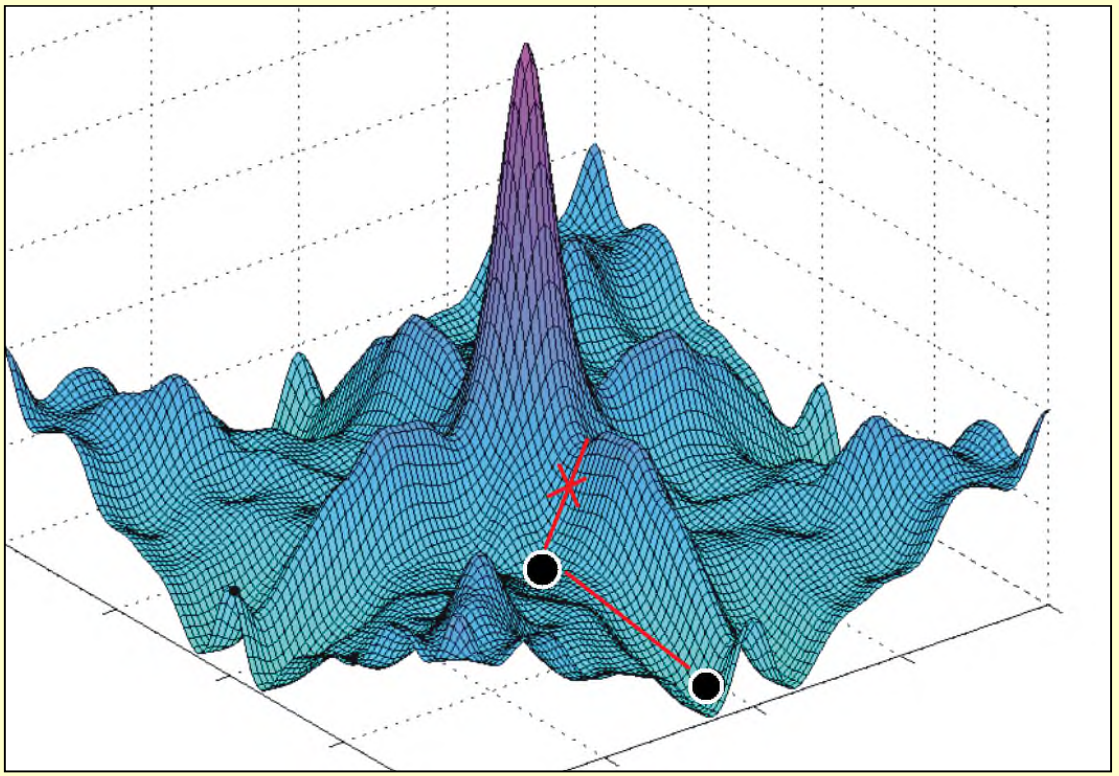


The metastable state is found first and the ground state is found shortly after

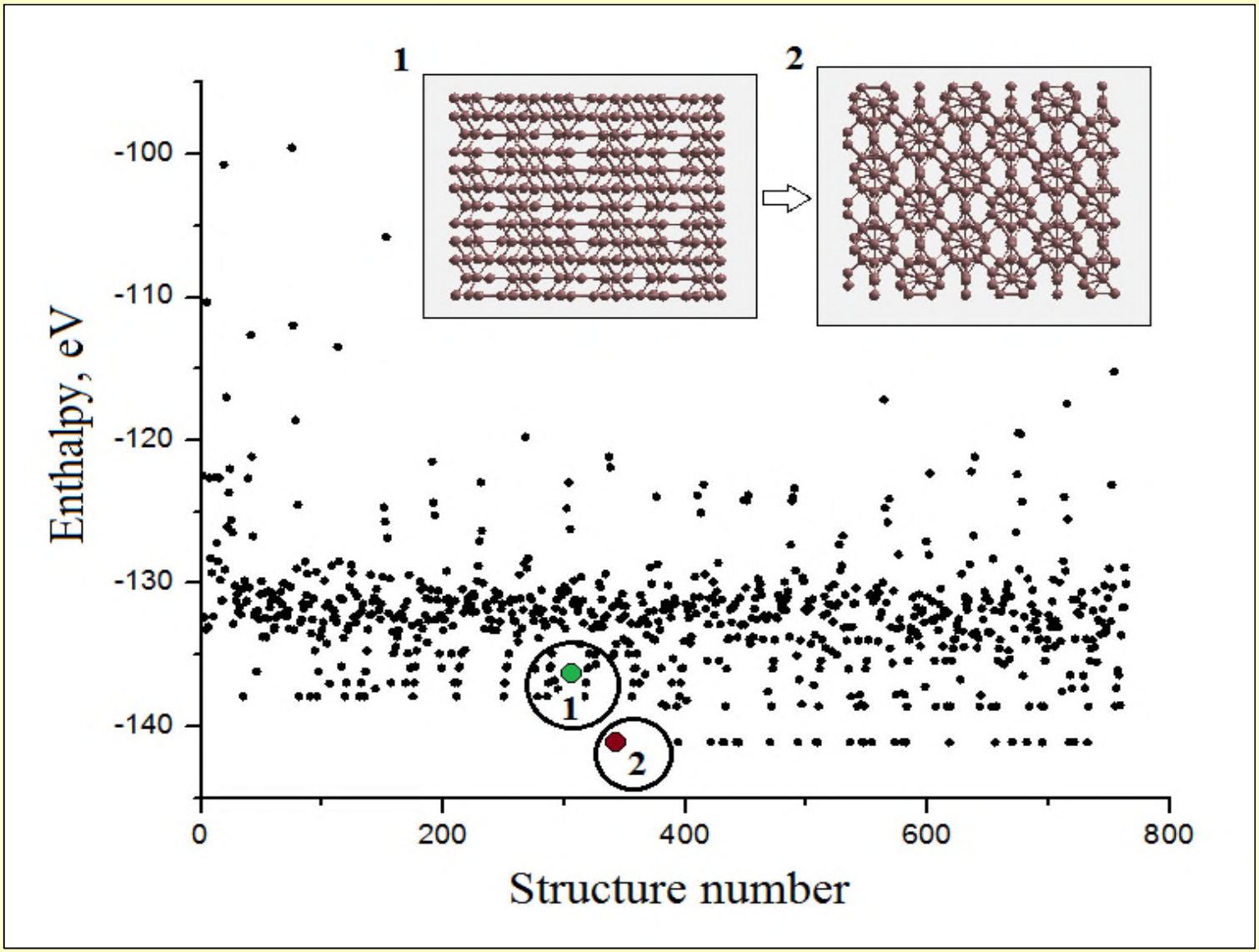
Soft-mode mutation

Atoms are moved along the eigenvector of the softest mode (both positive and negative directions need to be tried)

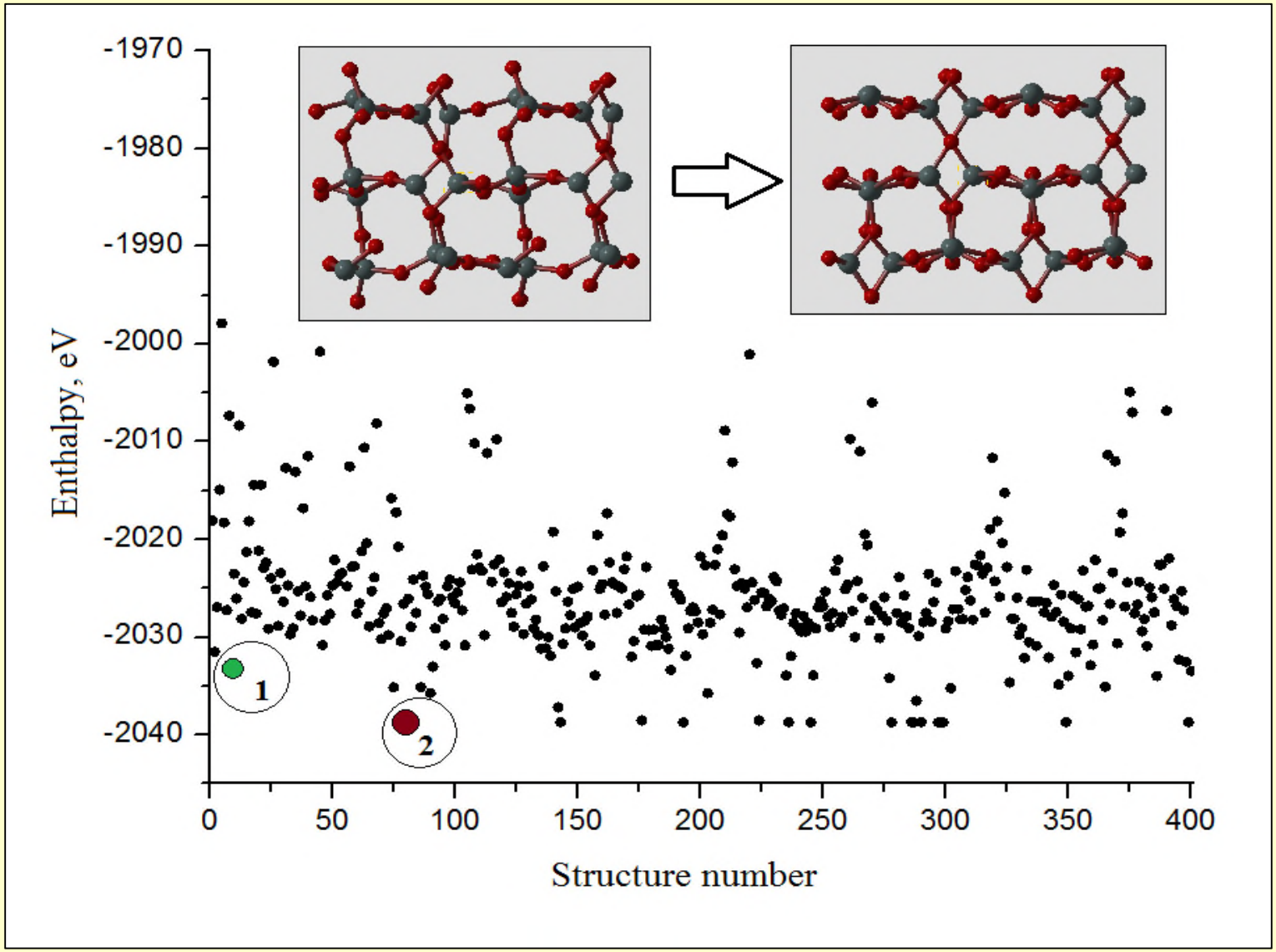
Requires the calculation of the dynamical matrix



Soft-mode mutation (γ-B_{28})



Soft-mode mutation (SiO_2-coesite)

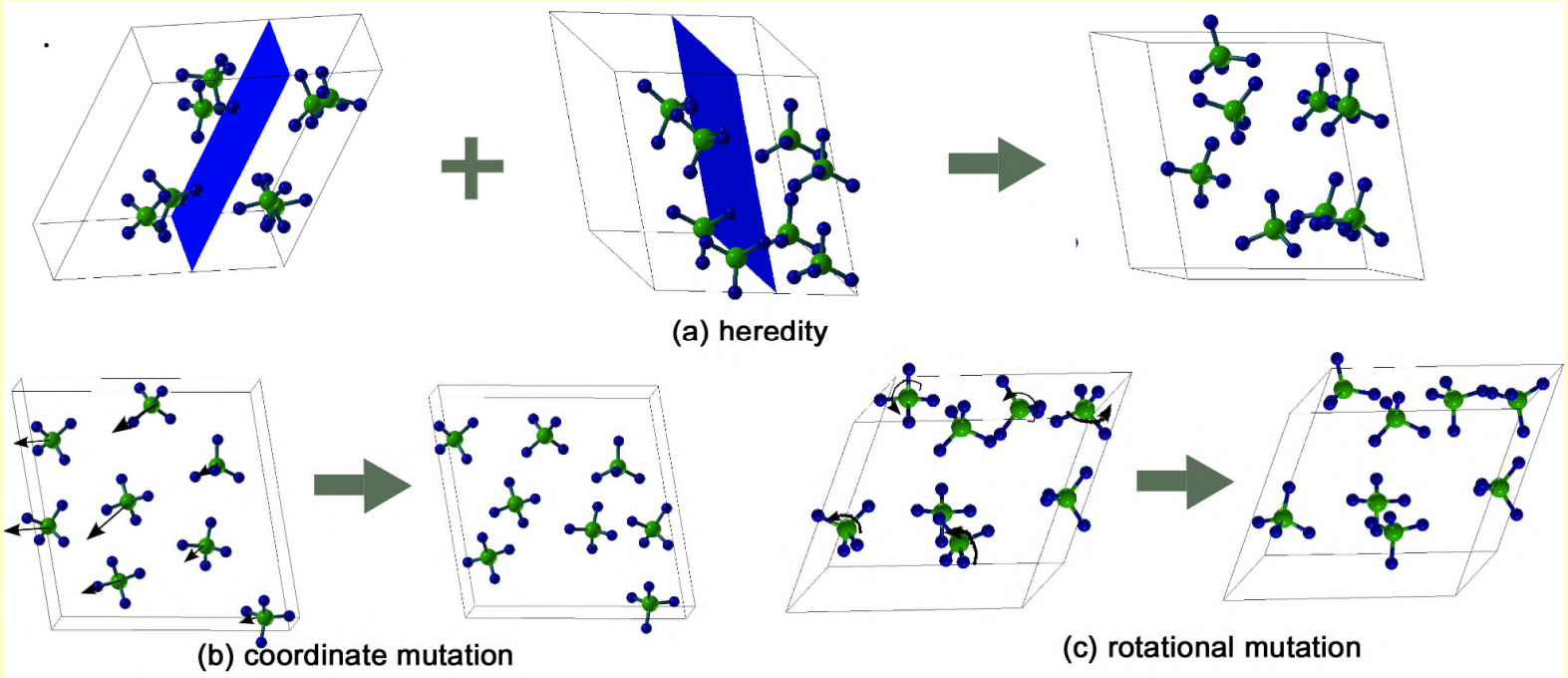


New modules

- **Optimization of properties**
- **Molecular crystals, nanoparticles**
- **Variable composition**
- **TPS, vcNEB**

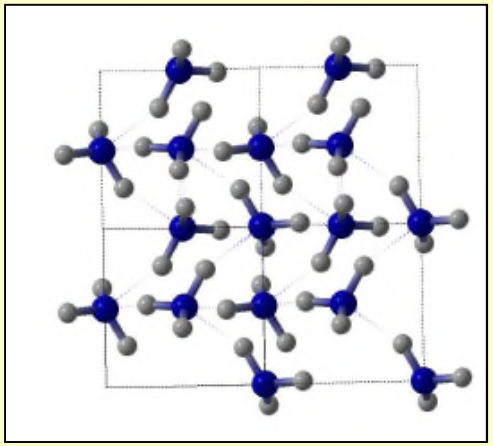
USPEX for molecular crystals (Zhu & ARO, 2012)

- Apply operators to positions and orientations of the molecules
- Take into account the size and shape of molecules
- Introduce rotational mutation
- Introduce conformational mutation
- Project softmutation into rotational and translational components

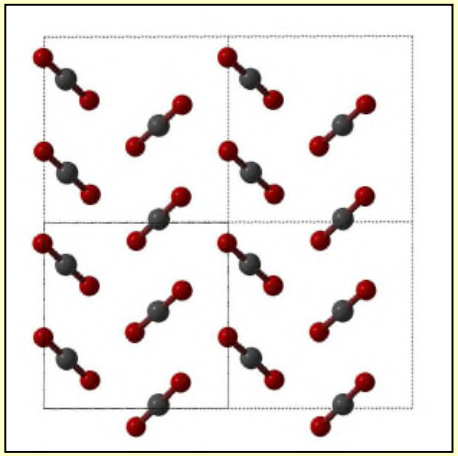


Molecular crystals

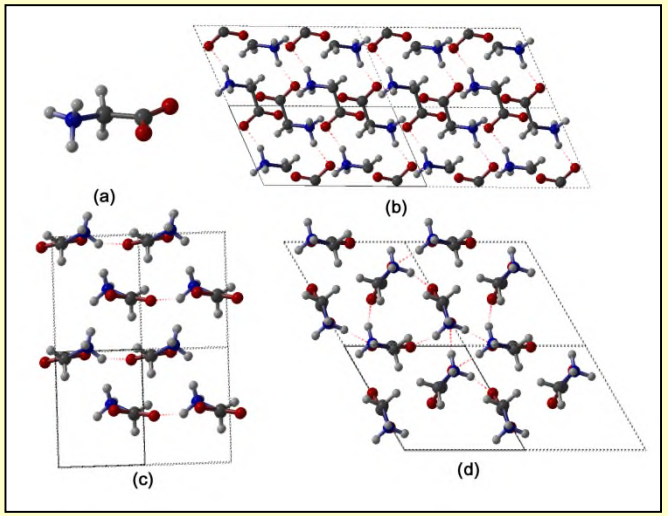
NH_3



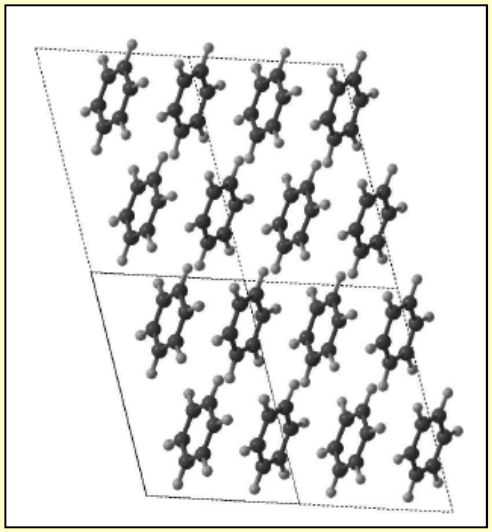
CO_2



Pharmaceuthical: Glycine



Benzene



$Mg(BH_4)_2$

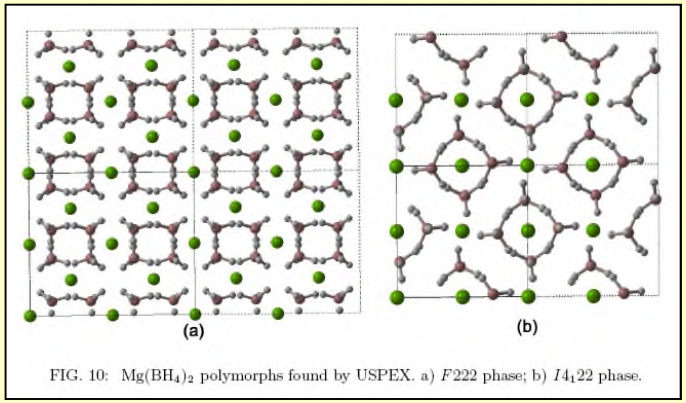
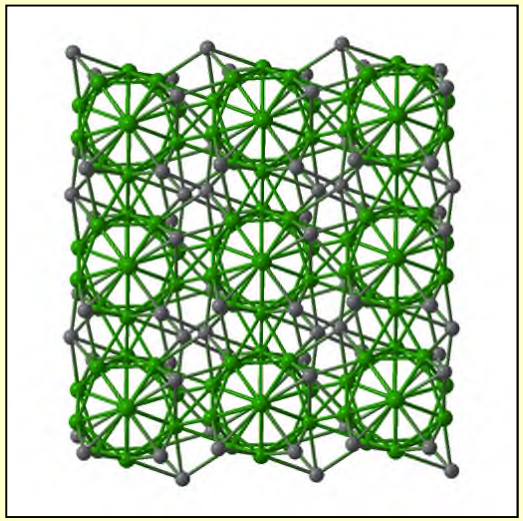


FIG. 10: $Mg(BH_4)_2$ polymorphs found by USPEX. a) $F222$ phase; b) $I4_122$ phase.

