How to Predict Crystal Structures

Artem R. Oganov (ARO)

STONY BROOK
STATE UNIVERSITY OF NEW YORK

(1) Department of Geosciences
(2) Department of Physics and Astronomy
(3) New York Center for Computational Sciences
State University of New York, Stony Brook, NY 11794-2100

Geology Department
Moscow State University
119992 Moscow, Russia.

Simple approaches to structure prediction

- **Pauling‘s rules. Parthe rules. Valence electron concentration.**
- **Bond valence model (I.D. Brown).**
- **Structure diagrams.**
- **Computational prediction**
  - **-random sampling**
  - **-simulated annealing**
  - **-metadynamics**
  - **-minima hopping**
  - **-evolutionary algorithms**

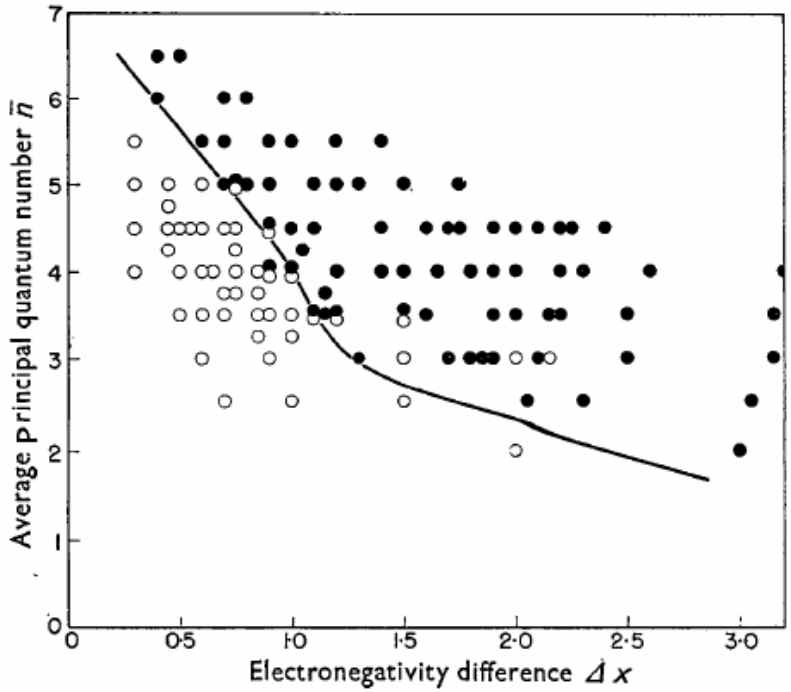
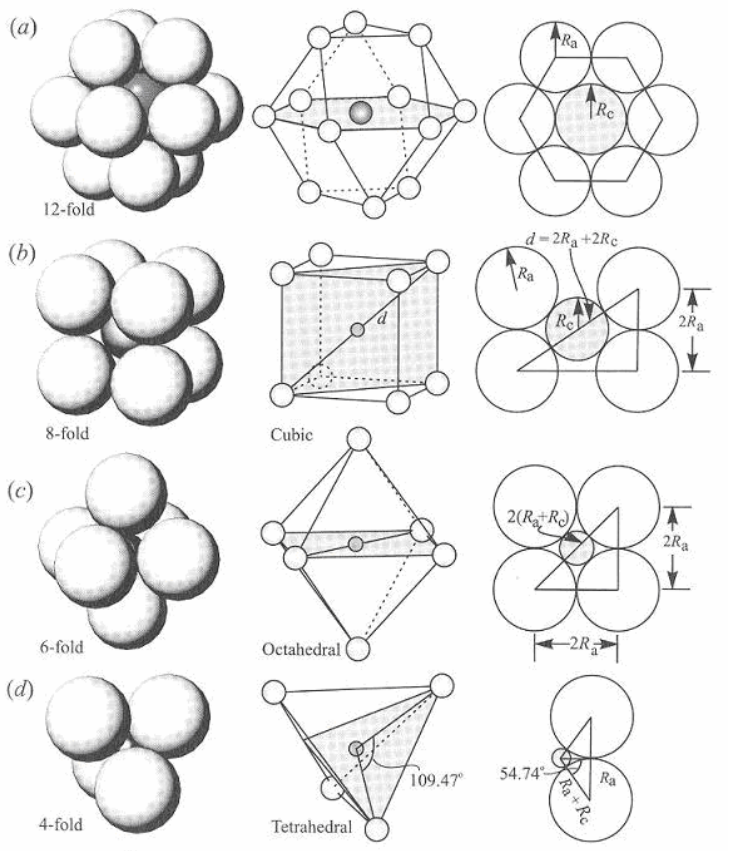
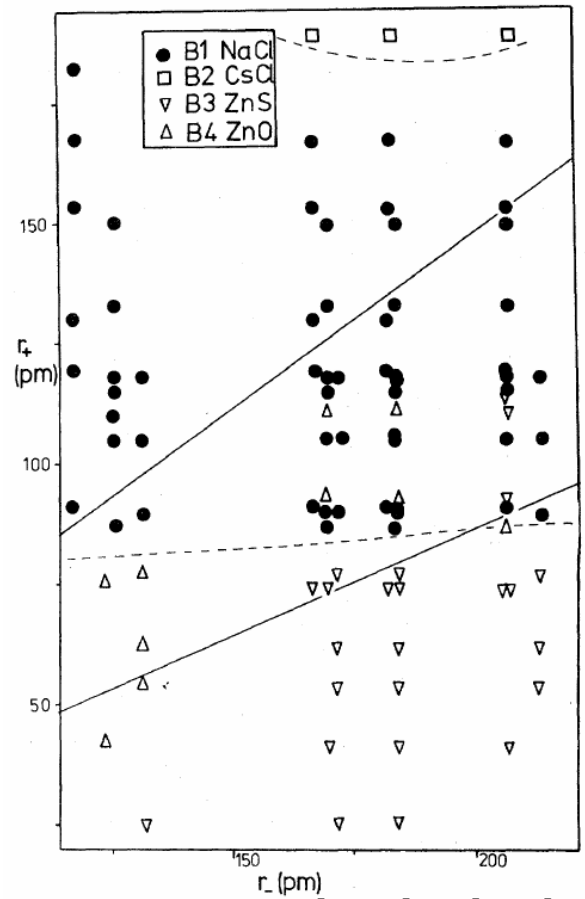


Fig. 1. AX structures with tetrahedral and octahedral coordination.

Mooser-Pearson diagram

Does 1st Pauling's rule work?





Structure separation by ionic radii ratio

A bit more on structure diagrams

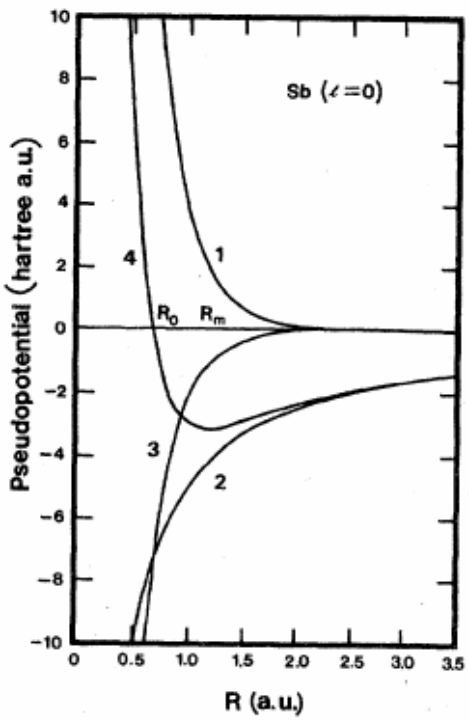
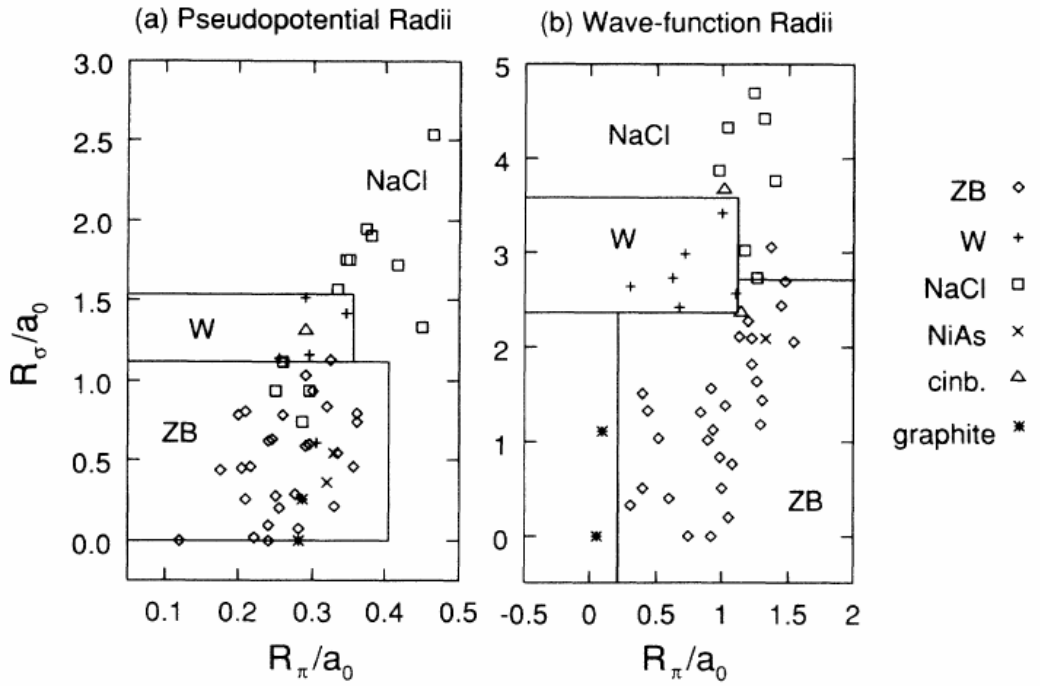


FIG. 1. Components of the atomic pseudopotential $v_{ps}^{(l)}(r)$ [Eq. (10)] for $l=0$ of the Sb atom: (1) Pauli potential $U_l(r)$, (2) the Coulomb attraction $-Z_v/r$, (3) core screening, and (4) the total pseudopotential. R_0 and R_m denote the points of crossing and minimum, respectively.