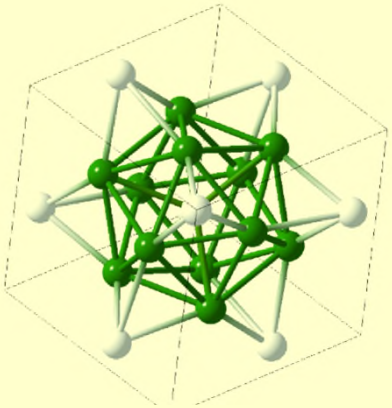
Q. Zhu et al, 2012

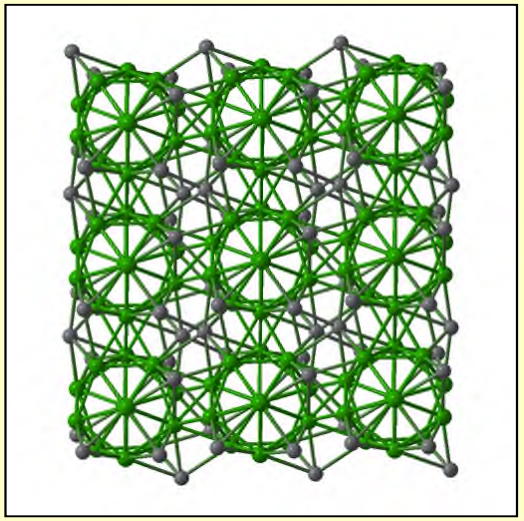
Methane



Molecular crystals: Methane at 10 GPa

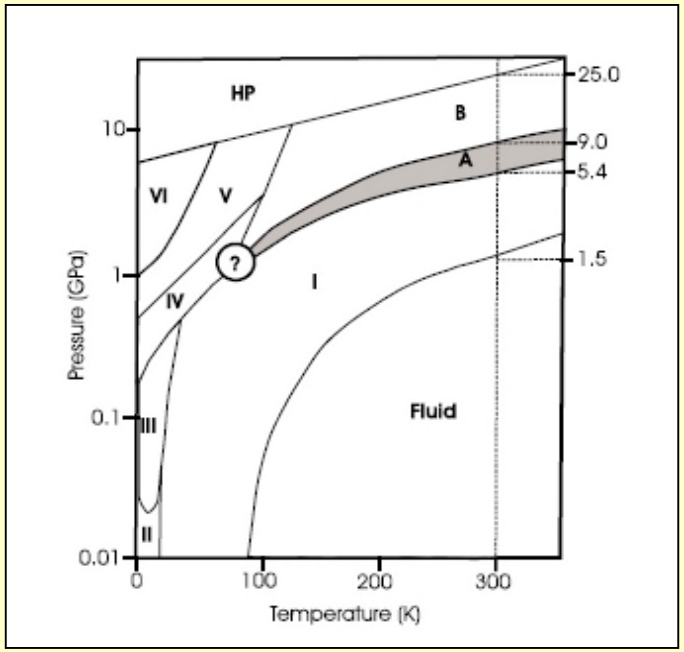
1 day, 8 cores, 105 atoms, first principles

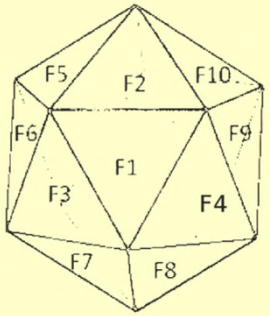




(111) view

21 molecules/cell
Nakahata, CPL, 1999
Refined by Sun et al., 2009





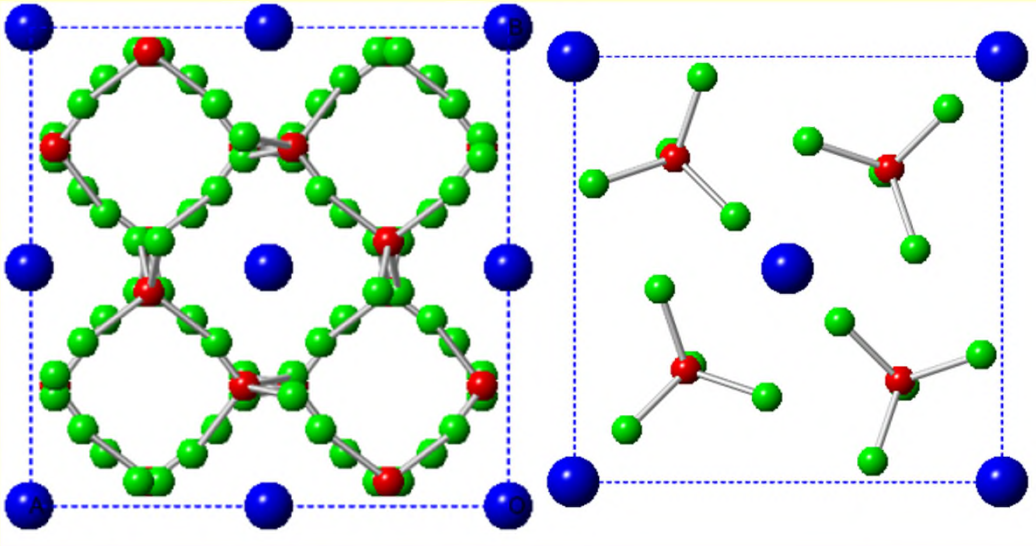
21 = 12 + 1 + 8

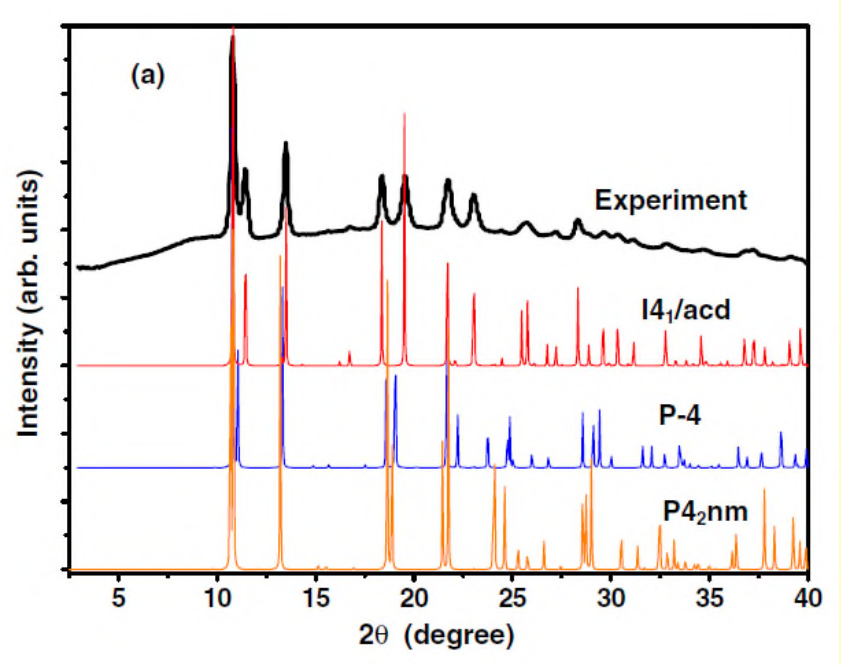
12: icosahedron site
1 : icosahedron center
8 : outside icosahedron

Zhu & ARO, 2012

Solved by: Maynard-Casely et al., 2010

δ-$Mg(BH_4)_2$: example of how theory corrects experimental structure determination





a **b** **c**

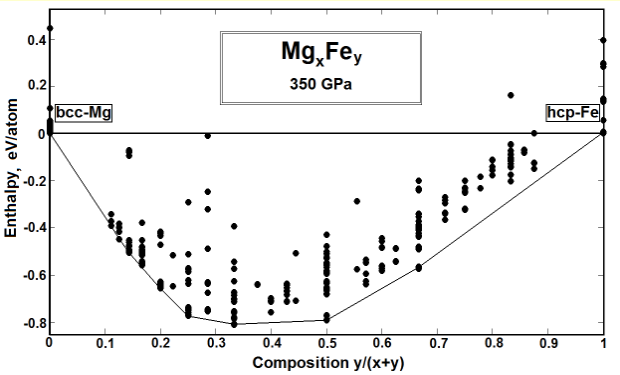
Theoretical $I4_1/acd$ (a) and "experimental" $P4_2nm$ (b) structures are very different, but have nearly identical powder XRD patterns (c).
The "experimental" structure is massively energetically unstable and is ruled out!

"Experimental" structure – [Filinchuk et al., *Angew. Chem.* (2011)]

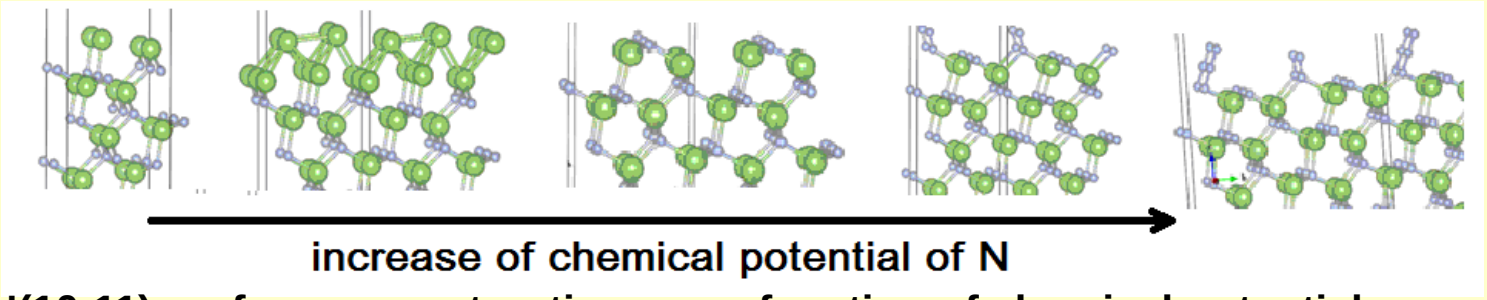
[Zhou, ARO, et al., *Phys. Rev. Lett.* (2012)]

Variable-composition searches: crucial for discovering new compounds and for surface phenomena

In general, need to include chemical composition as a variable!



Non-trivial ground states of Fe-Mg system at 350 GPa (Lyakhov, ARO et al., 2010)



GaN(10-11) surface reconstructions as a function of chemical potential (Zhu, ARO, et al., PRB 2013)

New developments of USPEX

A. Improved efficiency

B. Molecular crystals

C. Variable composition

D. Low-dimensional systems

-0D (nanoparticles)

-1D (polymers)

-2D (surfaces and 2D-crystals)

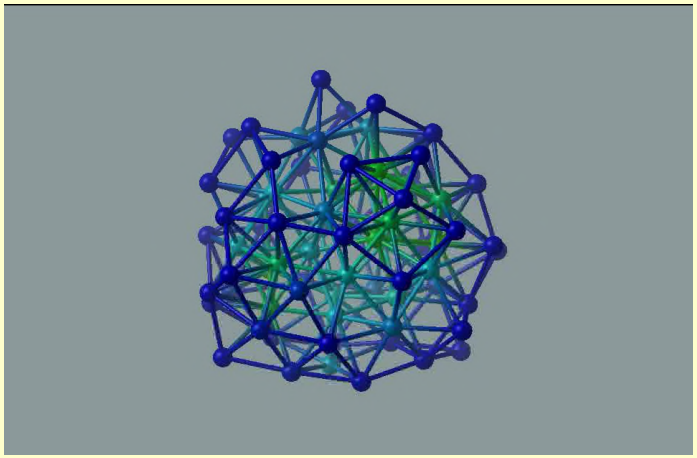
E. Evolutionary metadynamics

F. vc-NEB for transition pathways

G. Transition path sampling

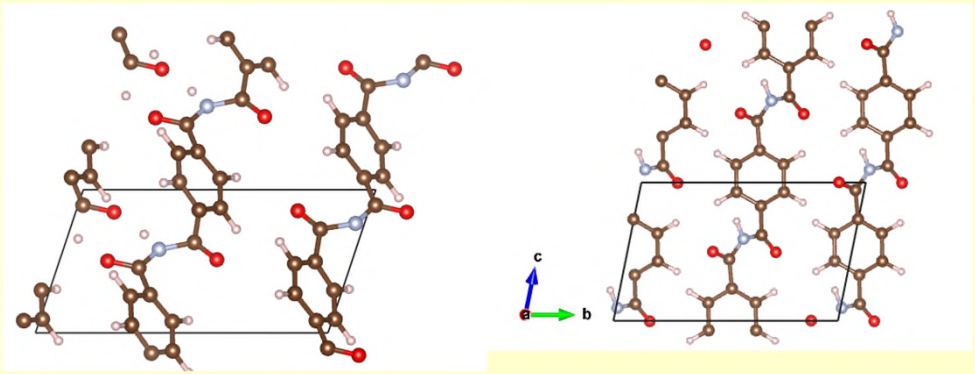
1D and 2D: Nanoparticles and polymers

Famous tough case: Lennard-Jones nanoparticle with 75 atoms



USPEX predicts ground state 3-130 times faster than best available methods (Lyakhov, ARO et al., 2012)

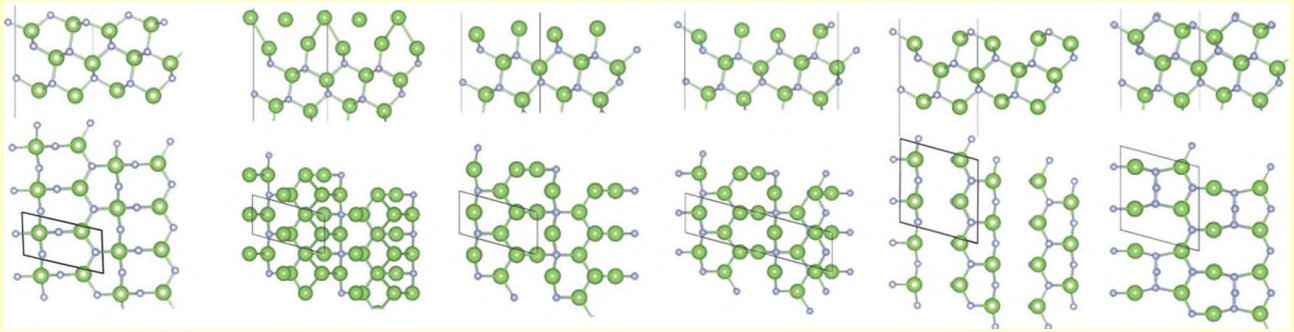
0-D systems



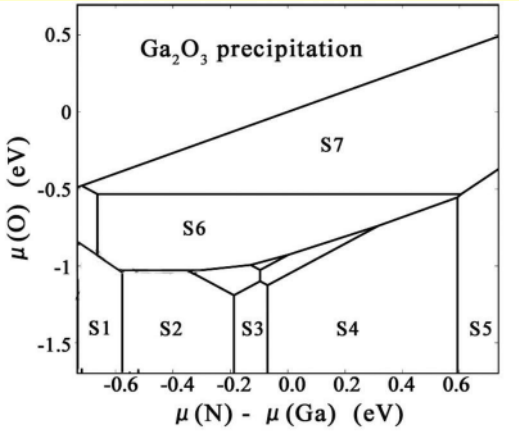
Predicted high-k dielectric polymers -NH-CO-C6H4-CO-

1-D systems

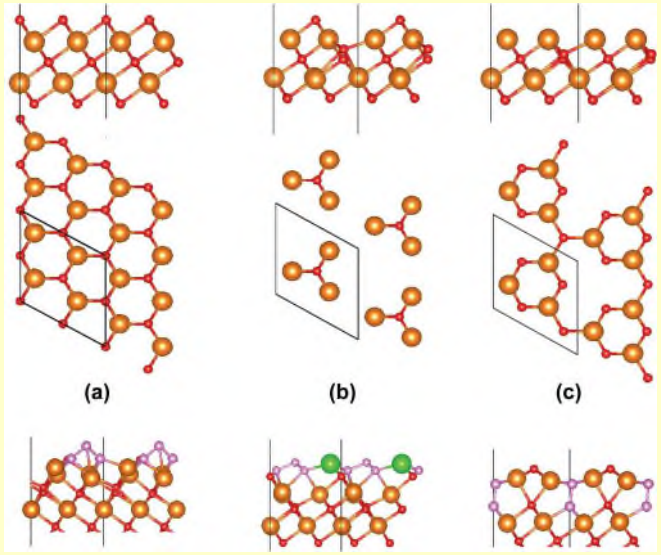
2D: Surfaces of crystals, new physics and chemistry… and medicine?