$$R_\sigma(A,B) = |\,(r_p^A + r_s^A) - (r_p^B + r_s^B)\,|$$

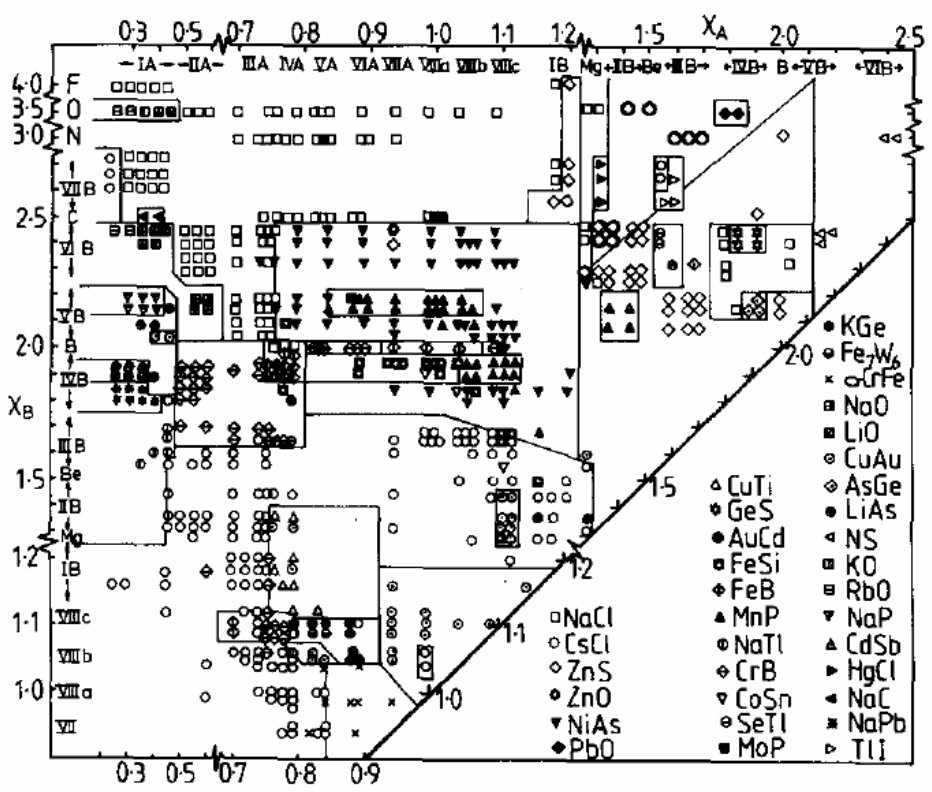
$$R_\pi(A,B) = |\,(r_p^A - r_s^A) + (r_p^B - r_s^B)\,|$$

Magic: Medeleev number and chemical scale

Table 1. The Mendeleev number m and chemical scale χ.

m		χ	m		χ	m		χ
1	He	0.00	36	Md	0.7125	70	Au	1.16
2	Ne	0.04	37	Fm	0.715	71	Ag	1.18
3	A	0.08	38	Es	0.7175	72	Cu	1.20
4	Kr	0.12	39	Cf	0.72	73	Mg	1.28
5	Xe	0.16	40	Bk	0.7225	74	Hg	1.32
6	Rn	0.20	41	Cm	0.725	75	Cd	1.36
7	Fr	0.23	42	Am	0.7275	76	Zn	1.44
8	Cs	0.25	43	Pu	0.73	77	Be	1.50
9	Rb	0.30	44	Np	0.7325	78	Tl	1.56
10	K	0.35	45	U	0.735	79	In	1.60
11	Na	0.40	46	Pa	0.7375	80	Al	1.66
12	Li	0.45	47	Th	0.74	81	Ga	1.68
13	Ra	0.48	48	Ac	0.7425	82	Pb	1.80
14	Ba	0.50	49	Zr	0.76	83	Sn	1.84
15	Sr	0.55	50	Hf	0.775	84	Ge	1.90
16	Ca	0.60	51	Ti	0.79	85	Si	1.94
17	Yb	0.645	52	Nb	0.82	86	B	2.00
18	Eu	0.655	53	Ta	0.83	87	Bi	2.04
19	Y†	0.66	54	V	0.84	88	Sb	2.08
20	Sc	0.67	55	Mo	0.88	89	As	2.16
21	Lu	0.675	56	W	0.885	90	P	2.18
22	Tm	0.6775	57	Cr	0.89	91	Po	2.28
23	Er	0.68	58	Tc	0.935	92	Te	2.32
24	Ho	0.6825	59	Re	0.94	93	Se	2.40
25	Dy	0.685	60	Mn	0.945	94	S	2.44
26	Tb	0.6875	61	Fe	0.99	95	C	2.50
27	Gd	0.69	62	Os	0.995	96	At	2.52
28	Sm	0.6925	63	Ru	1.00	97	I	2.56
29	Pm	0.695	64	Co	1.04	98	Br	2.64
30	Nd	0.6975	65	Ir	1.05	99	Cl	2.70
31	Pr	0.70	66	Rh	1.06	100	N	3.00
32	Ce	0.7025	67	Ni	1.09	101	O	3.50
33	La	0.705	68	Pt	1.105	102	F	4.00
34	Lw	0.7075	69	Pd	1.12	103	H	5.00
35	No	0.71						

† The structure maps would be marginally improved by inserting Y between Ho and Dy as suggested by their relative core sizes (cf table 17.7 of Wells (1975)).

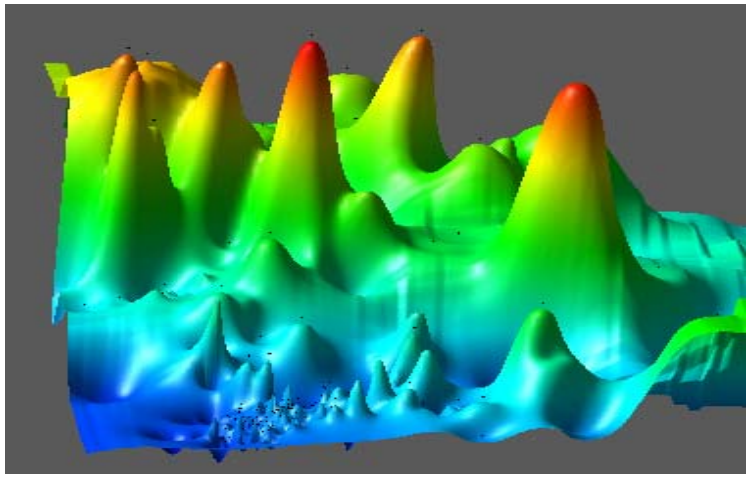


Pettifor diagram for AB compounds

Exciting statistics (Baur & Kassner, 1992)

Space-group No.	Space-group symbol	Frequency (inorganic)	Frequency (organic)
1	$P1$	146	635
2	$P\bar{1}$	1508	8733
3	$P2$	19	8
4	$P2_1$	224	3278
5	$C2$	156	463
6	Pm	13	1
7	Pc	74	196
8	Cm	80	30
9	Cc	244	501
10	$P2/m$	81	7
11	$P2_1/m$	462	332
12	$C2/m$	1180	254
13	$P2/c$	206	254
14	$P2_1/c$	2827	18885
15	$C2/c$	1326	3585
16	$P222$	14	3
17	$P222_1$	17	4
18	$P2_12_12$	62	271
19	$P2_12_12_1$	380	5679
20	$C222_1$	53	117
21	$C222$	18	4
22	$F222$	6	0
23	$I222$	8	14
24	$I2_12_12_1$	2	1
25	$Pmm2$	15	1
26	$Pmc2_1$	55	11
27	$Pcc2$	0	1
28	$Pma2$	18	1
29	$Pca2_1$	109	387
30	$Pnc2$	6	8
31	$Pmn2_1$	146	40
32	$Pba2$	26	16
33	$Pna2_1$	369	840
34	$Pnn2$	25	18
35	$Cmm2$	9	1
36	$Cmc2_1$	237	93
37	$Ccc2$	3	9
38	$Amm2$	52	1
39	$Abm2$	9	6
40	$Ama2$	38	12
41	$Aba2$	40	46
42	$Fmm2$	13	11
43	$Fdd2$	126	176
44	$Imm2$	49	7
45	$Iba2$	3	44
46	$Ima2$	26	5
47	$Pmmm$	212	0
48	$Pnnn$	2	3
49	$Pccm$	2	1
50	$Pban$	10	2
51	$Pmma$	57	7
52	$Pnna$	49	49
53	$Pmna$	27	8
54	$Pcca$	23	17
55	$Pbam$	265	13
56	$Pccn$	50	178
57	$Pbcm$	121	78
58	$Pnnm$	272	49
59	$Pmmn$	119	26
60	$Pbcn$	266	519
61	$Pbca$	466	2189
62	$Pnma$	2863	811
63	$Cmcm$	677	86
64	$Cmca$	218	77
65	$Cmmm$	103	4
66	$Cccm$	46	7
67	$Cmma$	23	2
68	$Ccca$	16	13
69	$Fmmm$	50	3
70	$Fddd$	111	47
71	$Immm$	190	3
72	$Ibam$	99	25
73	$Ibca$	15	15
74	$Imma$	140	5
75	$P4$	18	2
76	$P4_1$	21	79
77	$P4_2$	8	5
78	$P4_3$	4	24
79	$I4$	19	16
80	$I4_1$	5	13
81	$P\bar{4}$	12	11
82	$I\bar{4}$	149	76
83	$P4/m$	19	1
84	$P4_2/m$	20	8
85	$P4/n$	58	54
86	$P4_2/n$	56	87
87	$I4/m$	149	29
88	$I4_1/a$	179	153
89	$P422$	1	1
90	$P42_12$	5	3
91	$P4_122$	6	2
92	$P4_12_12$	87	160
93	$P4_222$	0	1
94	$P4_22_12$	13	16
95	$P4_322$	5	2
96	$P4_32_12$	29	65
97	$I422$	12	1
98	$I4_122$	5	2
99	$P4mm$	82	0
100	$P4bm$	23	0
101	$P4_2cm$	0	1
102	$P4_2nm$	15	3
103	$P4cc$	8	0
104	$P4nc$	0	6
105	$P4_2mc$	4	1
106	$P4_2bc$	2	6
107	$I4mm$	31	2
108	$I4cm$	6	4
109	$I4_1md$	22	5
110	$I4_1cd$	12	20
111	$P\bar{4}2m$	23	2
112	$P\bar{4}2c$	8	0
113	$P\bar{4}2_1m$	95	20
114	$P\bar{4}2_1c$	41	76
115	$P\bar{4}m2$	9	2
116	$P\bar{4}c2$	9	2
117	$P\bar{4}b2$	17	4
118	$P\bar{4}n2$	21	14
119	$I\bar{4}m2$	25	3
120	$I\bar{4}c2$	12	3
121	$I\bar{4}2m$	86	19
122	$I\bar{4}2d$	229	26
123	$P4/mmm$	259	2
124	$P4/mcc$	21	8
125	$P4/nbm$	5	0
126	$P4/nnc$	8	9
127	$P4/mbm$	179	4
128	$P4/mnc$	84	3
129	$P4/nmm$	354	10
130	$P4/ncc$	49	16
131	$P4_2/mmc$	22	3
132	$P4_2/mcm$	4	0
133	$P4_2/nbc$	5	4
134	$P4_2/nnm$	15	1
135	$P4_2/mbc$	56	5
136	$P4_2/mnm$	278	16
137	$P4_2/nmc$	43	10
138	$P4_2/ncm$	11	3
139	$I4/mmm$	1176	11
140	$I4/mcm$	343	3
141	$I4_1/amd$	301	8
142	$I4_1/acd$	56	27
143	$P3$	40	11
144	$P3_1$	29	44
145	$P3_2$	5	22
146	$R3$	89	77
147	$P\bar{3}$	78	51
148	$R\bar{3}$	500	235
149	$P312$	14	0
150	$P321$	76	5
151	$P3_112$	12	1
152	$P3_121$	149	56
153	$P3_212$	1	1
154	$P3_221$	31	21
155	$R32$	69	19
156	$P3m1$	104	0
157	$P31m$	31	2
158	$P3c1$	8	7
159	$P31c$	46	11
160	$R3m$	223	23
161	$R3c$	98	62
162	$P\bar{3}1m$	55	0
163	$P\bar{3}1c$	50	21
164	$P\bar{3}m1$	586	9
165	$P\bar{3}c1$	86	20
166	$R\bar{3}m$	858	18
167	$R\bar{3}c$	458	57
168	$P6$	3	0
169	$P6_1$	16	35
170	$P6_5$	9	27
171	$P6_2$	1	4
172	$P6_4$	0	2
173	$P6_3$	189	34
174	$P\bar{6}$	100	1
175	$P6/m$	14	0
176	$P6_3/m$	419	89
177	$P622$	11	0
178	$P6_122$	4	9
179	$P6_522$	0	4
180	$P6_222$	61	3
181	$P6_422$	11	0
182	$P6_322$	36	2
183	$P6mm$	0	1
184	$P6cc$	1	0
185	$P6_3cm$	48	1
186	$P6_3mc$	308	15
187	$P\bar{6}m2$	56	0
188	$P\bar{6}c2$	29	0
189	$P\bar{6}2m$	237	1
190	$P\bar{6}2c$	40	11
191	$P6/mmm$	498	1
192	$P6/mcc$	67	2
193	$P6_3/mcm$	216	0
194	$P6_3/mmc$	1254	11
195	$P23$	16	0
196	$F23$	49	1
197	$I23$	56	3
198	$P2_13$	163	31
199	$I2_13$	45	1
200	$Pm\bar{3}$	27	0
201	$Pn\bar{3}$	45	0
202	$Fm\bar{3}$	37	2
203	$Fd\bar{3}$	34	1
204	$Im\bar{3}$	100	3
205	$Pa\bar{3}$	210	49
206	$Ia\bar{3}$	60	3
207	$P432$	2	0
208	$P4_232$	12	0
209	$F432$	6	2
210	$F4_132$	7	1
211	$I432$	5	0
212	$P4_332$	34	2
213	$P4_132$	17	3
214	$I4_132$	10	0
215	$P\bar{4}3m$	89	3
216	$F\bar{4}3m$	352	1
217	$I\bar{4}3m$	144	15
218	$P\bar{4}3n$	88	8
219	$F\bar{4}3c$	24	7
220	$I\bar{4}3d$	277	6
221	$Pm\bar{3}m$	506	9
222	$Pn\bar{3}n$	3	0
223	$Pm\bar{3}n$	53	1
224	$Pn\bar{3}m$	25	3
225	$Fm\bar{3}m$	1532	10
226	$Fm\bar{3}c$	28	0
227	$Fd\bar{3}m$	1050	5
228	$Fd\bar{3}c$	19	5
229	$Im\bar{3}m$	91	10
230	$Ia\bar{3}d$	251	1