Structure and composition of surface phases of GaN (10-11)

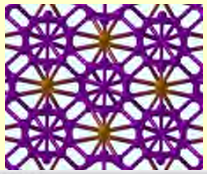


Phase diagram in presence of oxygen



Structure of (111) surface of MgO.

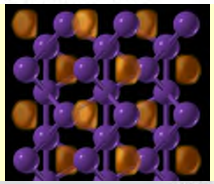
Applications of this method proved its great utlilty:



Vol 457|12 February 2009|doi:10.1038/nature07736 nature

Ionic high-pressure form of elemental boron

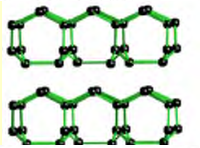
Artem R. Oganov[1,2]†, Jiuhua Chen[3,4], Carlo Gatti[5], Yanzhang Ma[6], Yanming Ma[2,7], Colin W. Glass[1], Zhenxian Liu[6], Tony Yu[3], Oleksandr O. Kurakevych[3] & Vladimir L. Solozhenko[3]



nature Vol 458|12 March 2009|doi:10.1038/nature07786

Transparent dense sodium

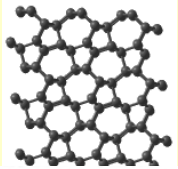
Yanming Ma[1,2], Mikhail Eremets[3], Artem R. Oganov[2,4]†, Yu Xie[2], Ivan Trojan[3], Sergey Medvedev[3], Andriy O. Lyakhov[2]†, Mario Valle[5] & Vitali Prakapenka[6]



PRL 102, 065501 (2009) PHYSICAL REVIEW LETTERS week ending 13 FEBRUARY 2009

Novel High Pressure Structures of Polymeric Nitrogen

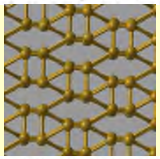
Yanming Ma,[1,2,*] Artem R. Oganov,[2,3] Zhenwei Li,[1] Yu Xie,[1] and Jani Kotakoski[4]



PRL 102, 175506 (2009) PHYSICAL REVIEW LETTERS week ending 1 MAY 2009

Superhard Monoclinic Polymorph of Carbon

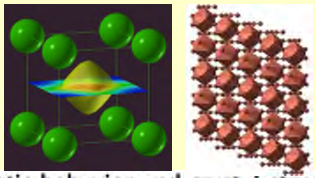
Quan Li,[1] Yanming Ma,[1,*] Artem R. Oganov,[2,3,†] Hongbo Wang,[1] Hui Wang,[1] Ying Xu,[1] Tian Cui,[1] Ho-Kwang Mao,[4,†] and Guangtian Zou[1]



PHYSICAL REVIEW B 76, 064101 (2007)

Structure of the metallic ζ-phase of oxygen and isosymmetric nature of the ε-ζ phase transition: *Ab initio* simulations

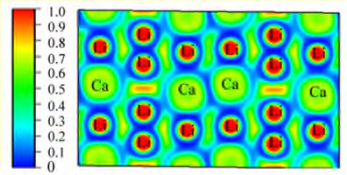
Yanming Ma,[1,2] Artem R. Oganov,[1,3,*] and Colin W. Glass[1]



PNAS

Exotic behavior and crystal structures of calcium under pressure

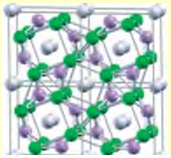
Artem R. Oganov[a,b,1], Yanming Ma[c], Ying Xu[c], Ivo Errea[d,e], Aitor Bergara[d,f,1], and Andriy O. Lyakhov[a]



PRL 104, 177005 (2010) PHYSICAL REVIEW LETTERS week ending 30 APRIL 2010

Novel High Pressure Structures and Superconductivity of $CaLi_2$

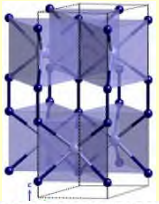
Yu Xie,[1,2] Artem R. Oganov,[2,3] and Yanming Ma[1,*]



PNAS

A little bit of lithium does a lot for hydrogen

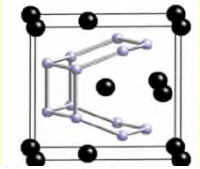
Eva Zurek[a,1], Roald Hoffmann[a,2], N. W. Ashcroft[b], Artem R. Oganov[c,d], and Andriy O. Lyakhov[c]



PHYSICAL REVIEW B 79, 132109 (2009)

Ultra-incompressible phases of tungsten dinitride predicted from first principles

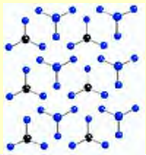
Hui Wang,[1] Quan Li,[1] Yinwei Li,[1] Ying Xu,[1] Tian Cui,[1] Artem R. Oganov,[2,3] and Yanming Ma[1,*]



PHYSICAL REVIEW B 79, 054101 (2009)

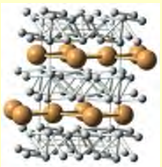
Absence of superconductivity in the high-pressure polymorph of MgB_2

Yanming Ma,[1,2,*] Yanchao Wang,[1] and Artem R. Oganov[2,3]



Dissociation of methane under high pressure

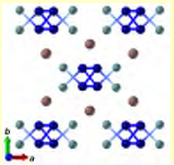
Guoying Gao,[1] Artem R. Oganov,[2,3,+] Yanming Ma,[1,*] Hui Wang,[1] Peifang Li,[1] Tian Cui,[1] Guangtian Zou[1]



PRL 102, 087005 (2009) PHYSICAL REVIEW LETTERS week ending 27 FEBRUARY 2009

Novel Structures and Superconductivity of Silane under Pressure

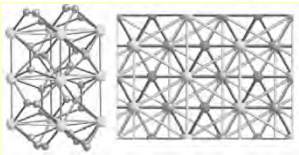
Miguel Martinez-Canales,[1,2] Artem R. Oganov,[3,4] Yanming Ma,[5] Yan Yan,[5] Andriy O. Lyakhov,[3] and Aitor Bergara[1,2,6]



PRL 101, 107002 (2008) PHYSICAL REVIEW LETTERS week ending 5 SEPTEMBER 2008

Superconducting High Pressure Phase of Germane

Guoying Gao,[1] Artem R. Oganov,[2,3] Aitor Bergara,[4,5] Miguel Martinez-Canales,[4,5] Tian Cui,[1] Toshiaki Iitaka,[6] Yanming Ma,[1,2,*] and Guangtian Zou[1]



PNAS

High-pressure crystal structures and superconductivity of Stannane (SnH_4)

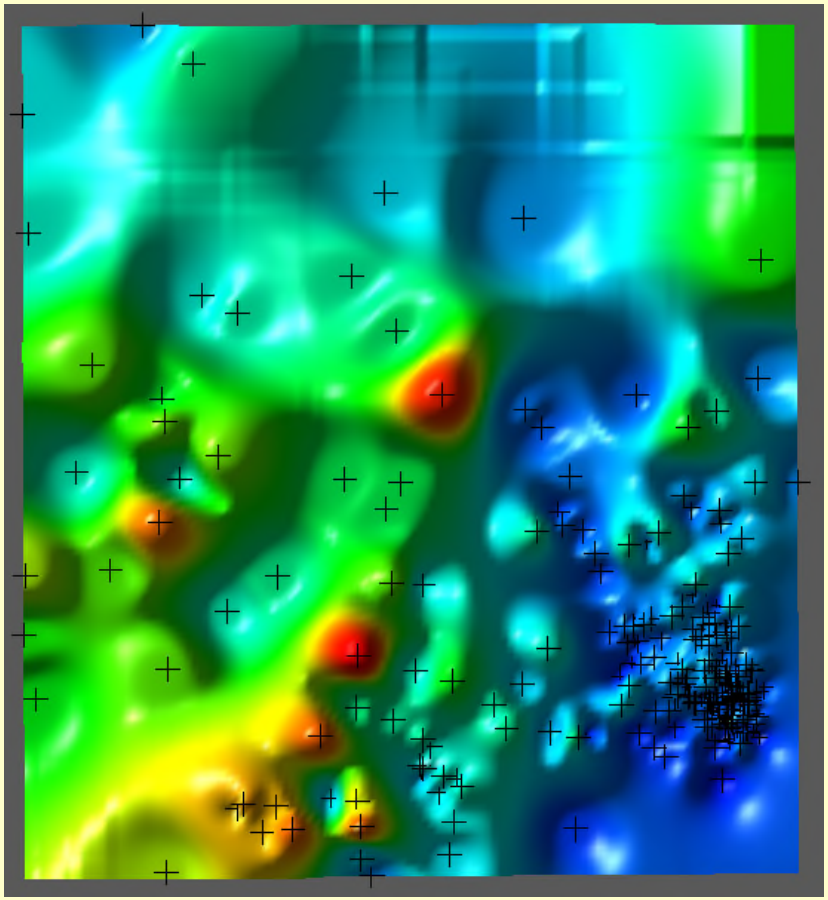
Guoying Gao[a], Artem R. Oganov[a,b], Peifang Li[a], Zhenwei Li[a], Hui Wang[a], Tian Cui[a], Yanming Ma[a,1], Aitor Bergara[c,d,1], Andriy O. Lyakhov[b], Toshiaki Iitaka[e], and Guangtian Zou[a]

Earth and Planetary Science Letters 261 (2007) 391–399

High-pressure phases of $CaCO_3$: Crystal structure prediction and experiment

Artem R. Oganov[a,*], Colin W. Glass[a], Shigeaki Ono[b]

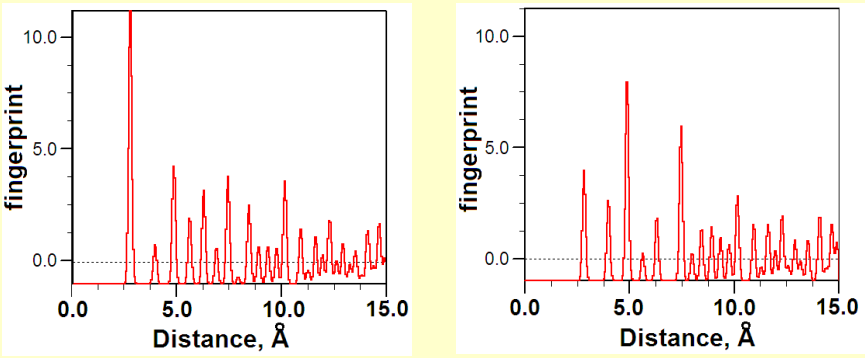
2. Why does it work?



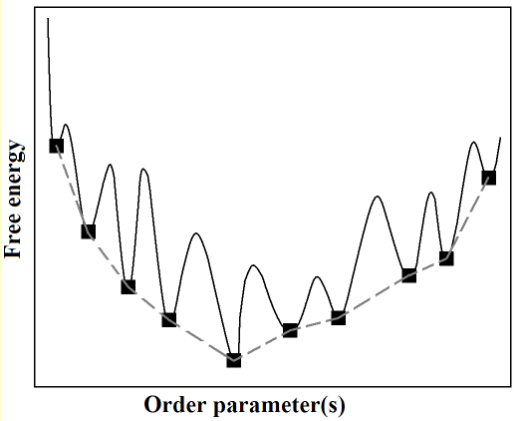
ARO & Valle, J.Chem.Phys. 130, 104504 (2009)

Fingerprint theory is the basis of our analysis

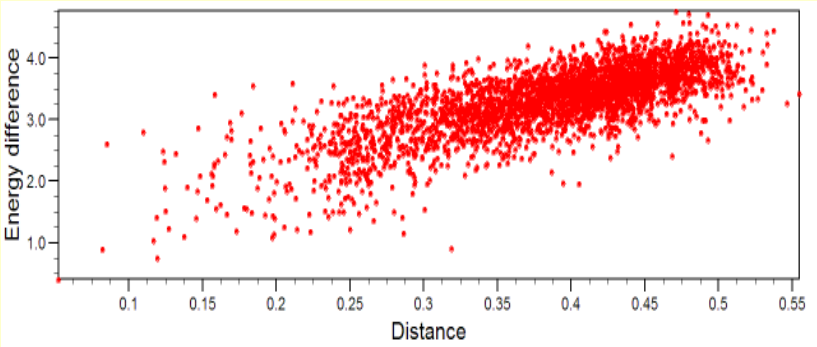
Fingerprint function is a 1D-descriptor of the structure: diffraction spectrum, PCF, ...



Difference between 2 structures is given by „distance“, e.g.: $$dist(i,j) = \left(\sum_k |fp_{i_k} - fp_{j_k}|^p \right)^{\frac{1}{p}}$$



Pedagogical cartoon

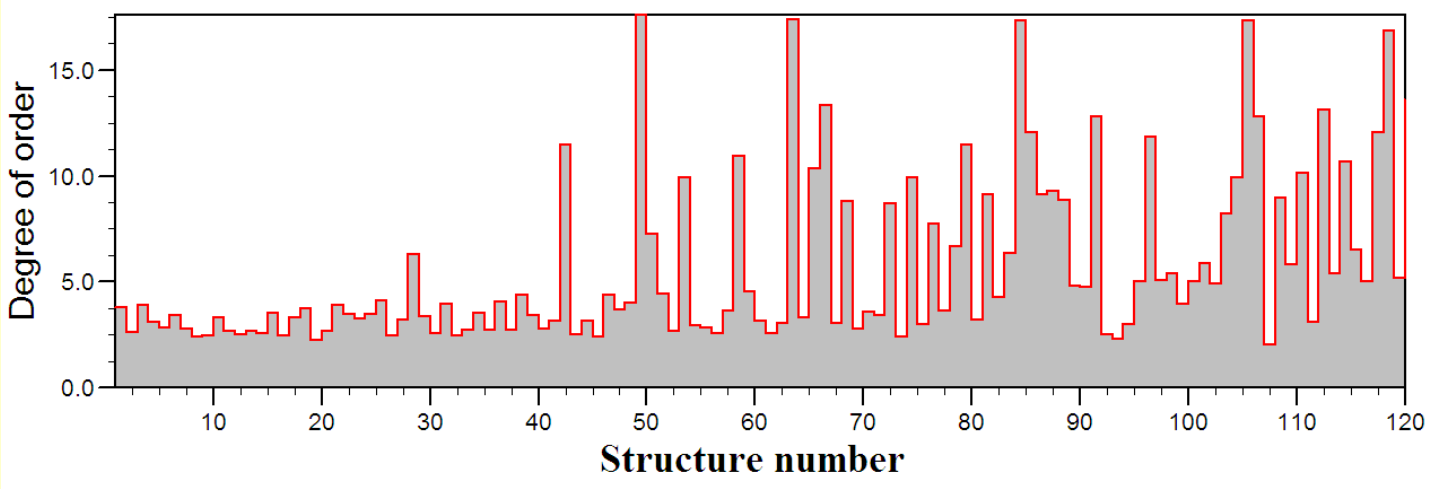


Real system (GaAs): correlation of energy and the distance from the ground-state structure

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

Feature of evolution: emergence of order from chaos

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

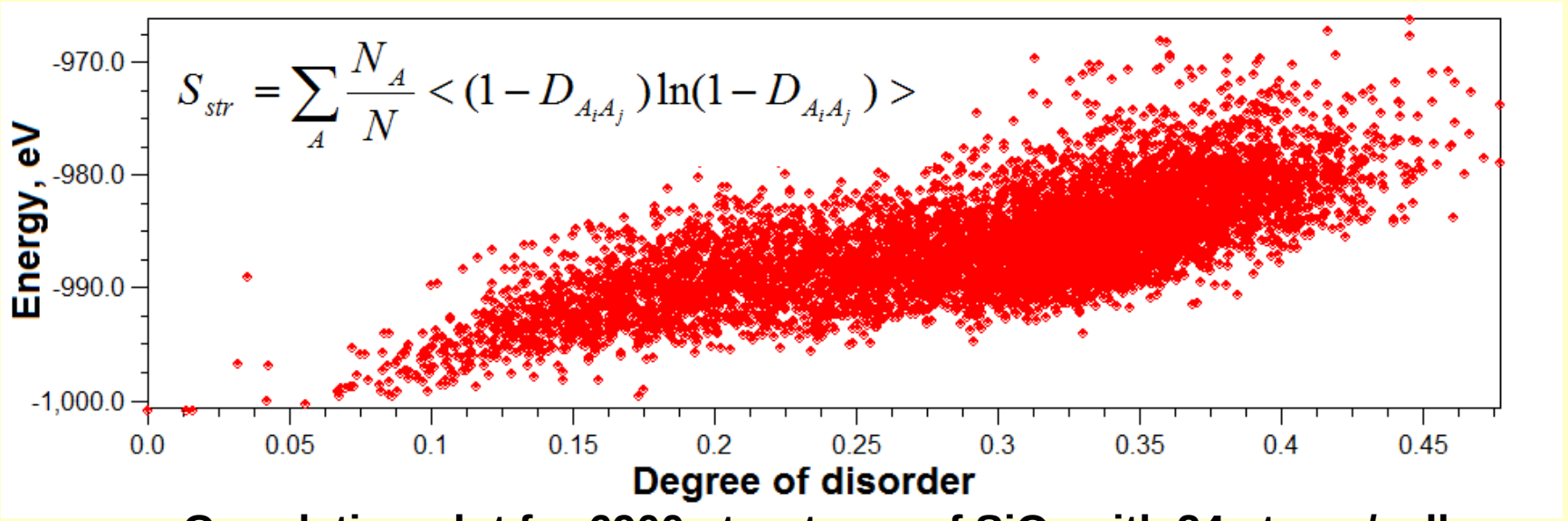


Increase of order during evolutionary simulation of GaAs

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

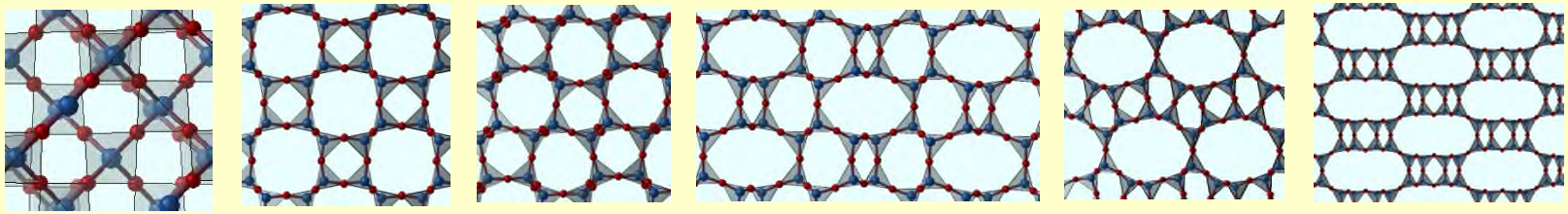
Statistical confirmation of Pauling‘s 5th rule:

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



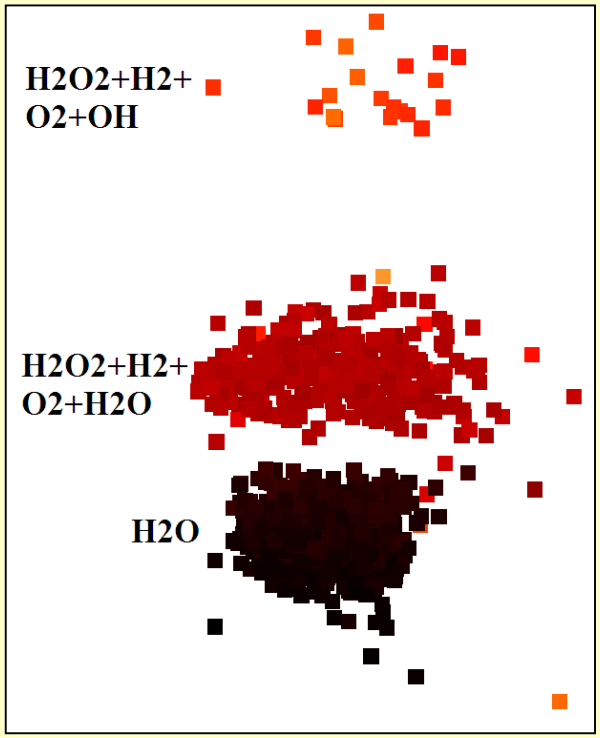
Correlation plot for 6900 structures of SiO_2 with 24 atoms/cell

Some of the (many) remarkable silicate frameworks:

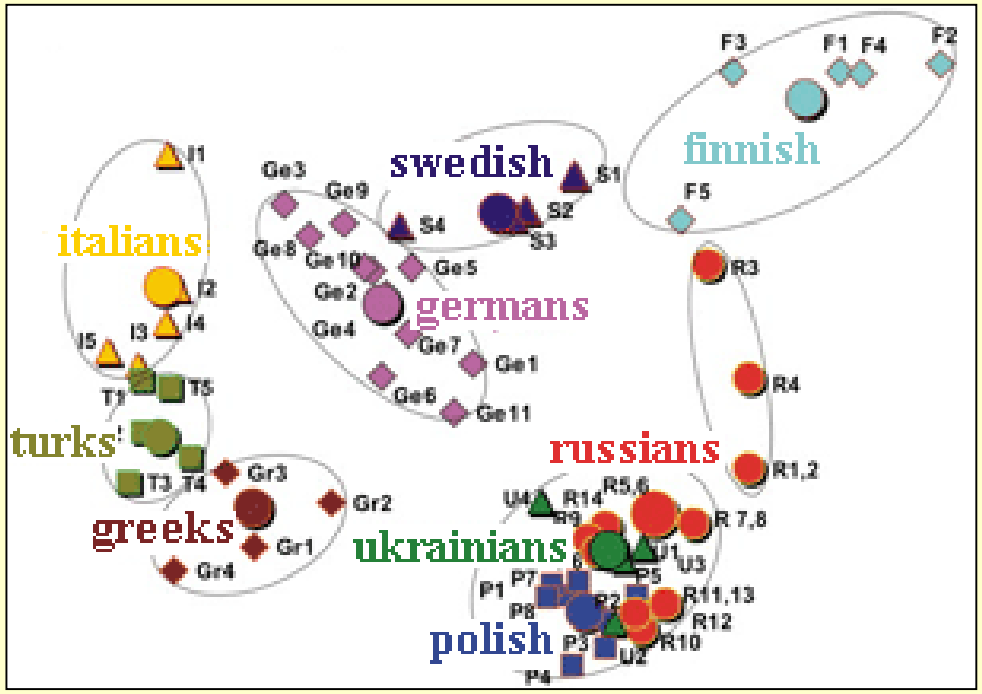


Increasing energy

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).

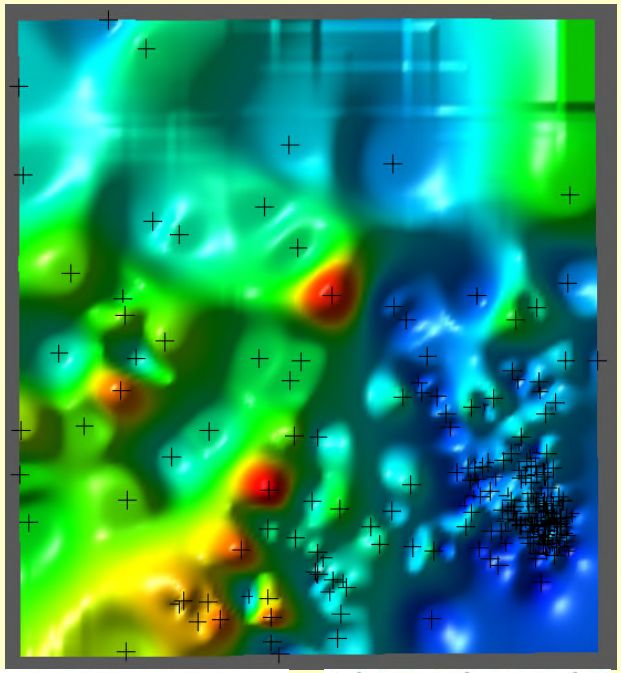


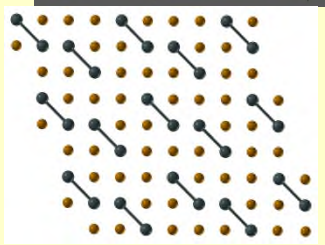
DNA grouping in Europe

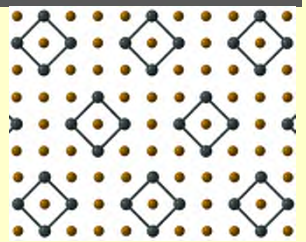
[ARO & Valle, J. Chem. Phys. 130, 104504 (2009)]

Visualizing energy landscapes

Au_8Pd_4 - simple



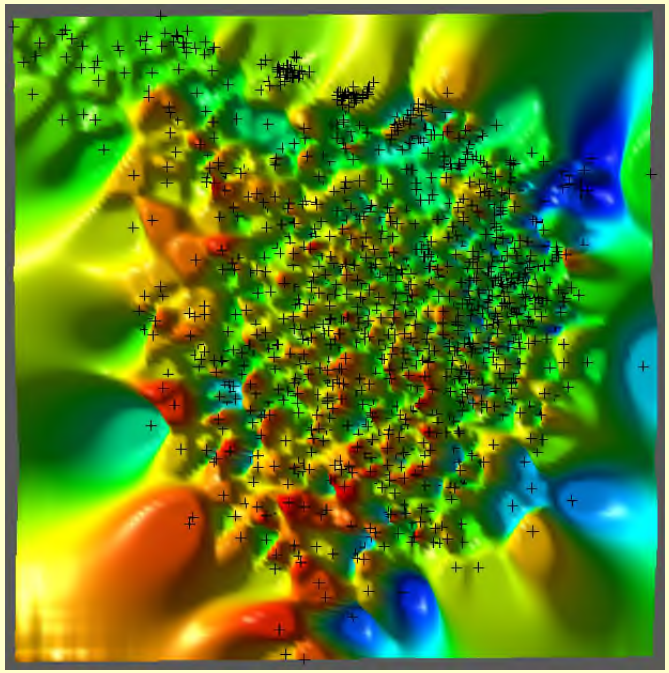


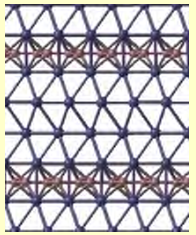


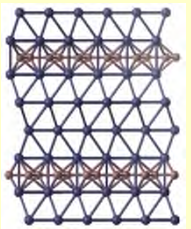
-61.960 eV
From USPEX

-61.957 eV
Cluster expansion

L_4J_8 - complex







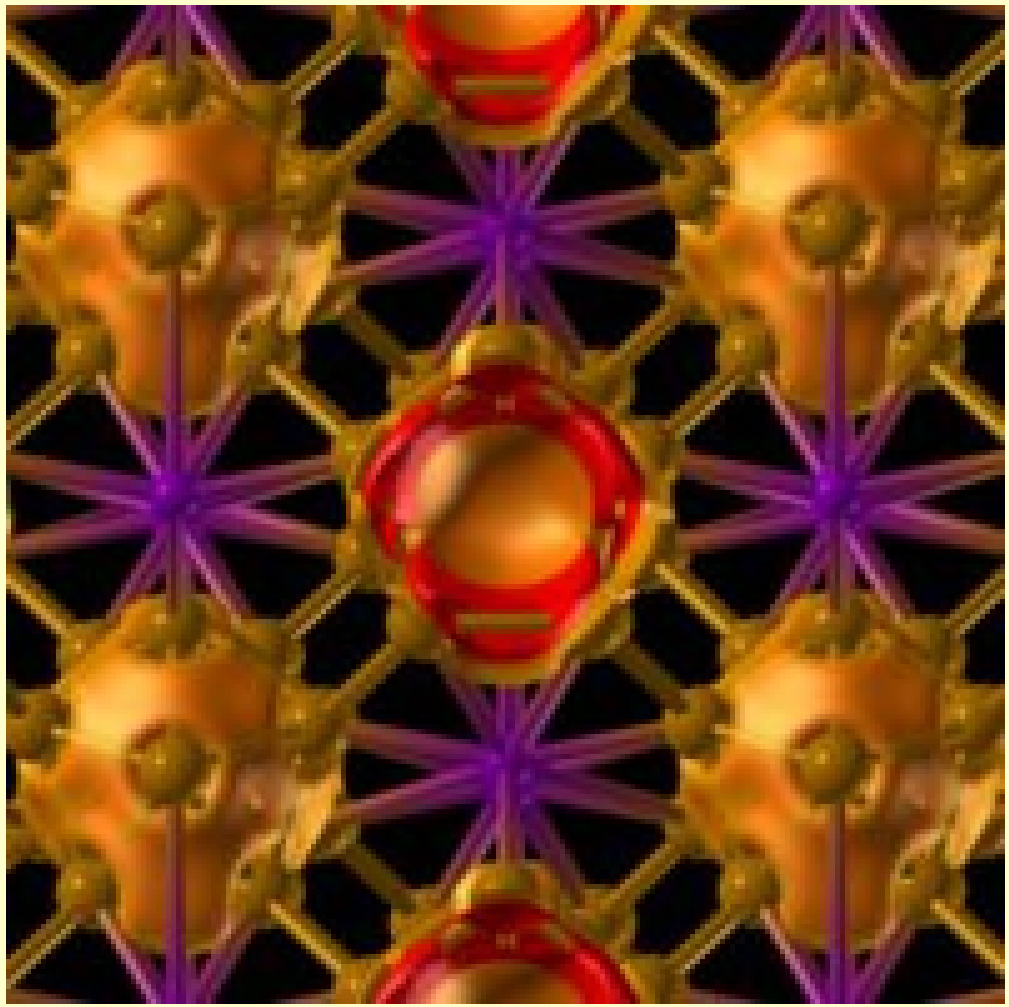
-99.12ε

-99.05ε

Binary Lennard-Jones crystal (R_L:R_J=1:2)

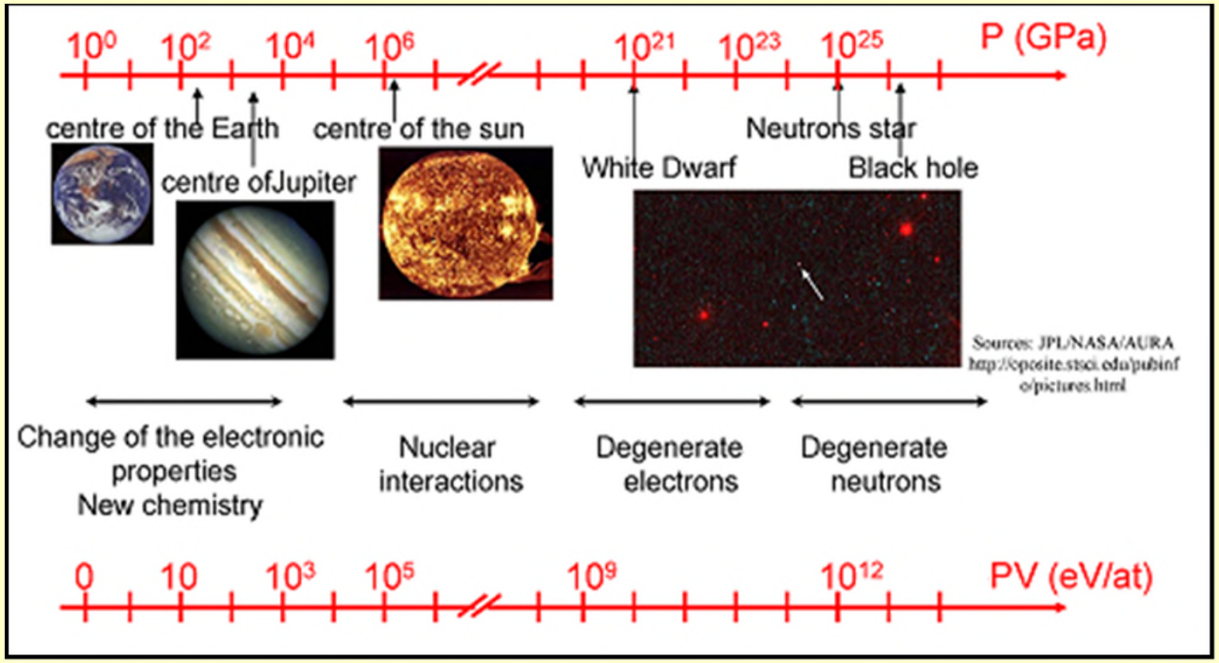
[ARO & Valle, J. Chem. Phys. 130, 104504 (2009)]

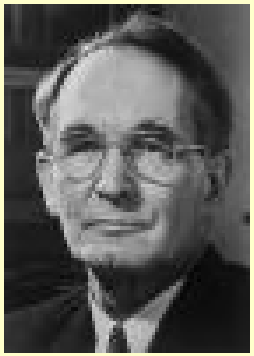
3. Predicting new materials



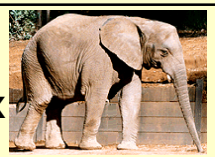
-Matter under pressure
-Materials with target properties

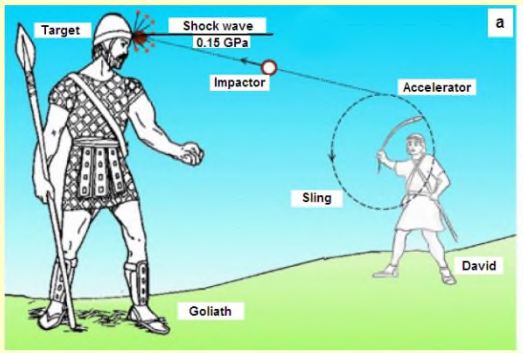
Matter under pressure: new phenomena and ubiquity in nature

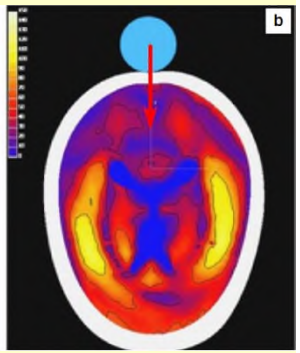




P.W. Bridgman
1946 Nobel Prize for Physics

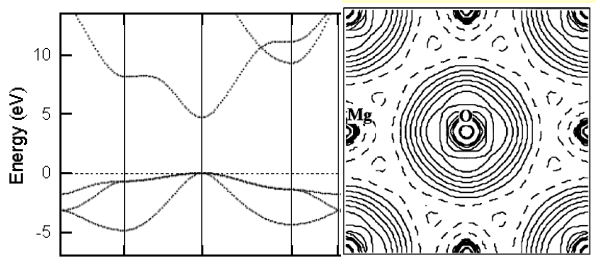
Units: 100 GPa = 1 Mbar = 200x  / 





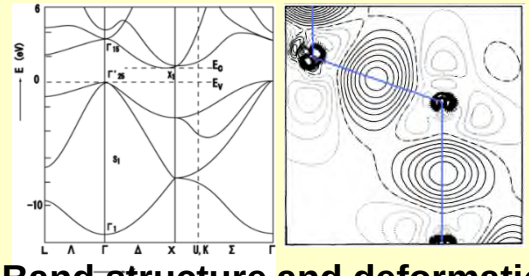
Types of chemical bonding

IONIC



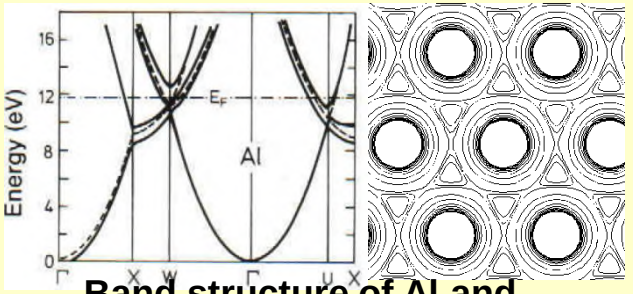
Band structure and deformation electron density of MgO