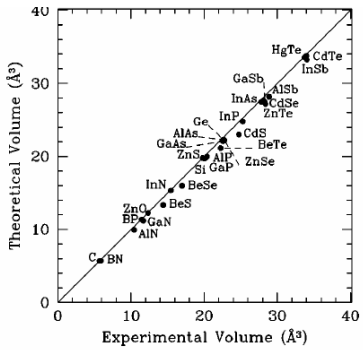
To predict stable structure, we combine global optimization with density-functional calculations



Task: find structure with lowest possible thermodynamic potential:

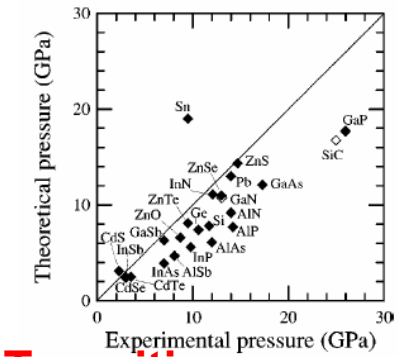
- ***E***
- ***H=E+PV***
- ***F=E-TS***
- ***G=E+PV-TS***

Approximate density functionals (LDA, GGA) in many cases have sufficient accuracy



Volumes

LDA: Mujica‘03



Transition pressures

LDA: Mujica‘03

Crystal structure prediction: major unsolved problem.

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

Are Crystal Structures Predictable?

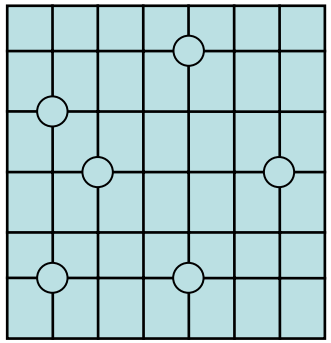
ANGELO GAVEZZOTTI*

"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

Need to find GLOBAL energy minimum.

Trying all structures is impossible:

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

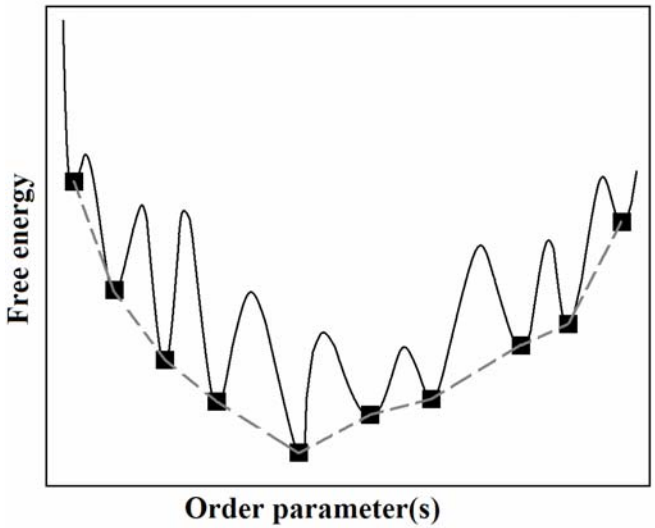


N_{atoms}	Variants	CPU time
1	**1**	**1 sec.**
10	**10^{11}**	**10^{3} yrs.**
20	**10^{25}**	**10^{17} yrs.**
30	**10^{39}**	**10^{31} yrs.**

Crystal structure prediction: What are we facing?

- **Find lowest free energy structure from chemical composition**
- **High-dimensional problem. Dimensionality $d = 3N + 3$.**
- **Very sensitive to small changes**
- **Thus: HUGE and 'noisy' search space**

- **Don't have to search the whole configuration space**
- **Global minimum surrounded by many very good local minima**
- **Can assume some overall shape to which we can tune an approach**
- **Can easily calculate the energies from first principles**



Example of a (very) simple landscape

After local optimization intrinsic dimensionality of landscape is reduced:

$d^* = 3N + 3 - \kappa$

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 $Mg_4N_4H_4$.

Complexity $C \sim \exp(\beta d^*)$

[Valle & ARO, in press (2010)]

Random sampling
(Freeman & Catlow, 1992; 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.
- No „learning“ - only current position as source of information!

Metadynamics (Martonak, Laio, Parrinello 2003)

- Tabu search with reduced dimensionality

$$G^t(\mathbf{h}) = G(\mathbf{h}) + \sum_{t'<t} We^{\frac{|h-h^{t'}|^2}{2\delta h^2}} \qquad \mathbf{h}^{t+1} = \mathbf{h}^t + \delta h \frac{\phi^t}{|\phi^t|}$$

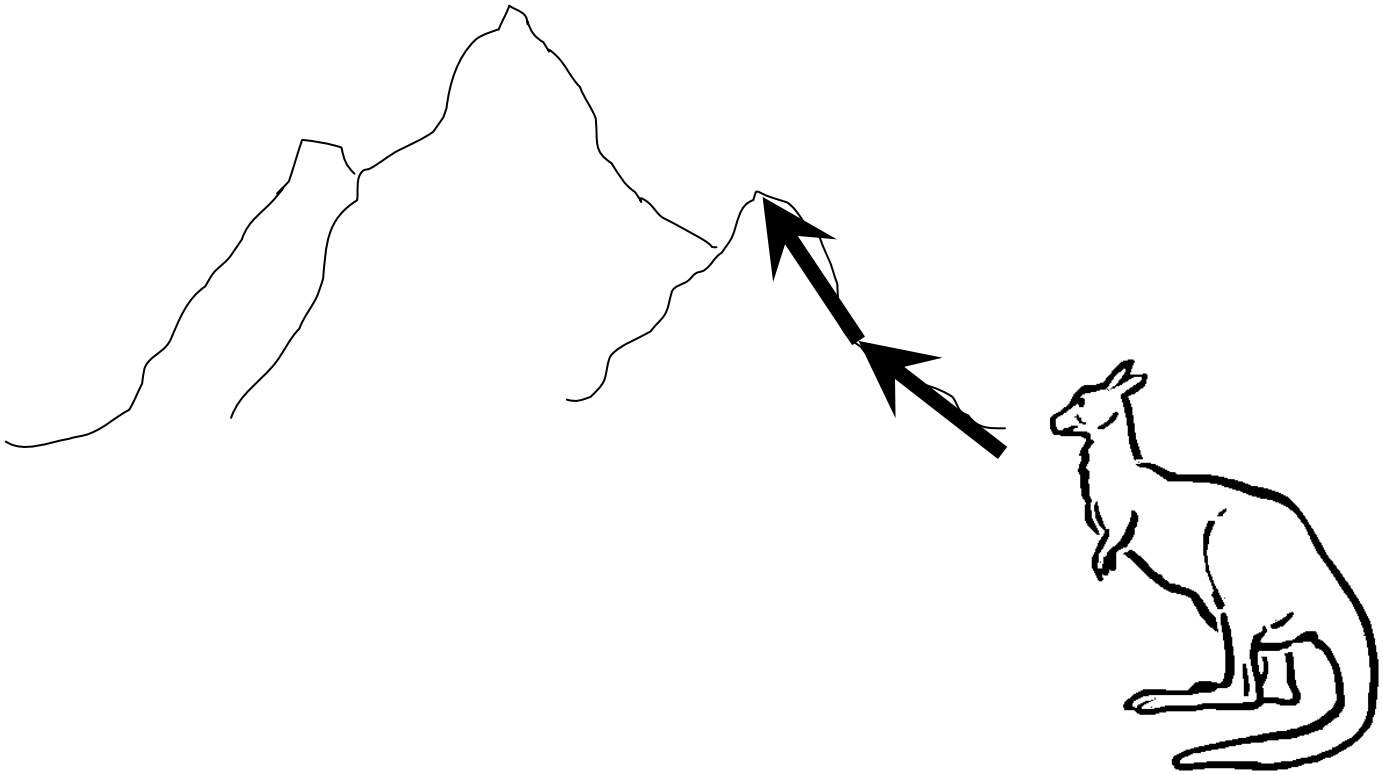
Minima hopping (Gödecker 2004)

- Keep history of visited minima. Escape minima with MD, using feedback to control temperature
- Promising, but so far applied only to clusters.