COVALENT



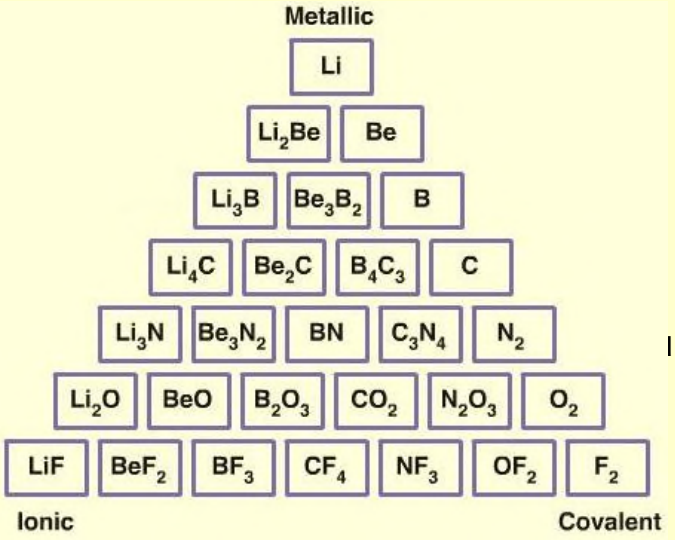
Band structure and deformation electron density of Si

METALLIC



Band structure of Al and valence electron density of Cu

- **Ionic: atoms have charges. Electrons localize on anions. Purely ionic bonding cannot exist.**
- **Covalent: shared electron pairs between the atoms. Directional.**
- **Metallic: delocalized, due to electron gas. Under sufficient pressure all matter should metallize.**
- **van der Waals: universal (present in all materials).**

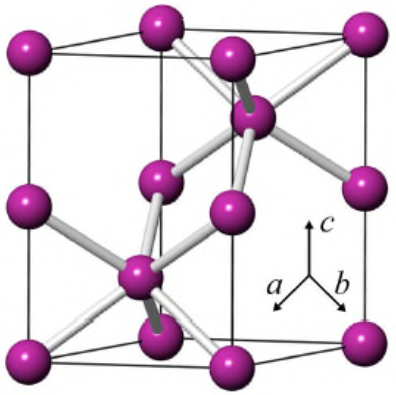


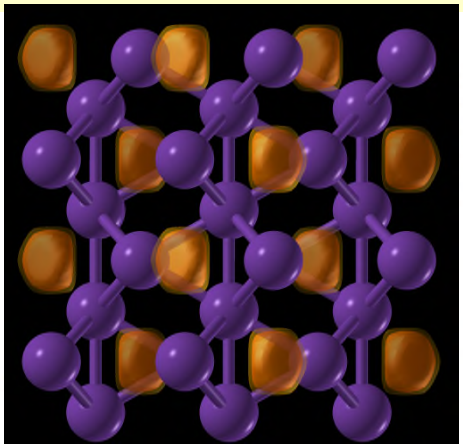
van Arkel – Ketelaar triangle

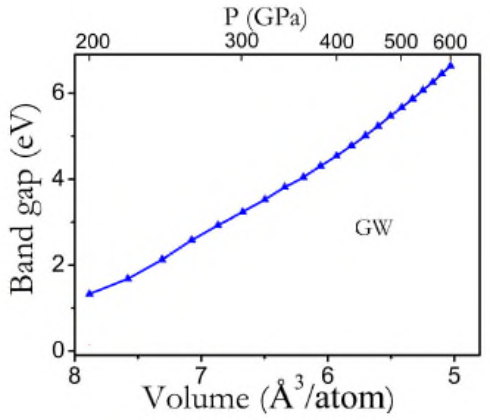
Metals under pressure

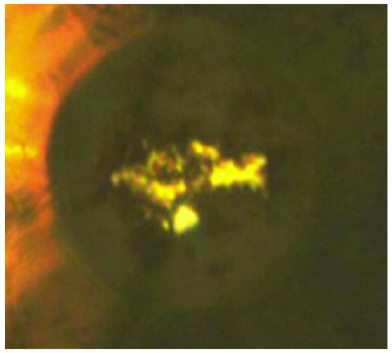
Na

- **Studied Fe, Na, Li, K, Rb, Cs, Ca, $CaLi_2$.**
- **Competition between steric (close packing), valence-electronic (Hume-Rothery), and core-electronic effects.**
- **Often open and low-symmetry structures emerge.**
- **Surprise: core electrons become essential and cause demetallization of Na and Li. Na becomes transparent at 200 GPa (Ma, Eremets, Oganov, Nature 2009).**





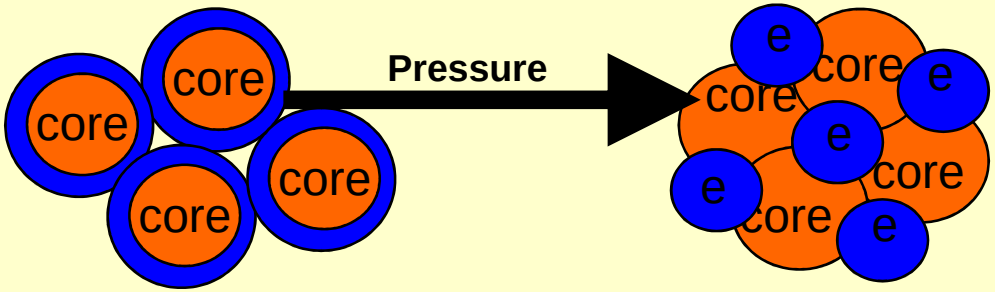




199 GPa

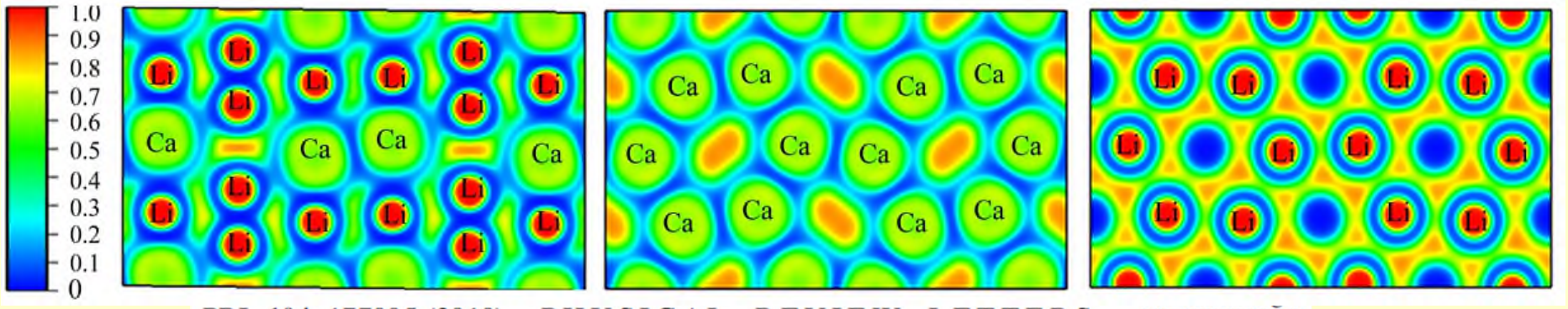
Localized interestitial electron pairs make Na insulating.

Explanation: Models of Ashcroft (1999, 2008)



$CaLi_2$: another illustration of the importance of core electrons

- **Feng (2007), Debessai (2008), Tse (2009) gave mutually inconsistent results.**
- **Our study (Xie et al., 2010) reconciled theory and experiment and found unique new structures with Li-Li pairing.**



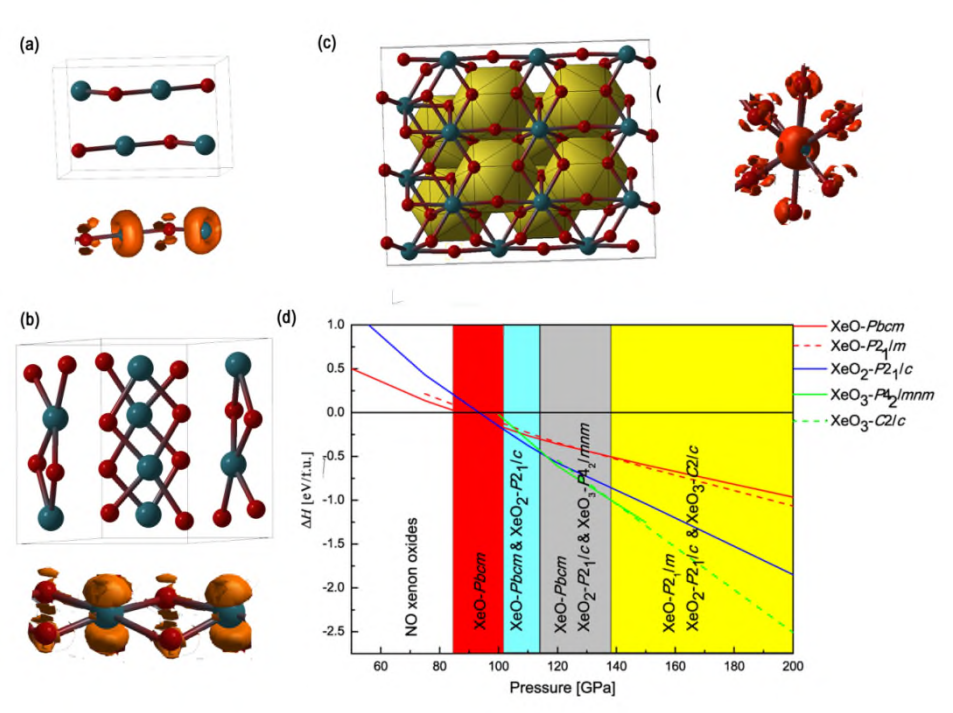
PRL 104, 177005 (2010) PHYSICAL REVIEW LETTERS 30 APRIL 2010

Novel High Pressure Structures and Superconductivity of $CaLi_2$

Yu Xie,[1,2] Artem R. Oganov,[2,3] and Yanming Ma[1,*]

Ionic solids under pressure

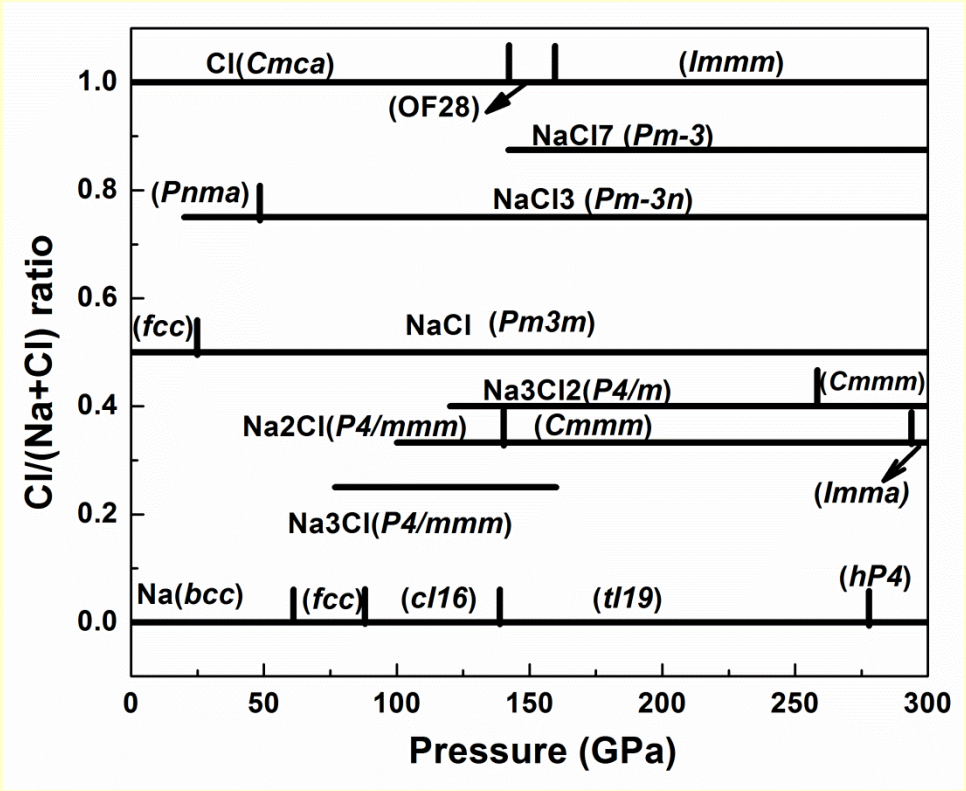
- Studied $CaCO_3$, $MgCO_3$, TiO_2, $MgSiO_3$, Al_2O_3,…
- Tendency to close packing, increase of coordination – as expected.
- Metallization under pressure (e.g., MgO at 21 TPa) – as expected.
- Xe oxides become stable at >80 GPa. Unexpectedly strong (~50%) Xe→O charge transfer.
- Oxidation state increases with pressure: Xe^{2+} -> Xe^{4+} -> Xe^{6+}



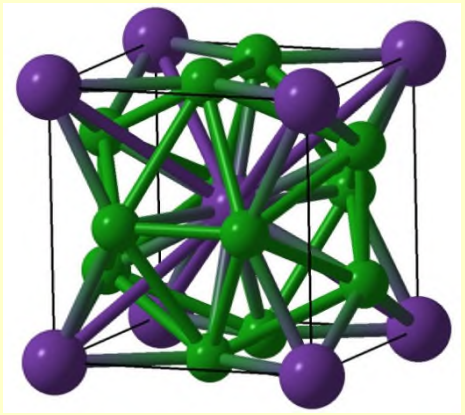
Surprise: significantly ionic stable XeO_n compounds
(Zhu, Jung, & ARO, *Nature Chemistry*, 2013)

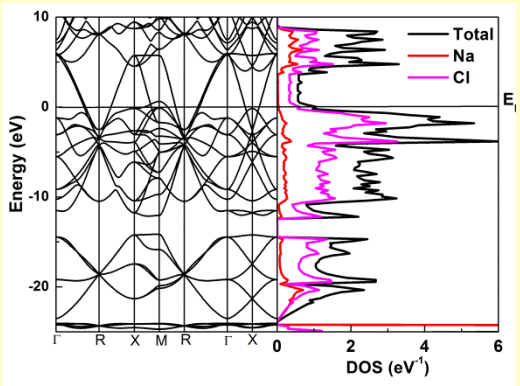
Ionic solids under pressure

- **Na-Cl system: compounds Na_3Cl, Na_2Cl, Na_3Cl_2, NaCl, $NaCl_3$, $NaCl_7$ are all stable under pressure (Zhang, ARO, et al. http://arxiv.org/abs/1211.3644). Confirmed by experiment!**



Phase stability in the Na-Cl system

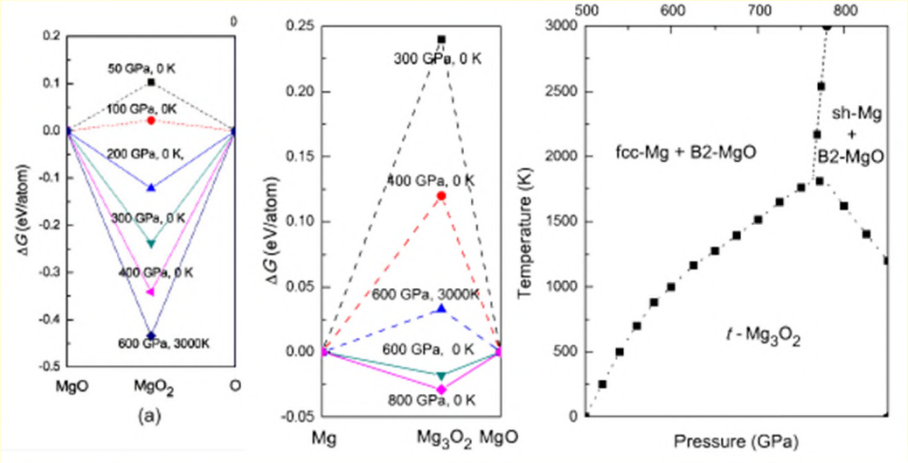




Atomic and electronic structure of cubic NaCl3

Ionic solids under pressure

Mg-O system: compounds Mg_3O_2, MgO, MgO_2 are all stable under pressure (Zhu, ARO, 2013).



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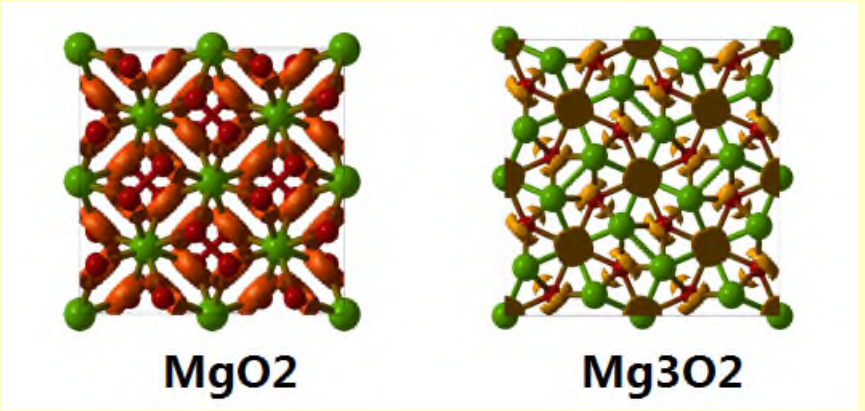


Crystal structure and electron localization function of MgO_2 and Mg_3O_2

van der Waals solids under pressure

- Studied Xe, CO_2, CH_4, SiH_4, GeH_4, SnH_4, glycene, graphane (CH).
- Polymerization of molecules (CO_2, CH_4, SiH_4, GeH_4, SnH_4) – as expected.
- Metallization (Xe, CO_2, CH_4, SiH_4, GeH_4, SnH_4) – as expected.