Evolutionary algorithms

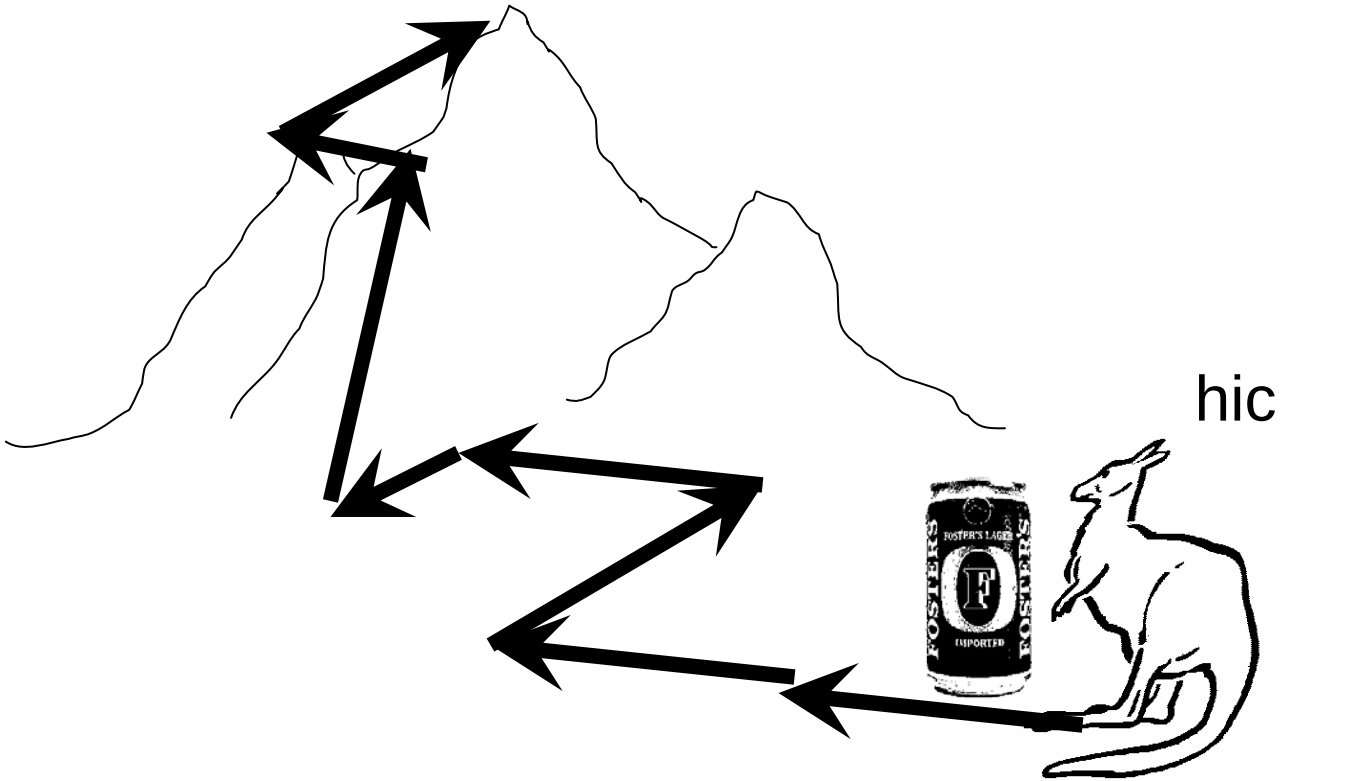
- Balance between exploration and exploitation. „Learning“ power.
- Depend critically on representation, variation operators etc.
- Early methods – Bush (1995), Woodley (2004), Gottwald & Likos (2005).
- Modern algorithm – ARO & Glass (2006).

Global optimisation methods: Kangaroo's climb to Mt. Everest (thanks to R. Clegg)



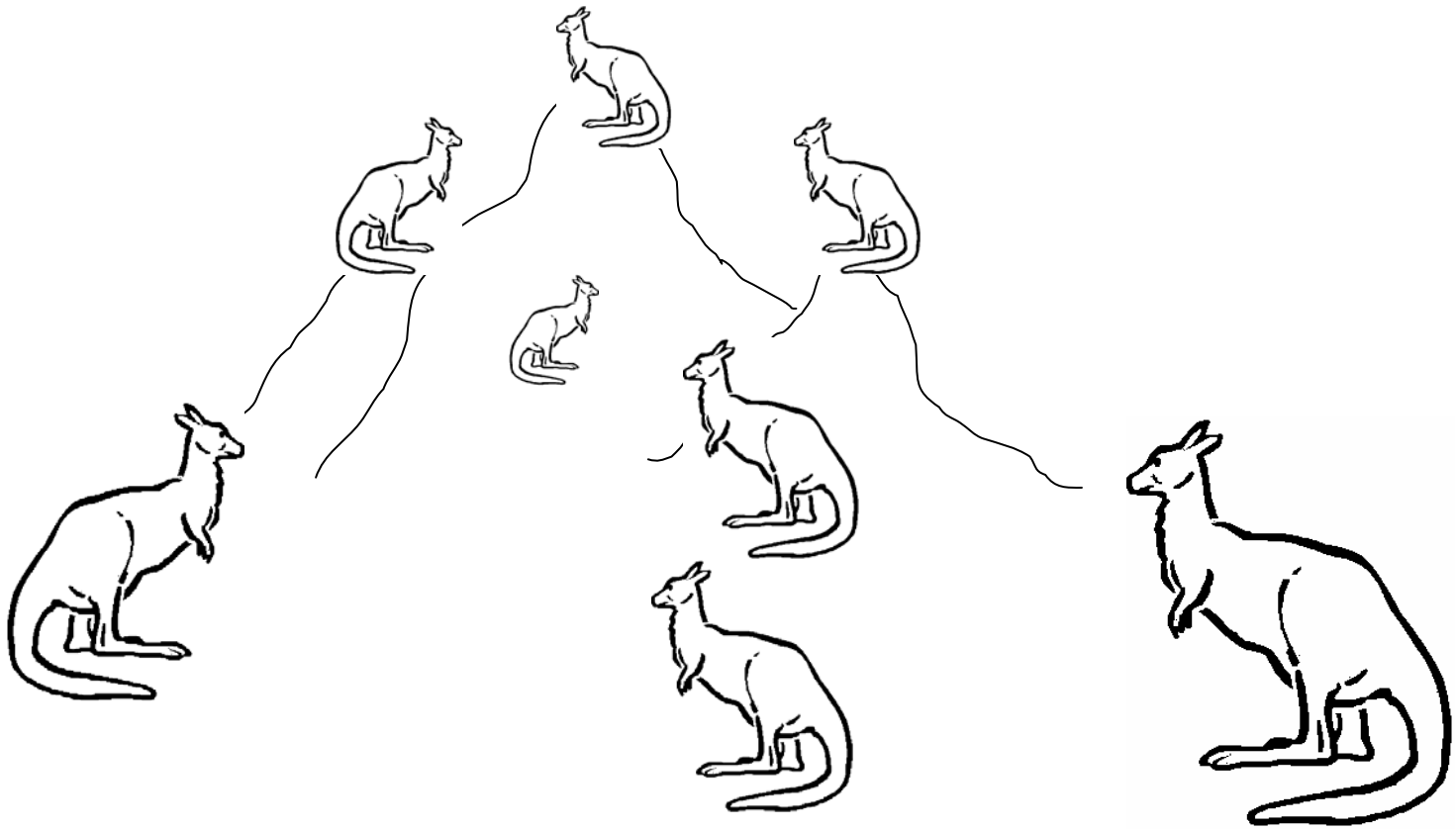
Hill climbing is like dropping a kangaroo somewhere on the surface of the earth, telling it to only hop uphill and hoping it will get to the top of mount Everest.

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



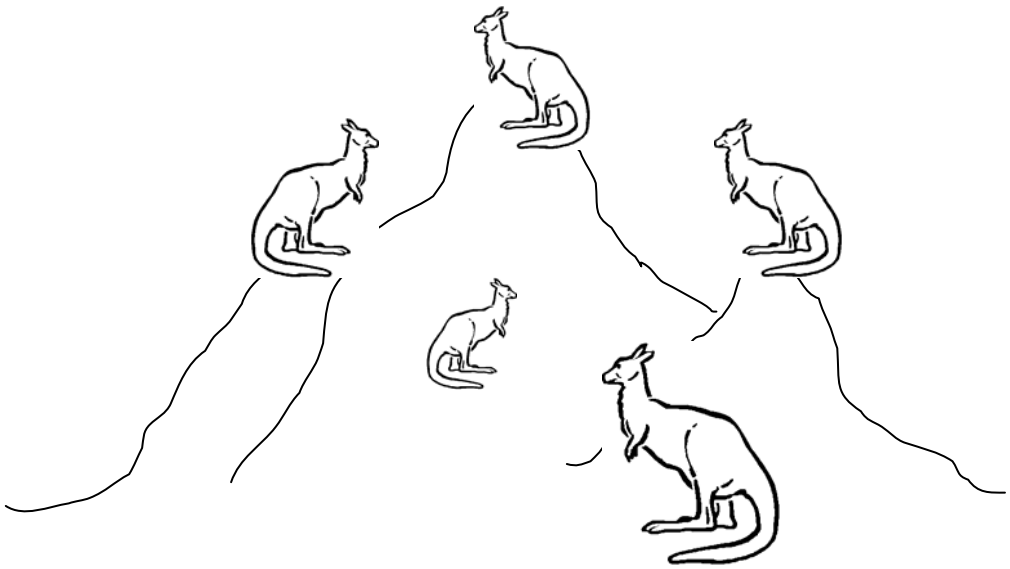
Simulated Annealing is like doing the same but getting the kangaroo very very drunk first.

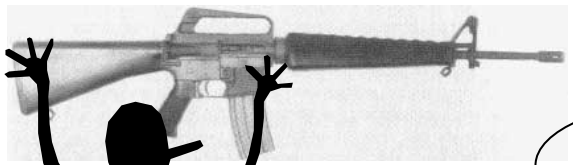
Global optimisation methods: Kangaroo's climb to Mt. Everest

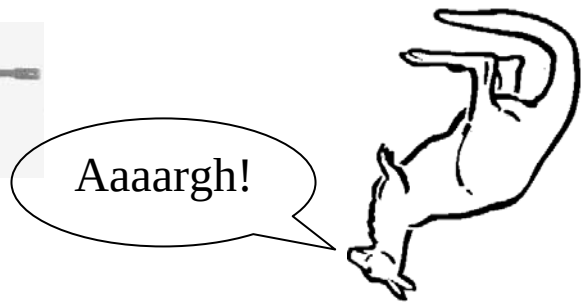


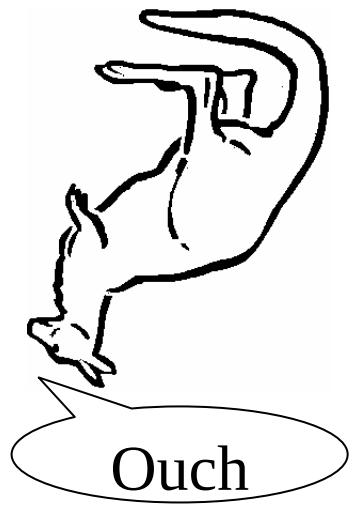
Evolutionary Algorithms are like taking a whole plane load of kangaroos and letting them reproduce freely (not pictured).....

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



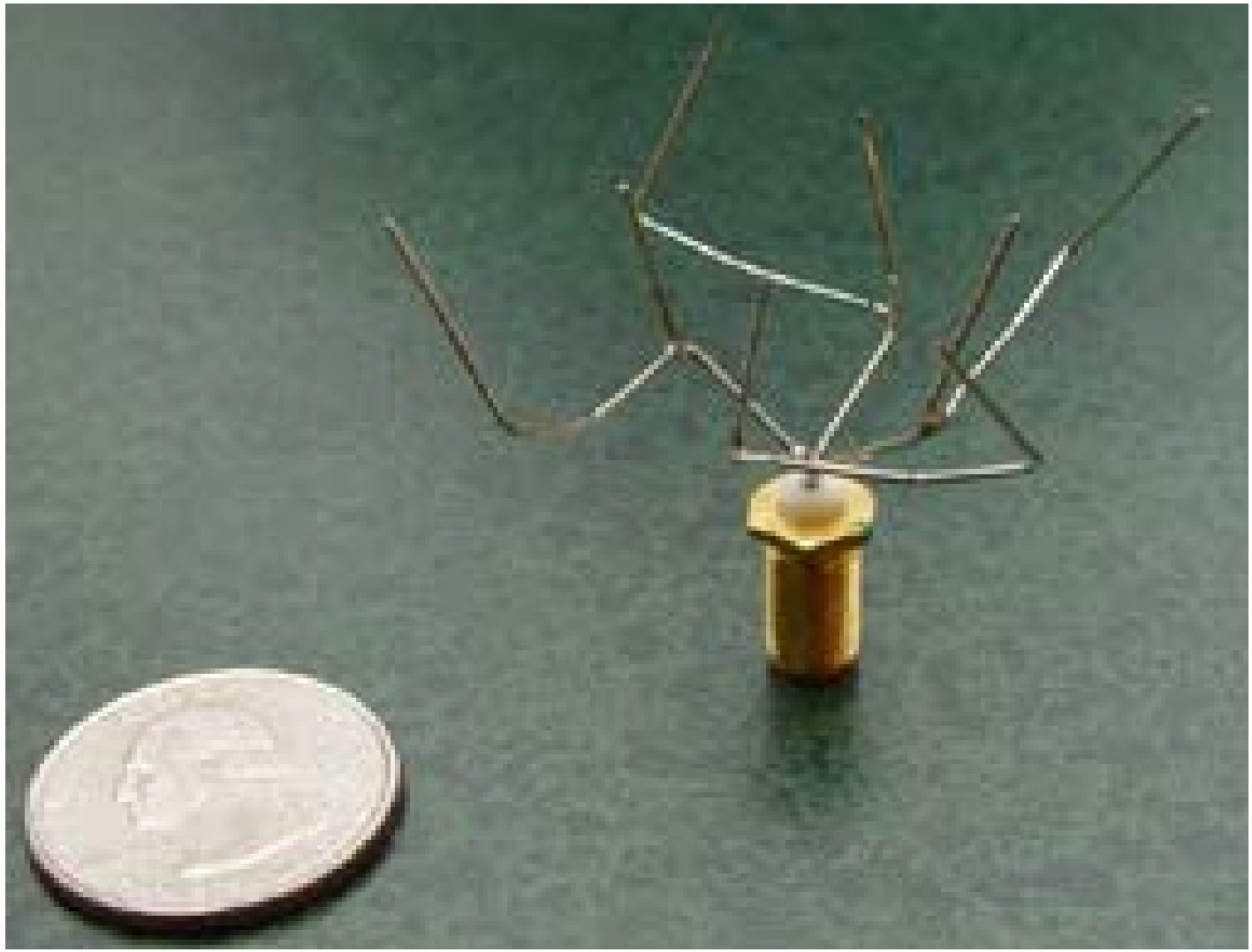






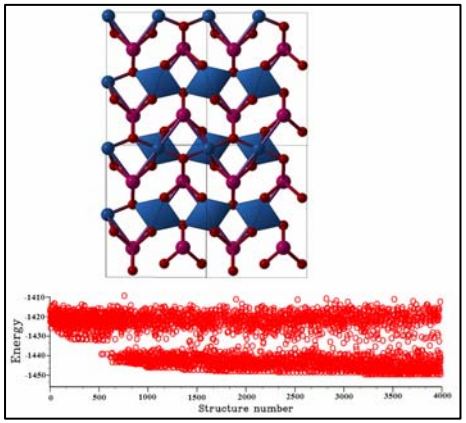
....and regularly shooting the ones at lower altitudes.

NASA:
Antenna designed with an evolutionary algorithm outperforming any human design

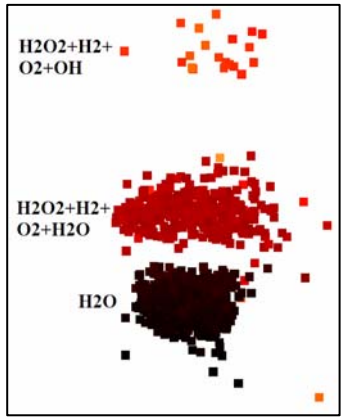


Purely theoretical crystal structure prediction is now possible

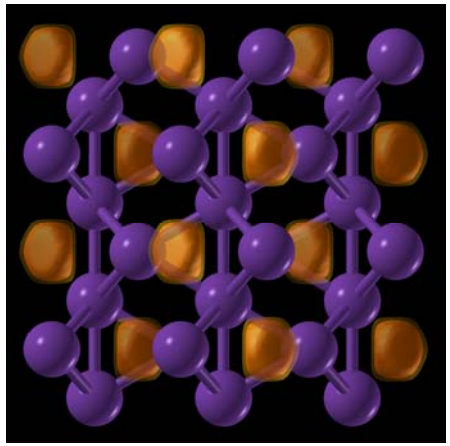
1. Evolutionary algorithm USPEX



2. Analysing results

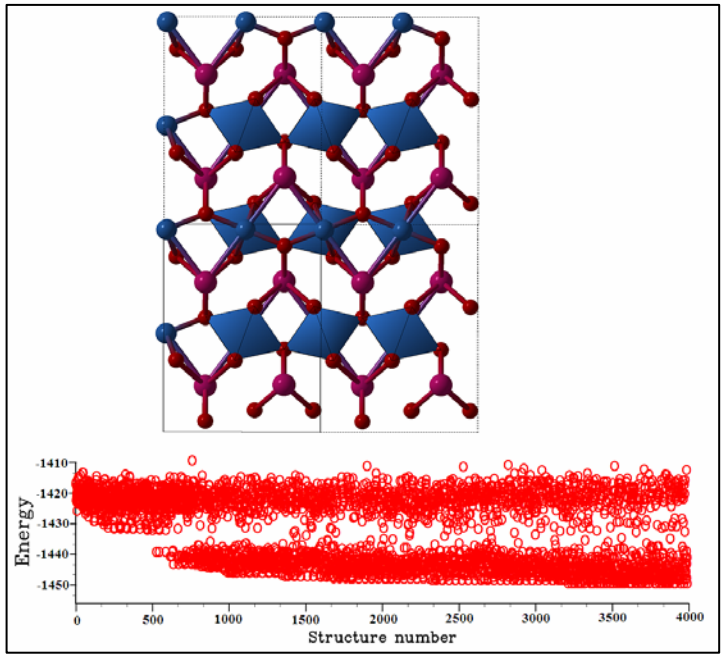


3. Some applications



1. Evolutionary algorithm USPEX

(Universal Structure Predictor: Evolutionary Xtallography)