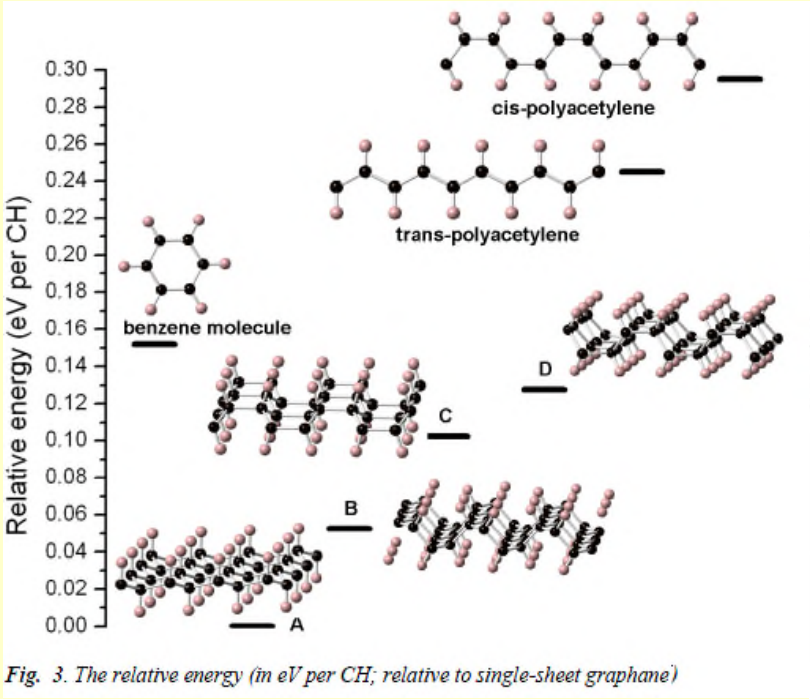


Fig. 3. The relative energy (in eV per CH; relative to single-sheet graphane)

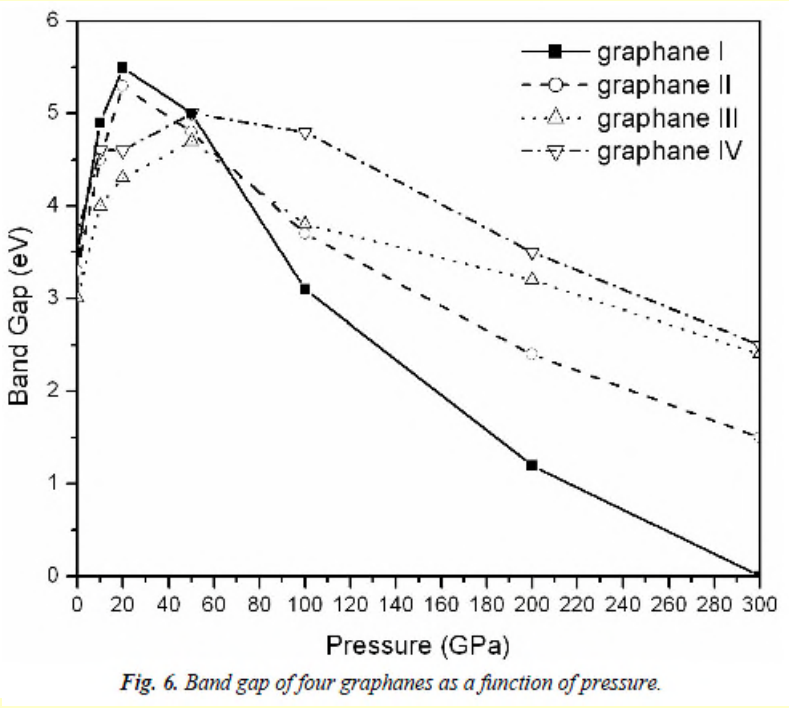
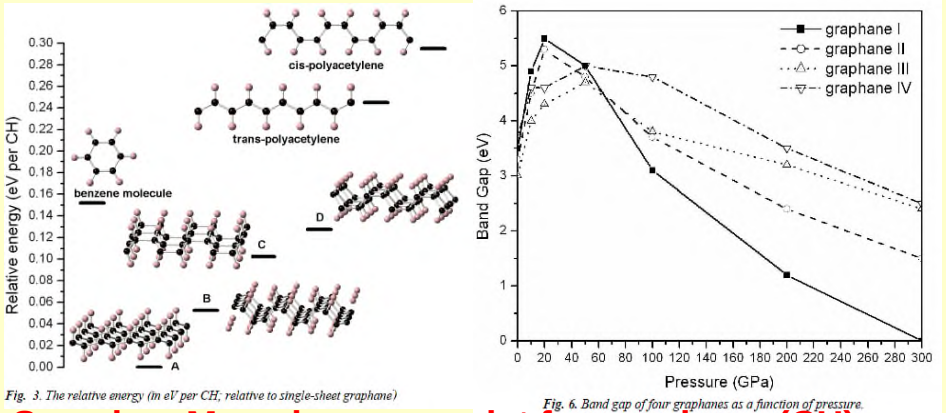


Fig. 6. Band gap of four graphanes as a function of pressure.

Surprise: Many isomers exist for graphane (CH). Graphane is more stable than benzene (C_6H_6). (Wen, Hoffmann, ARO, 2011)

van der Waals solids under pressure

- **Studied Xe, CO_2, CH_4, SiH_4, GeH_4, SnH_4, glycene, graphane (CH).**
- **Polymerization of molecules (CO_2, CH_4, SiH_4, GeH_4, SnH_4) – as expected.**
- **Metallization (Xe, CO_2, CH_4, SiH_4, GeH_4, SnH_4) – as expected.**



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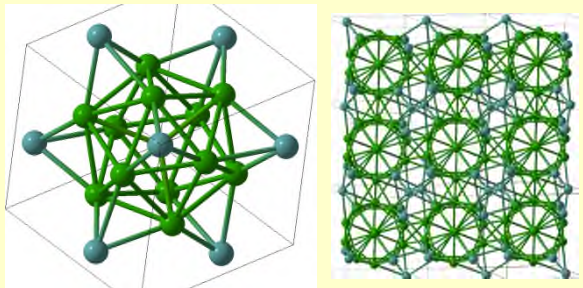
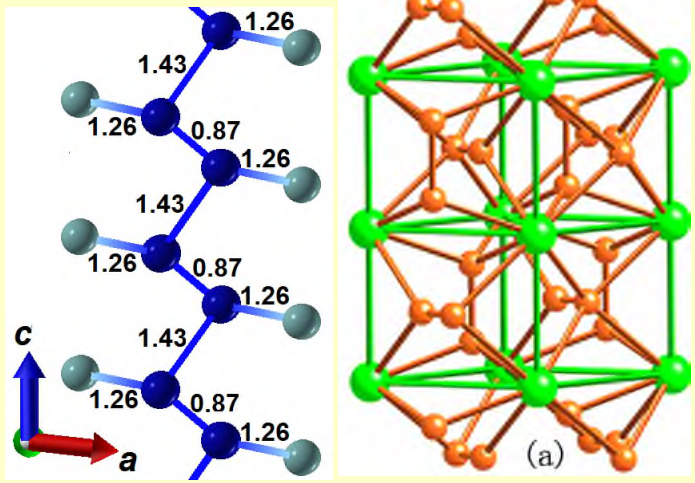


Surprise: Icosahedral structure for plastic phase of methane at ~10 GPa (Zhu, ARO, 2012).
Consistent with (Maynard-Caseley, 2010).



Surprise: ubiquitous formation of perhydrides under pressure (GeH_4 – left, SnH_4 – right, LiHn).
H-H distances of ~0.80-0.90 A.

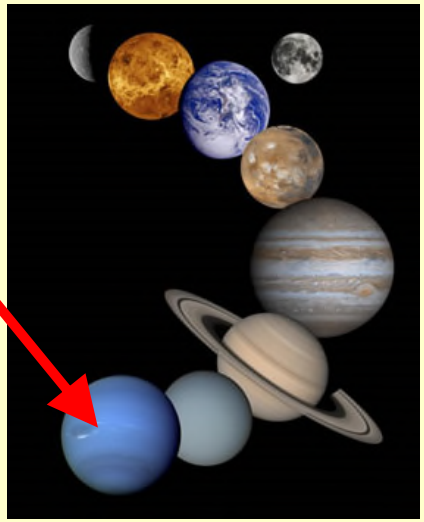
Planet Neptune has an internal source of heat. What is it?

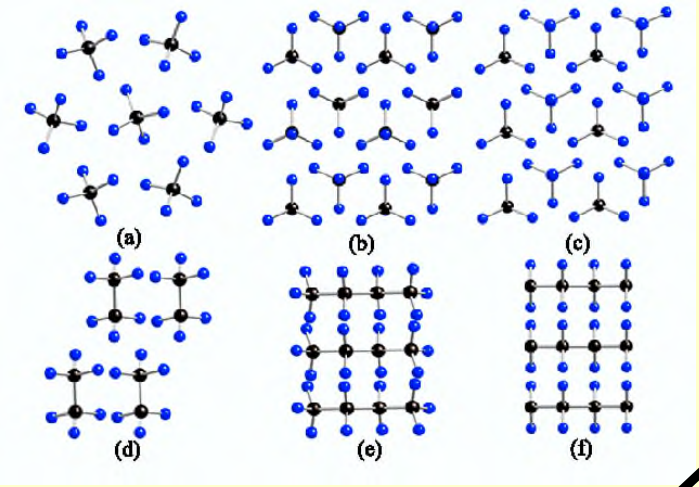
CH_4

- Uranus and Neptune: H_2O:CH_4:NH_3 = 59:33:8.
- Neptune has internal heat source (Hubbard'99).
- Ross'81 (and Benedetti'99):

CH_4=C(diamond) + $2H_2$. <u>Sinking of diamond – main source of heat in Neptune?</u>

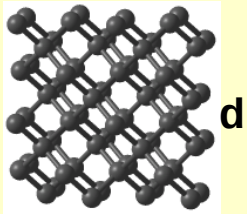
- Theory (Ancilotto'97; Gao'2010) confirms this.



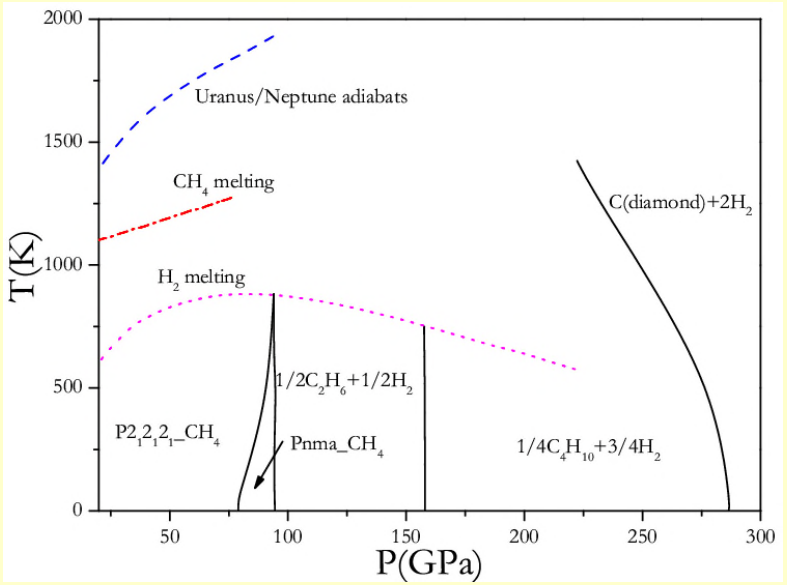


methane

hydrocarbons



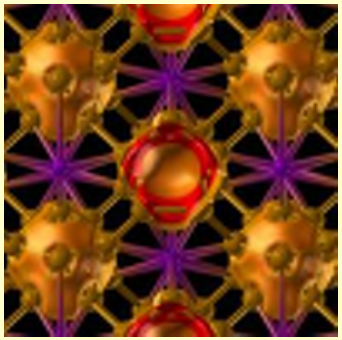
diamond



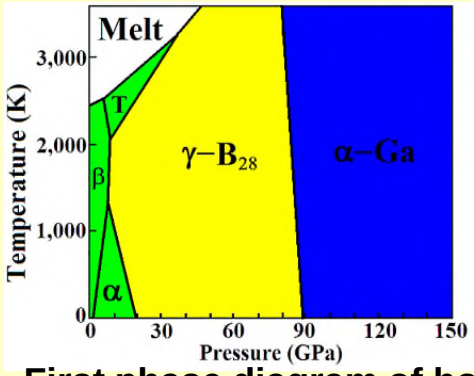
[Gao, ARO et al., *J. Chem. Phys.* 133, 144508 (2010)]

Covalent solids under pressure

- Studied B, C, N, O, Cl, CO_2, WN_2, MgB_2, B-C, B-P.
- Multiple bonds become less favorable, coordination increases under pressure (N, Cl, CO_2).
- Metallization (B, C, N, O, Cl).
- Surprise: before metallization – formation of unusual partially ionic states (B, H).



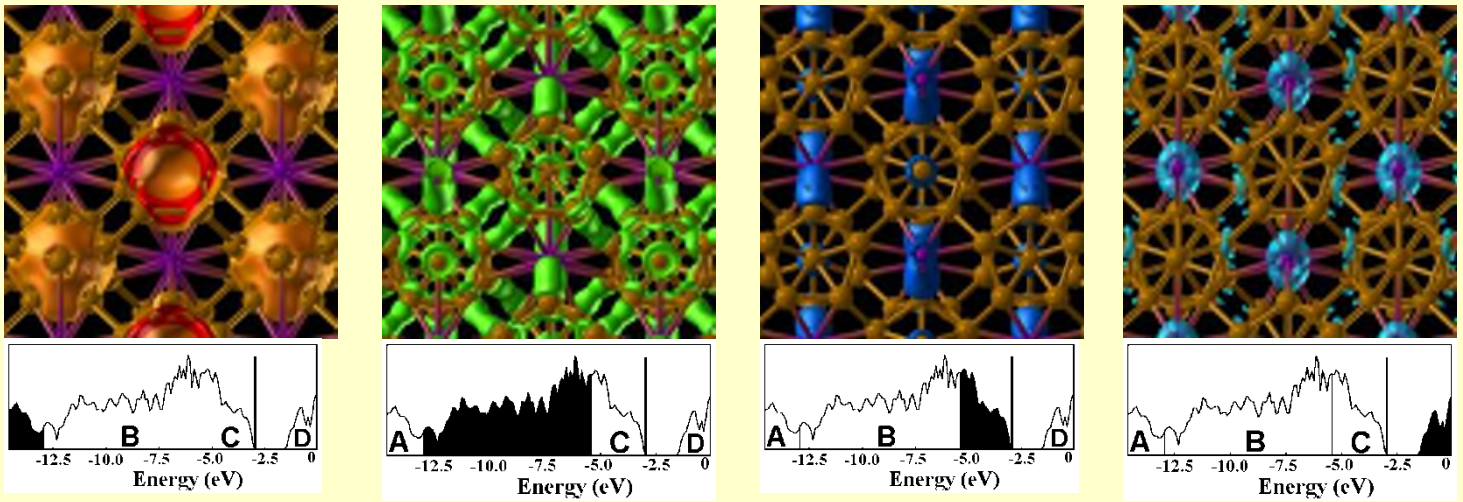
NaCl-like structure of γ-B_{28}
(Oganov et al., Nature 2009)



First phase diagram of boron
(Oganov et al., Nature 2009)

Non-trivial chemistry of boron – field for new discoveries

B



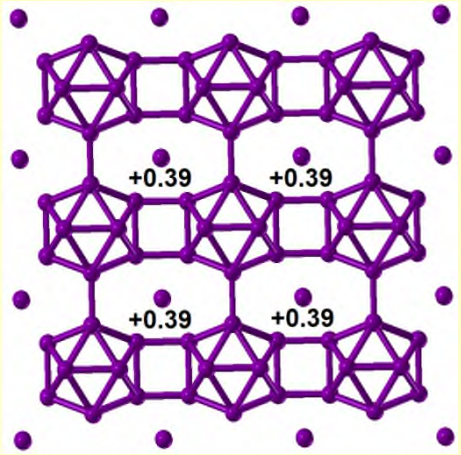
Charge separation between B_{12}-icosahedra and B_2-pairs is clear from DOS

Theoretical (Oganov, 2009 & 2011) and experimental (Mondal, 2011) atomic charges in γ-B_{28}

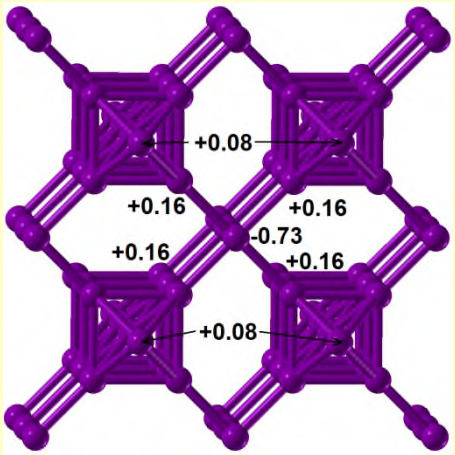
Site	GGA	EXX	HSE06	Experiments (Mondal, 2011)	
B1	+0.26	+0.34	+0.31	+0.41	+0.81
B2	-0.18	-0.31	-0.21	-0.19	-0.19
B3	+0.00	-0.04	+0.00	+0.06	-0.03
B4	+0.07	+0.25	+0.07	-0.14	-0.44
B5	+0.04	+0.11	+0.04	+0.00	+0.05

Charge transfer (i.e. partial ionicity) – uniquitous in metastable structures of boron