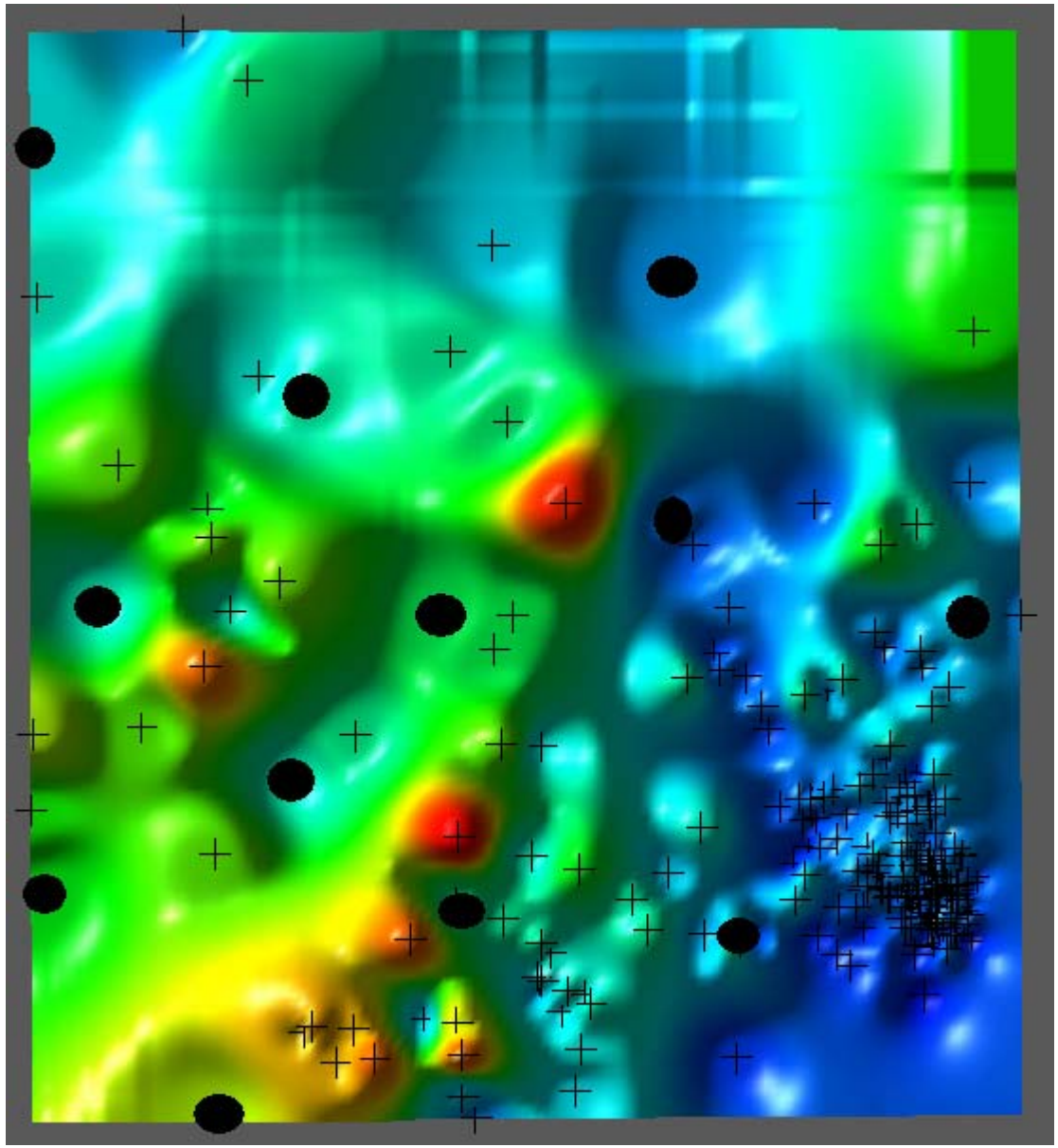


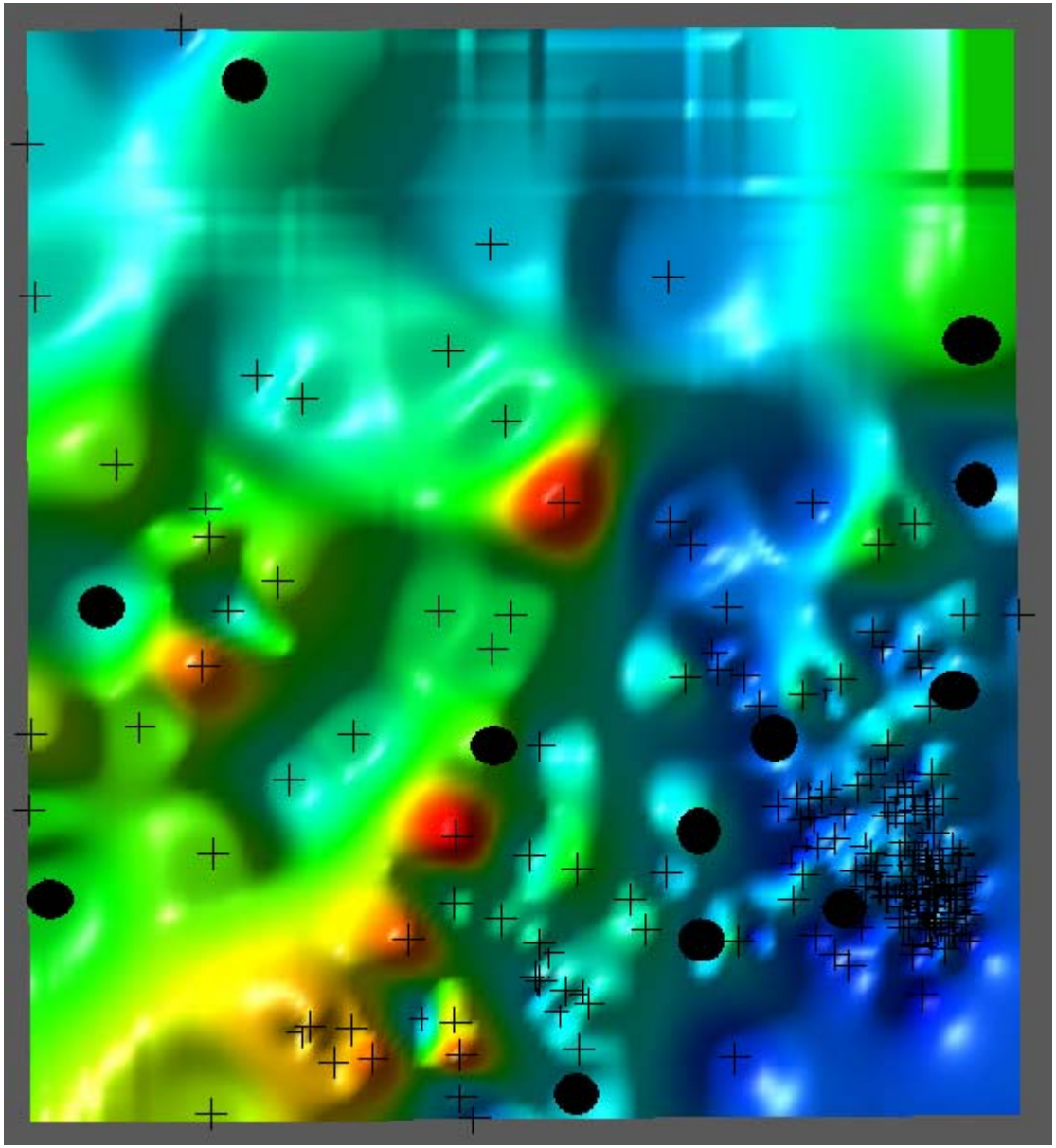
ARO, Glass (2006). *J. Chem. Phys.* **124**, art. 244704.
Glass, ARO, Hansen (2006). *Comp. Phys. Comm.* **175**, 713.