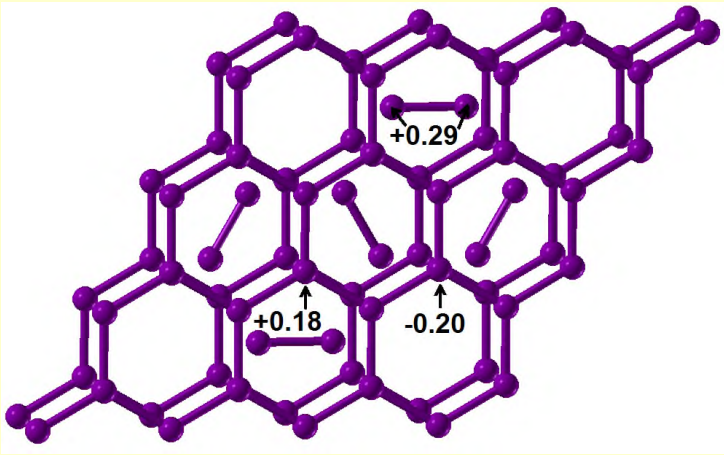
B



Icosahedra are negatively, single B-atoms positively charged



One B atom has 4 single bonds, achieved due to -1 charge on that atom

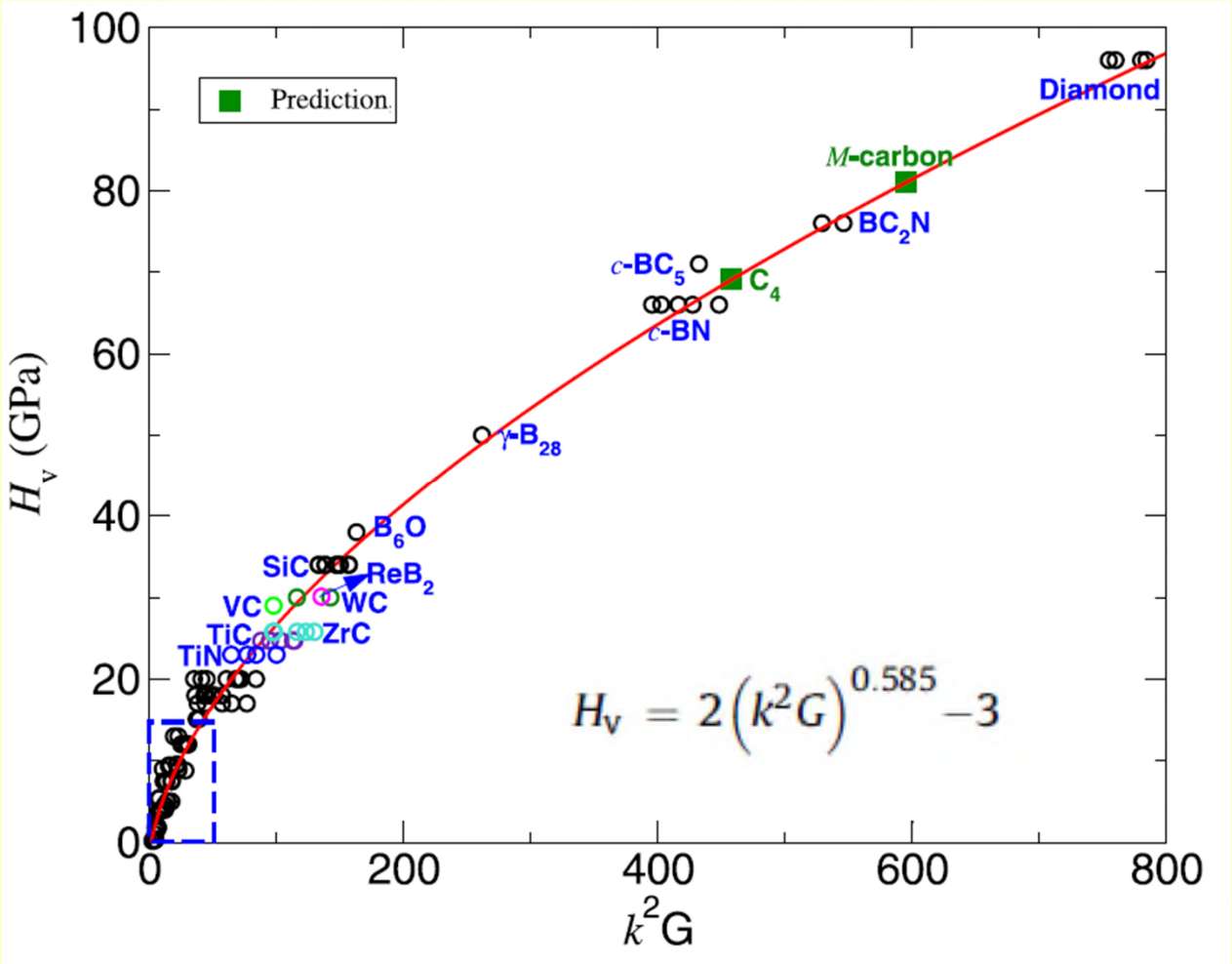


Graphene sheets require 4 electrons/atom. This is achieved by charge transfer

[ARO et al., J. Superhard Mater. (2011)]

Boron is the basis for novel superhard materials. γ-B_{28} is one of the hardest known materials

B



Overview of hard materials (Chen, 2011)

γ-B_{28} has hardness of 50 GPa (Solozhenko, ARO, 2008)

Optimization of physical properties:

Replacing Edisonian trial-and-error way of discovering new materials

"*I have not failed (ten thousand times)*. I've just found 10000 ways that won't work"

(T.A. Edison)

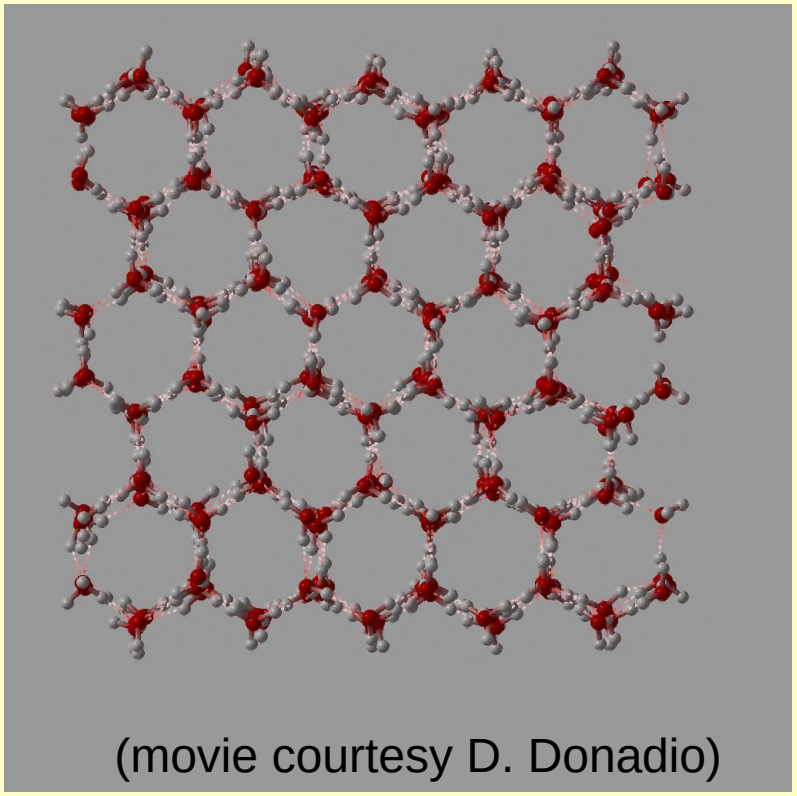
Relevant USPEX input

enthalpy : optType

Possible values:

- **enthalpy (default)**
- **volume**
- **hardness**
- **struc_order**
- **aver_dist**
- **diel_sus**
- **gap**
- **diel_gap**
- **mag_moment**
- **struc_entropy**

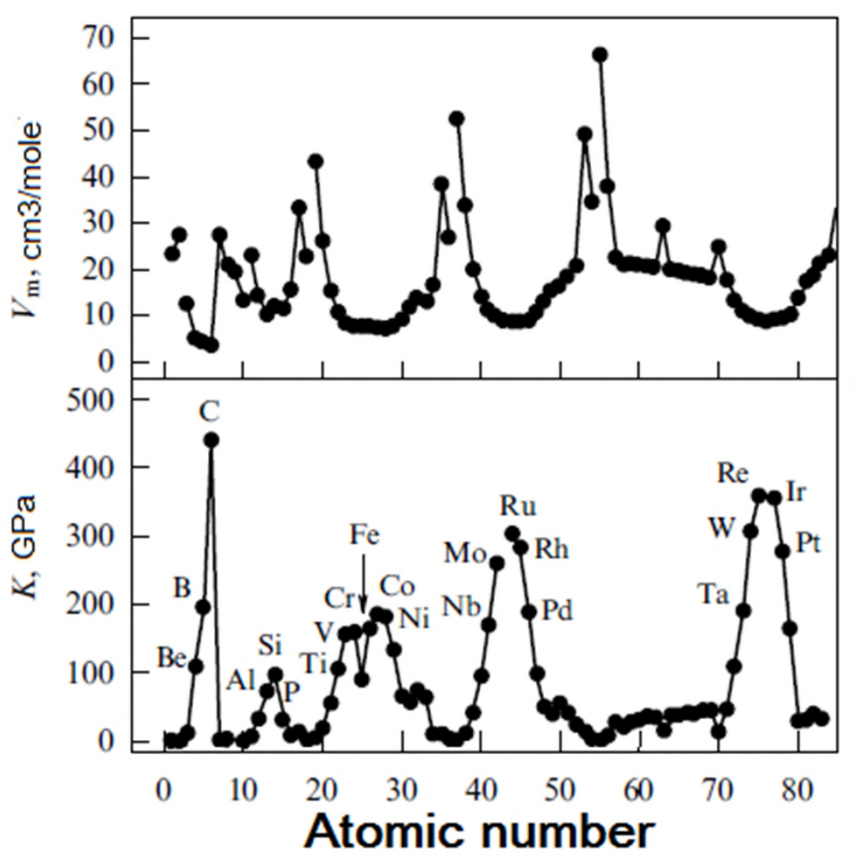
Examples of interesting properties:
Why is ice lighter than water?



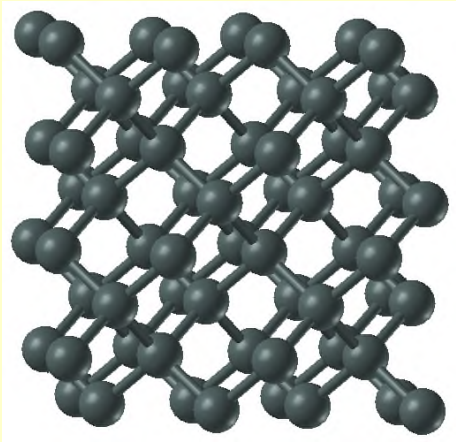
(movie courtesy D. Donadio)

Structure of ice contains large empty channels, which explain its low density.

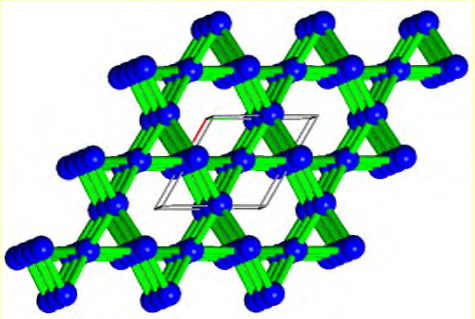
Looking for the densest possible material: carbon allotrope(s) denser than diamond



Diamond has the highest bulk modulus and lowest atomic volume among all elements (and compounds) From Brazhkin (2009).



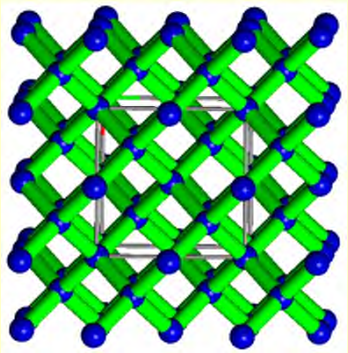
diamond structure



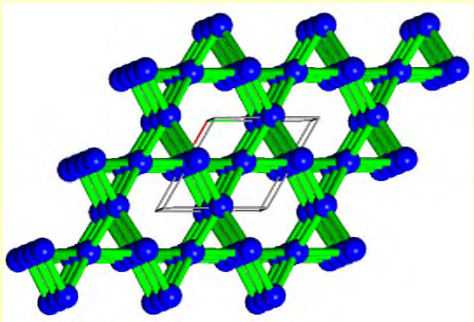
new structure, 3.2% denser than diamond!
(Zhu, ARO, et al., PRB 2011)

Finding materials with target properties: optimizing the density (rather than energy)

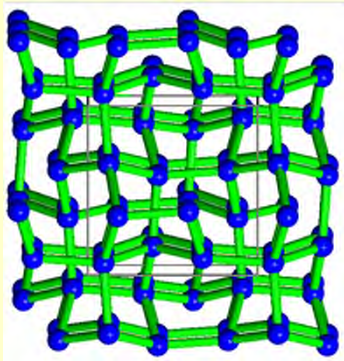
- Diamond has the highest hardness, highest bulk modulus and lowest atomic volume among all materials [Brazhkin (2009)]. Can this be improved?
- We found 3 interesting denser-than-diamond structures (by 1.1-3.2%). Structural analogy between C and SiO_2.



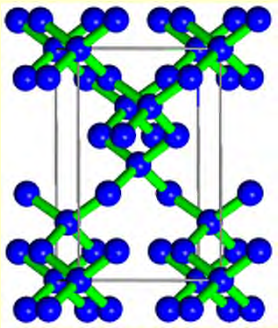
diamond structure



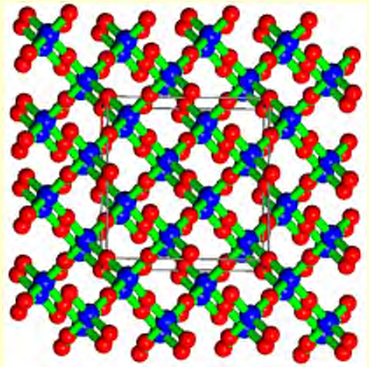
hP3 structure



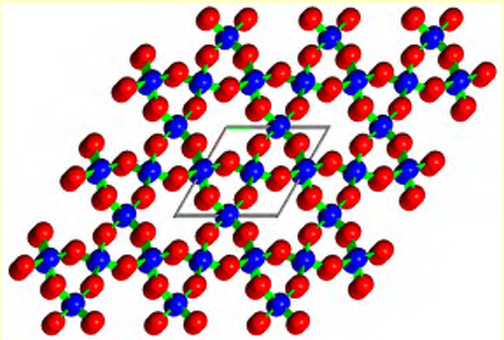
tP12 structure



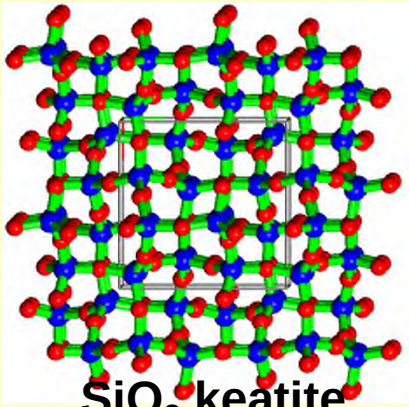
tI12 structure



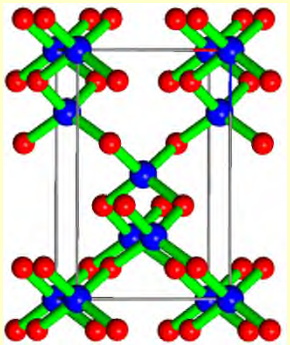
SiO_2 cristobalite structure



SiO_2 quartz structure

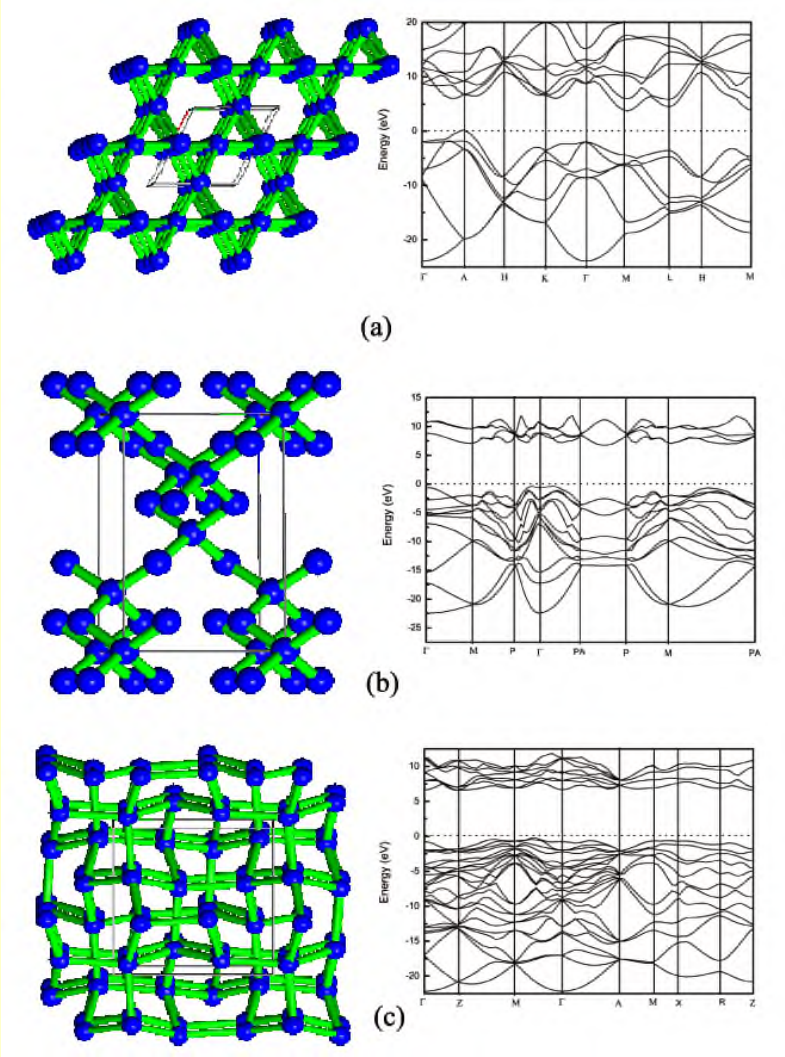


SiO_2 keatite structure



High-pressure SiS_2 phase

Superdense carbon allotropes [Zhu, ARO, et al., PRB 2011]

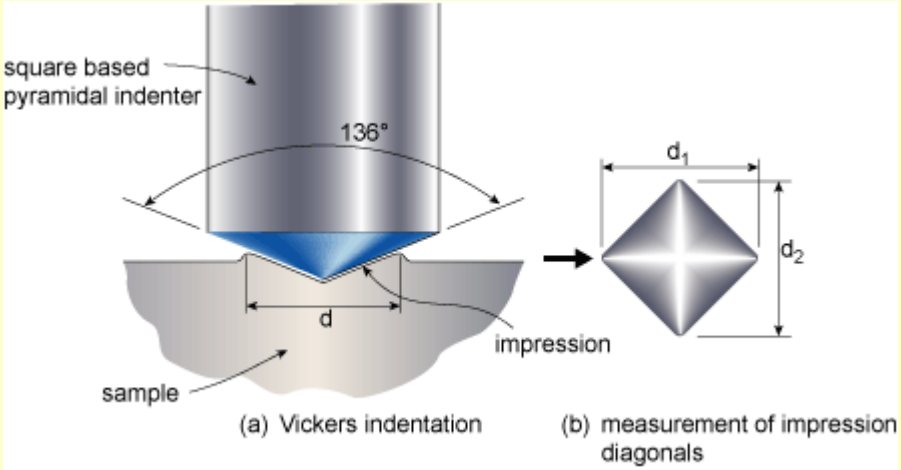


(1) sp^3 hybridization
(2) superhard
(3) huge refractive indices (up to 2.8!)
(4) strong dispersion of light
(6) tP12 is the widest-gap form of carbon (7.3 eV)

TABLE II. Energy relative to diamond (δE), volume (V), bulk modulus (B_0), average bond length (d), hardness(H), static dielectric constant ϵ_s for the investigated structures. Experimental data are in parentheses

Allotropes	δE eV/atom	V Å^3/atom	B_0 GPa	d Å	H GPa	Band gap eV	ϵ_s
Diamond	0	5.70 (5.68)	431.1 (446)	1.545 (1.54)	94.3 (96±5)	5.4 (5.5)	5.57 (5.68)
Lonsdaleite	0.024	5.71	437.3	1.548	93.2	5.0	5.52
M-carbon	0.159	5.97	392.7	1.551	89.8	5.0	5.52
bct-4	0.196	6.01	411.4	1.549	91.1	3.8	5.42
bc8	0.697	5.60	389.6	1.588	88.8	3.5	6.67
*h*P3	1.113	5.49	432.7	1.603	87.6	3.0	7.73
*t*I12	1.140	5.48	425.0	1.603	87.2	5.5	7.87
*t*P12	0.883	5.64	396.0	1.583	88.3	7.3	7.08

Theory of hardness? Yes!