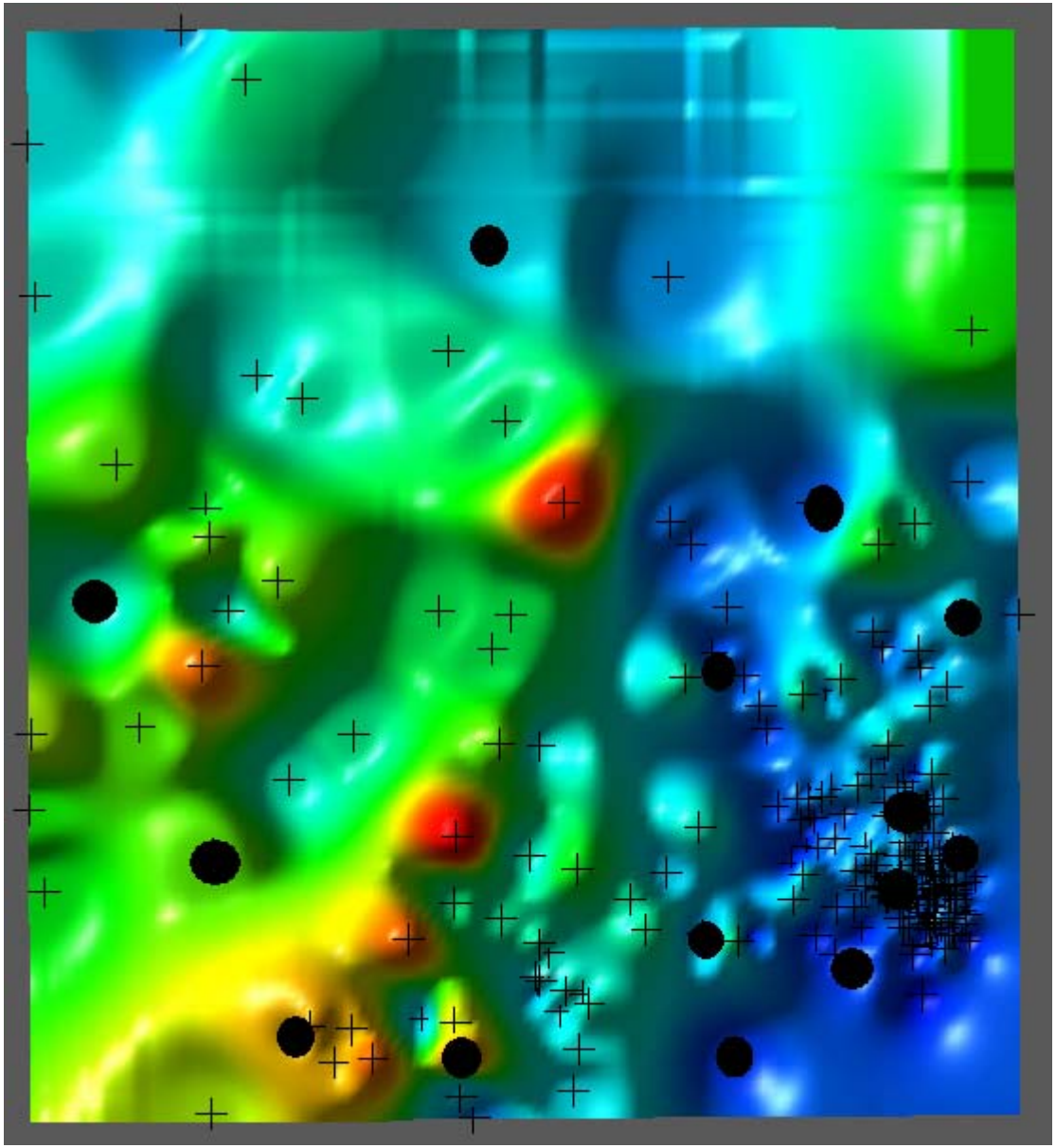
RESEARCH NEWS

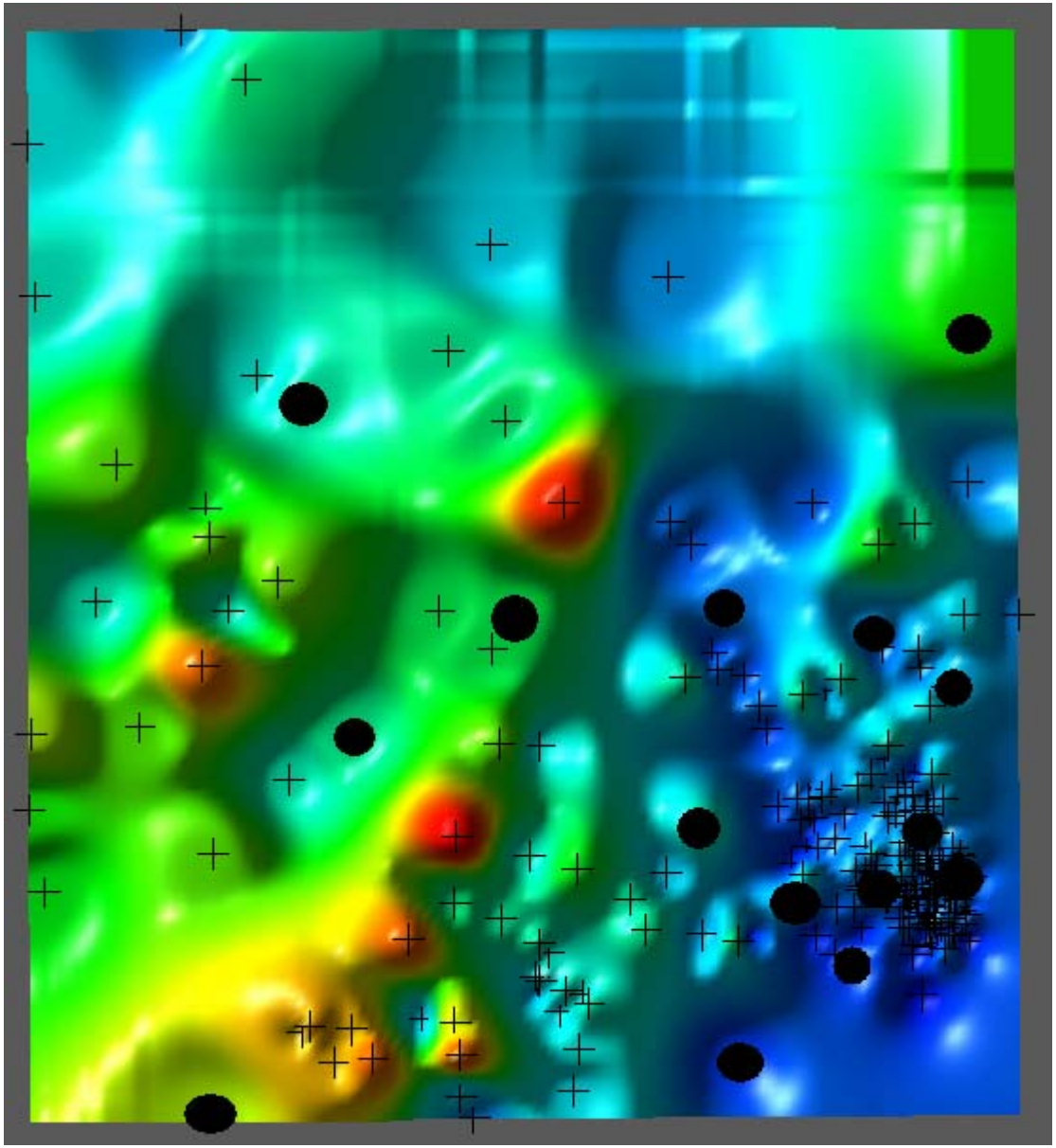
Crystal structure prediction – evolutionary or revolutionary crystallography?

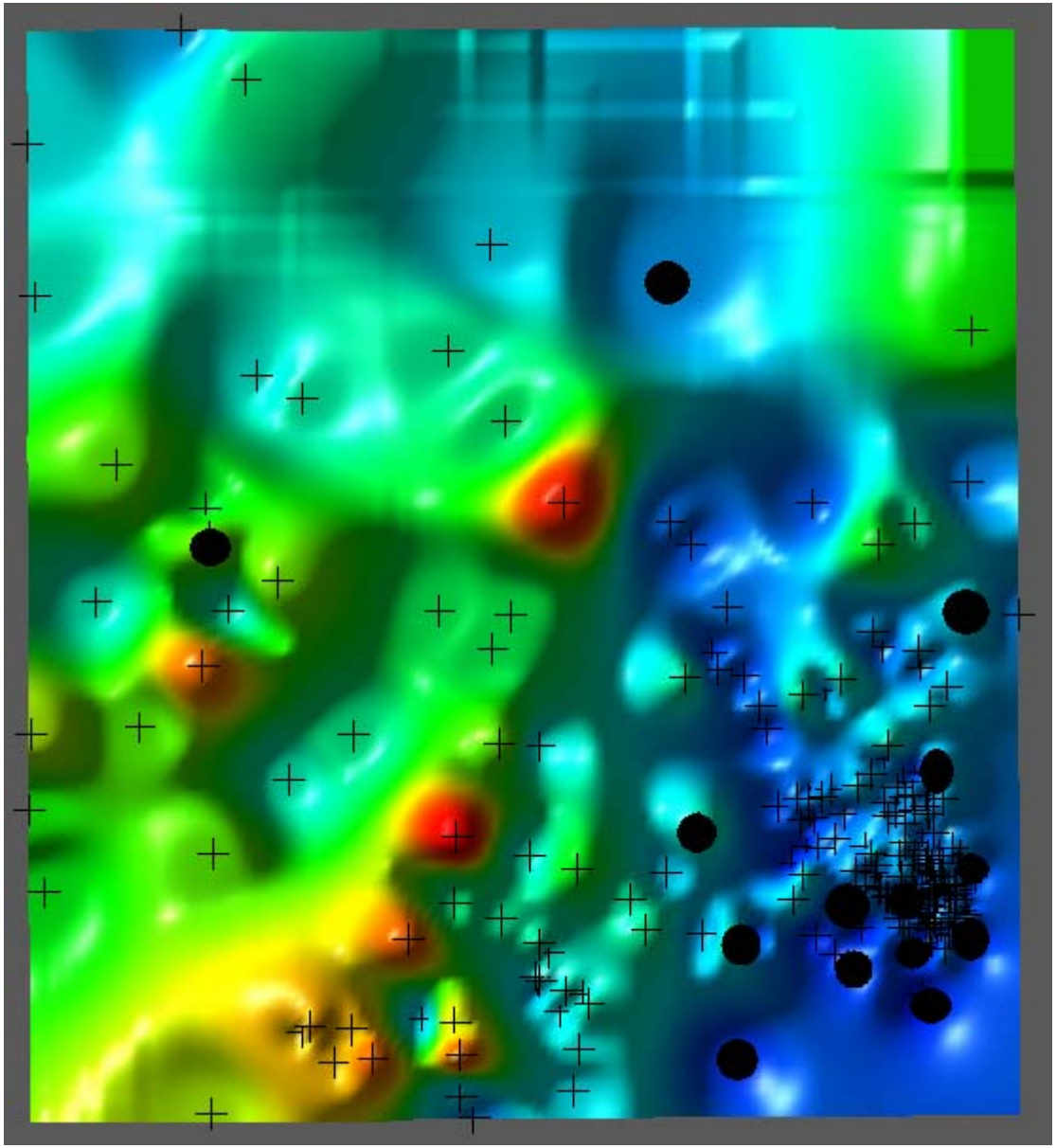
S. L. Chaplot and K. R. Rao CURRENT SCIENCE, VOL. 91, NO. 11, 10 DECEMBER 2006





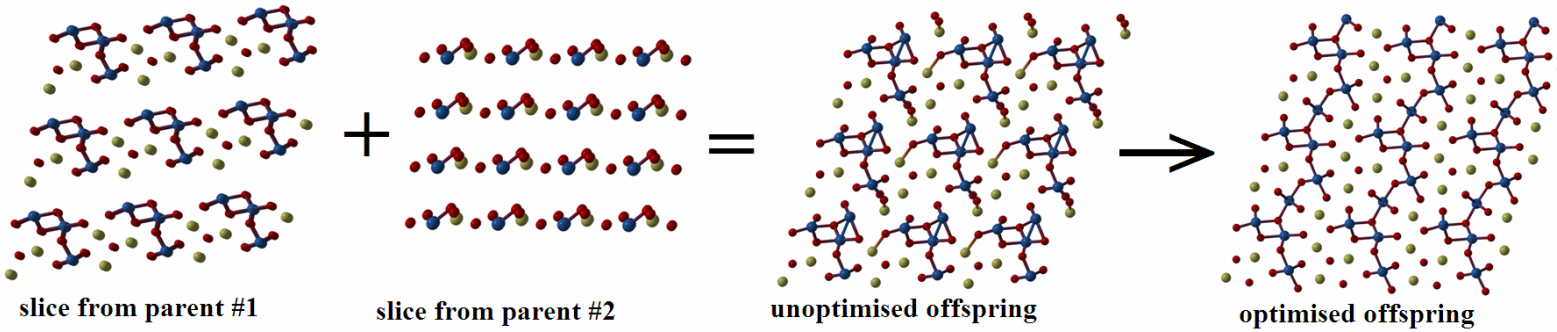




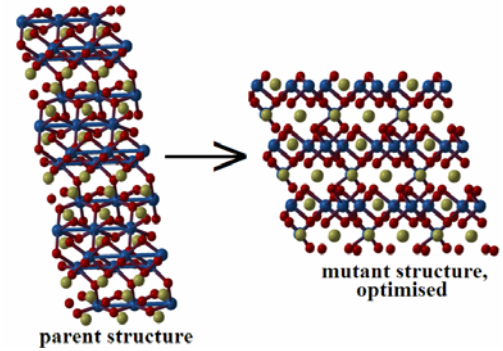


Basics of USPEX

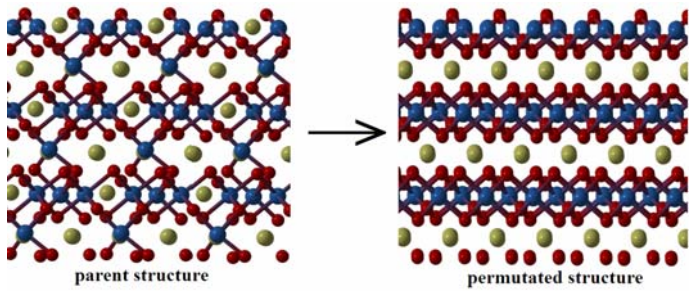
- (Random) initial population
- Preselection to discard unphysical or redundant structures
- Relax all structures (VASP, SIESTA, GULP). Fitness value – relaxed (free) energy
- Select lowest-energy structures as parents for new generation
- Survival of the fittest