Single-bond crystals:

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

Multibond crystals:

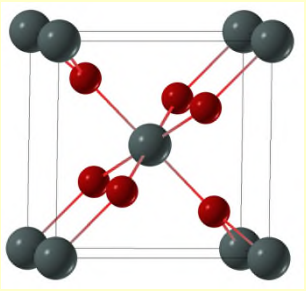
$$H_k(\mathrm{GPa}) = \frac{423.8}{V} n \left[\prod_{a,b=1}^{n} N_{ab} X_{ab} e^{-2.7 f_{i(ab)}} \right]^{1/n} - 3.4$$

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

$$X_k = \sqrt{\frac{\chi_i^k \chi_j^k}{CN_i^k CN_j^k}}$$

Material	Model of Li et al. (2009)	Lyakhov & ARO (2011)	Exp.
Diamond	91.2	89.7	90
Graphite	57.4	0.17	0.14
TiO_2 rutile	12.4	12.3	8-10
β-Si_3N_4	23.4	23.4	21
SiO_2 stishovite	31.8	30.8	33

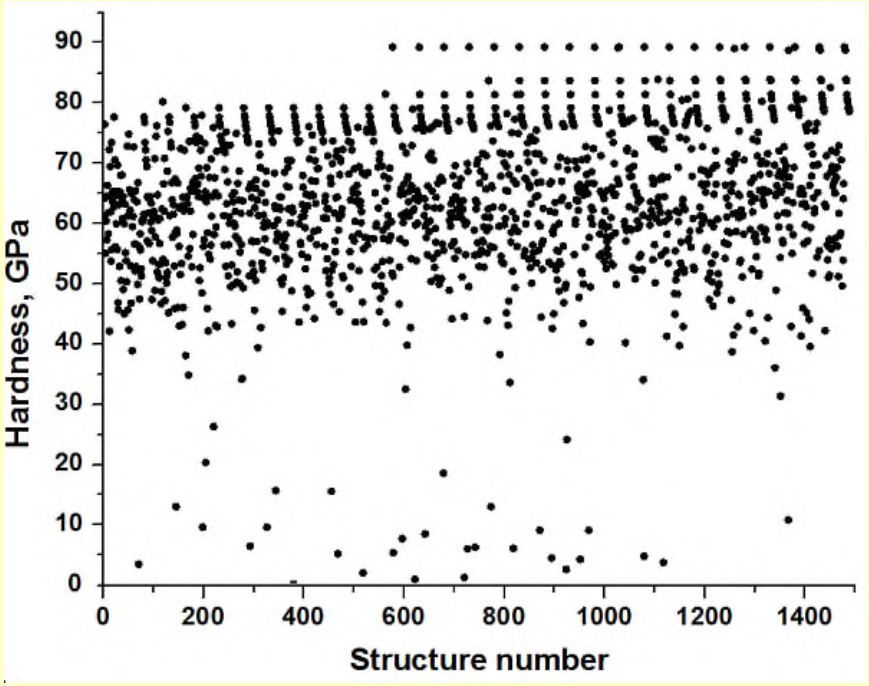
Lyakhov & ARO (2011) – augmented model of Li (2009) by bond valence model and graph theory.



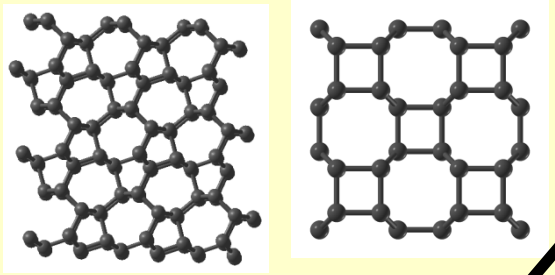
Special Issue "Theory of superhard materials" (editor – A.R. Oganov)

Journal of Superhard Materials, 2010, Vol. 32, No. 3, © Allerton Press, Inc., 2010.

Is diamond the hardest structure for carbon? Yes [Lyakhov & ARO, PRB 2011].



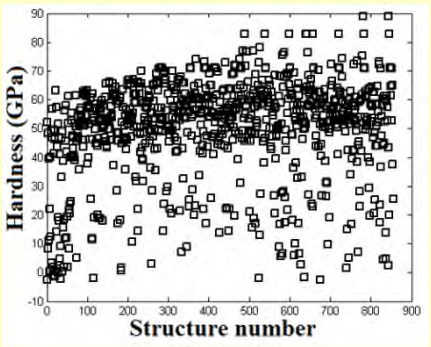
Simulation for carbon, 16 atoms/cell

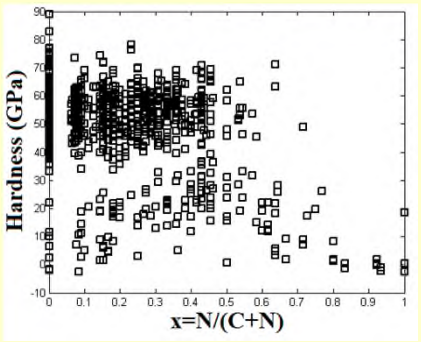


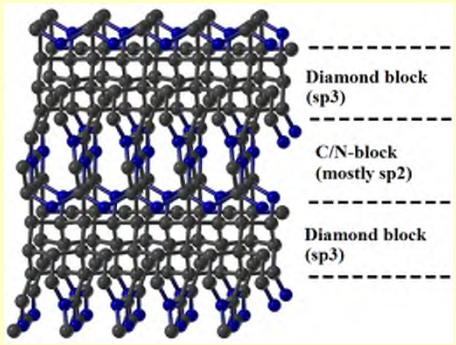
All of the hardest structures are sp^3-hybridized

Structure	Knoop hardness, GPa	Enthalpy, eV/atom
Diamond	89.7	0.000
Lonsdaleite	89.1	0.026
C2/m	84.3	0.163
I4/mmm	84.0	0.198
Cmcm	83.5	0.282
P2/m	83.4	0.166
$I2_12_12_1$	82.9	0.784
Fmmm	82.2	0.322
Cmcm	82.0	0.224
$P6_522$	81.3	0.111

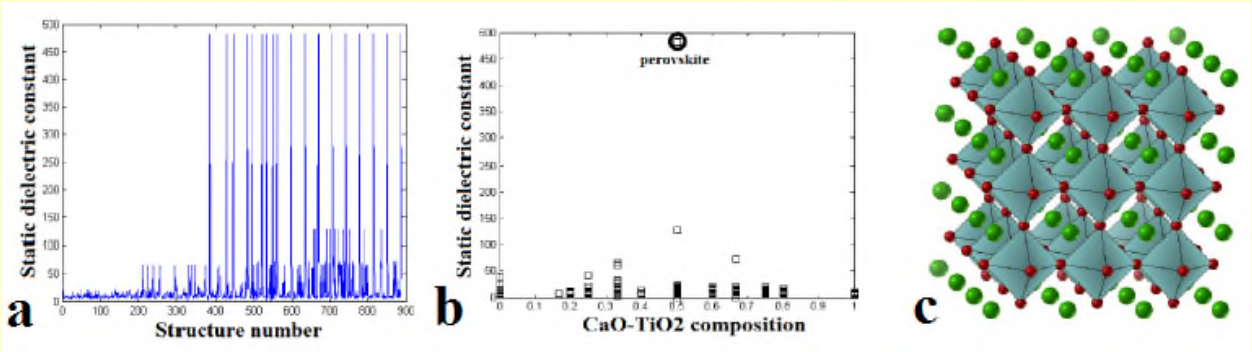
USPEX can optimize properties of variable-composition systems







Our calculations (ARO, 2012) clearly show that carbon nitrides cannot be harder than diamond, thus ending the old quest (Liu & Cohen, 1989; Teter & Hemley, 1995).



Our calculations (ARO, 2012) show that in the CaO-TiO_2 system $CaTiO_3$ perovskite has the highest dielectric constant.

Looking for the hardest materials… What is the hardest oxide?

- **Leger (Nature 1996) – SiO_2 stishovite (33 GPa).**
- **Dubrovinsky (Nature 2001) – TiO_2-cotunnite (38 GPa).**
- **He (Appl.Phys.Lett. 2002) – B_6O (45 GPa).**

Materials science

The hardest known oxide

A material as hard as diamond or cubic boron nitride has yet to be identified[1–6], but here we report the discovery of a cotunnite-structured titanium oxide which represents the hardest oxide known. This is a new polymorph of titanium dioxide, where titanium is nine-coordinated to oxygen in the cotunnite

Table 1 Hardness of polycrystalline materials

Material	*Bulk modulus (GPa)*	*Hardness* (GPa)*	*Ref.*
B_4C	200	30 (30)	3
SiC	248	29 (29)	3
Al_2O_3	252	20 (19)	7
SiO_2, stishovite	291	32 (33)	7
WC	421	30 (30)	8
Cubic BN	369	(32)	3
Cotunnite-type TiO_2†	431	38	
Sintered diamond	444	(50)	3

*Literature data are given in parentheses. The uncertainty in measured hardness is less than 3 GPa.
†Measurements were made at 157 ± 2 K.

L. S. Dubrovinsky*, N. A. Dubrovinskaia*, V. Swamy†, J. Muscat†, N. M. Harrison‡, R. Ahuja§, B. Holm§, B. Johansson§||
*Institute of Earth Sciences, Uppsala University, S-752 36 Uppsala, Sweden
e-mail: leonid.dubrovinsky@geo.uu.se
†CSIRO Minerals, Box 312, Clayton South,

Suggestion of TiO_2 is clearly incorrect – (1) it is unstable at 1 atm (!),
(2) Experiments of Dubrovinsky were low-quality
(bulk modulus is 43% overestimated – Al-Khatatbeh (2009), Hamane-Nishio (2010))
(3) No phase of TiO_2 can be harder than ~15 GPa.

Pseudo-hard TiO_2: Dubrovinsky et al. (Nature 2001) overestimated bulk modulus by 43%, hardness by 140%

Materials science

The hardest known oxide

A material as hard as diamond or cubic boron nitride has yet to be identified[1–6], but here we report the discovery of a cotunnite-structured titanium oxide which represents the hardest oxide known. This is a new polymorph of titanium dioxide, where titanium is nine-coordinated to oxygen in the cotunnite

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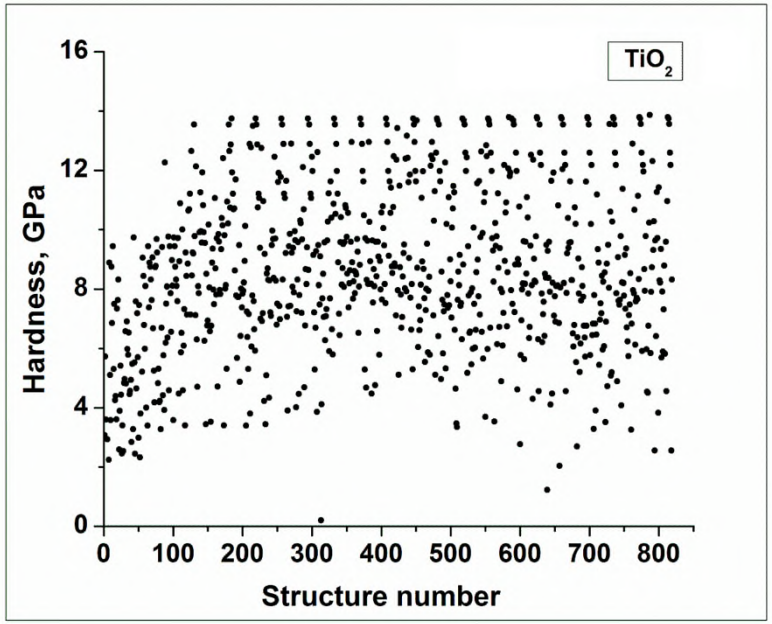
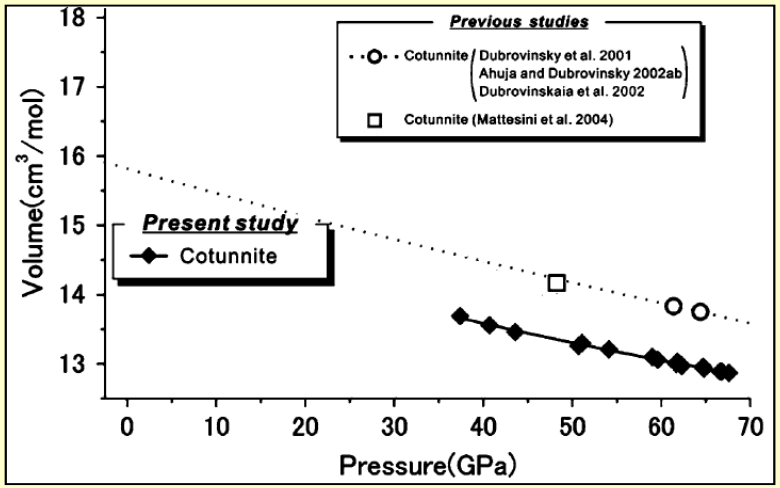
e-mail: leonid.dubrovinsky@geo.uu.se
†CSIRO Minerals, Box 312, Clayton South,

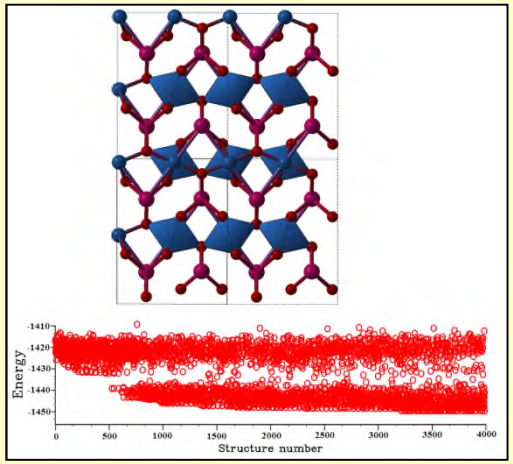


Lyakhov & ARO (2011)

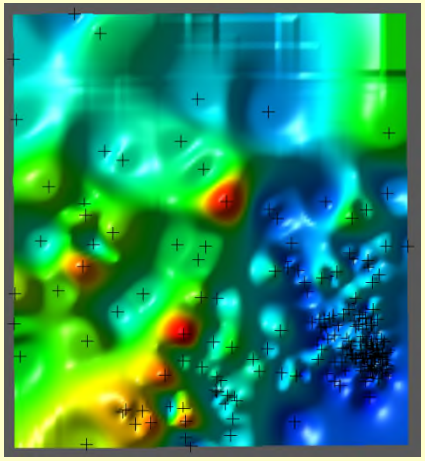


Nishio-Hamane (2010): bulk modulus is ~300 GPa, not 431 GPa.

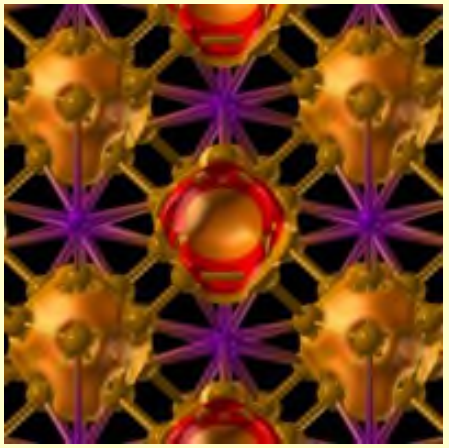
New developments in crystal structure prediction extend the range of problems that can be solved



Powerful methods for crystal structure prediction



Fingerprints - new language for crystallography



Predicted new materials and phenomena