(1) Heredity

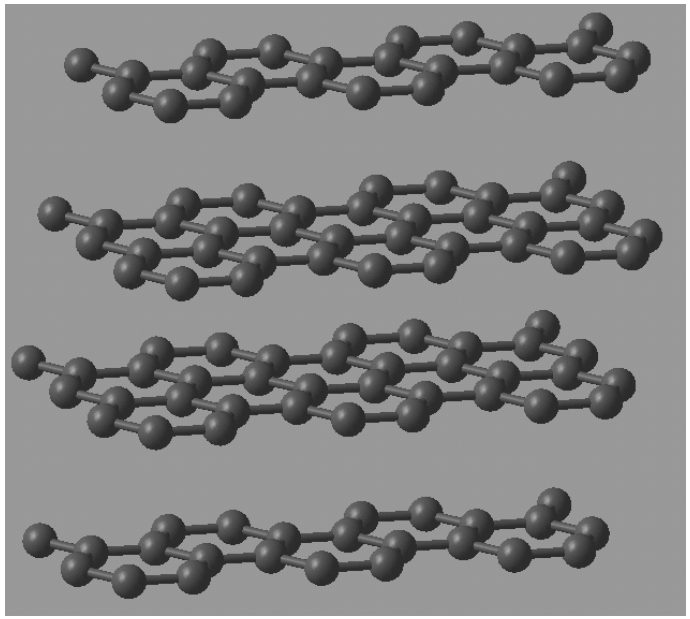


(2) Lattice mutation

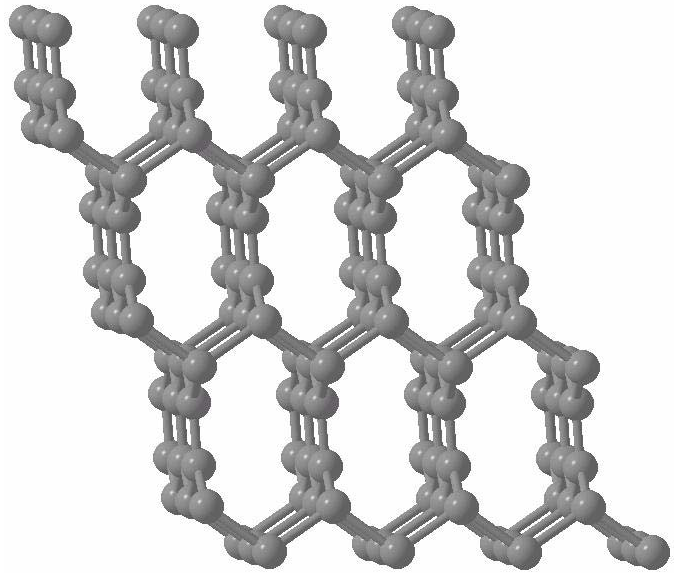


(3) Permutation

Test 1: „Who would guess that graphite is the stable allotrope of carbon at ordinary pressure?“ (Maddox, 1988)

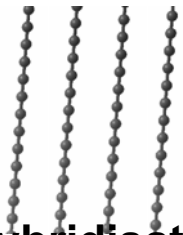


Graphite, correctly predicted to be the stable phase at 1 atm

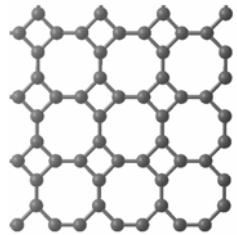


Metastable sp^2 forms, harder than diamond?
First proposed by R.Hoffmann (1983)

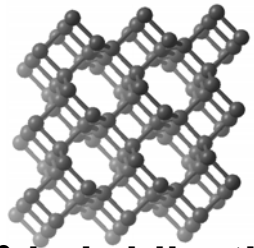
Low-energy structures reveal chemistry



sp-hybridisation (carbyne)



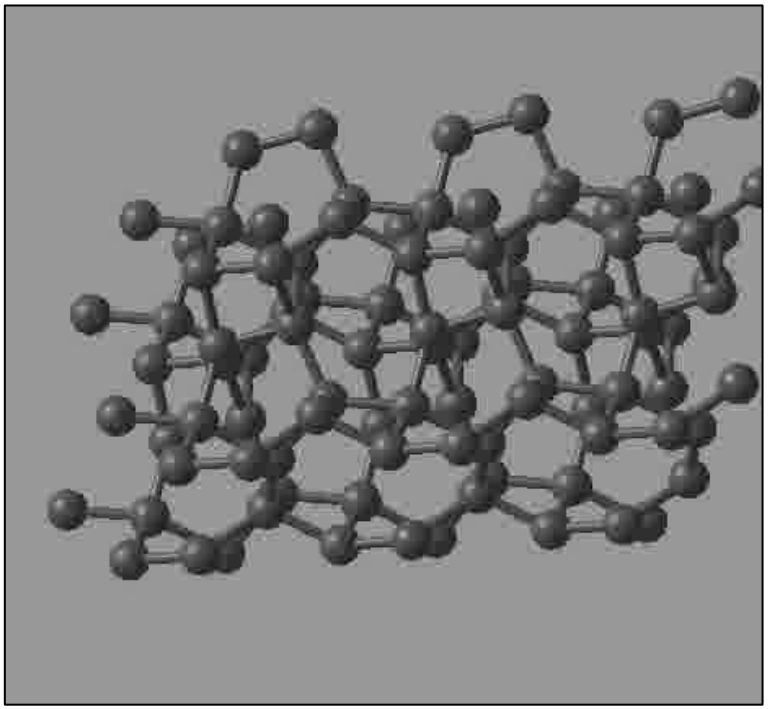
sp^2-hybridisation



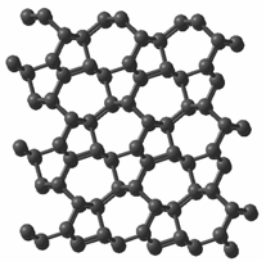
sp^3-hybridisation

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

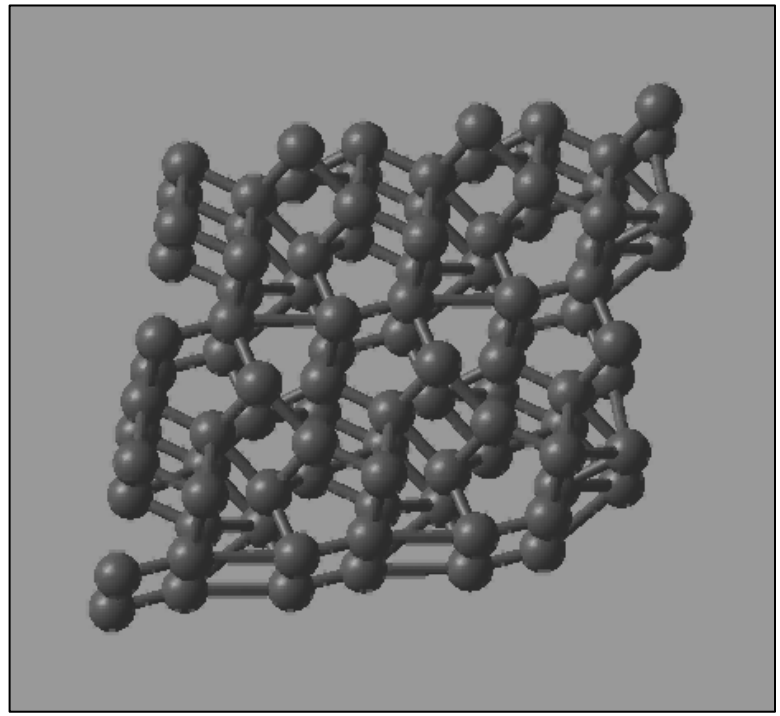
Test 1: High-pressure phases of carbon are also successfully reproduced



100 GPa: diamond is stable



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



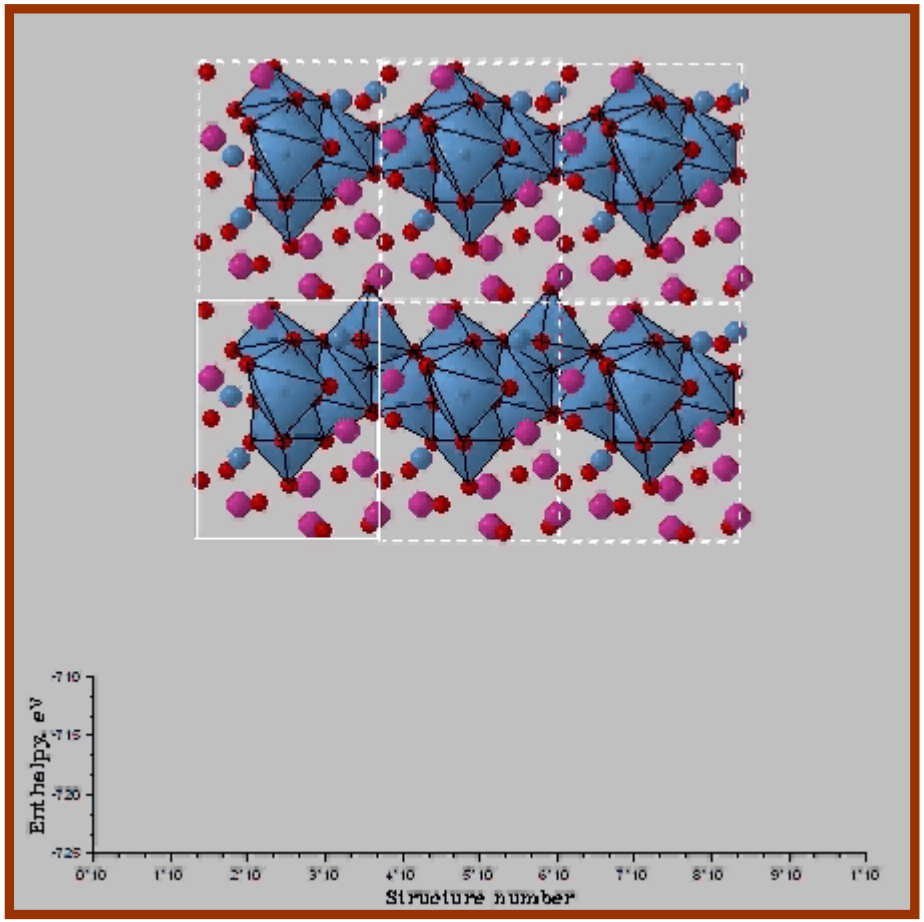
2000 GPa: bc8 phase, potentially important in astrophysics

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

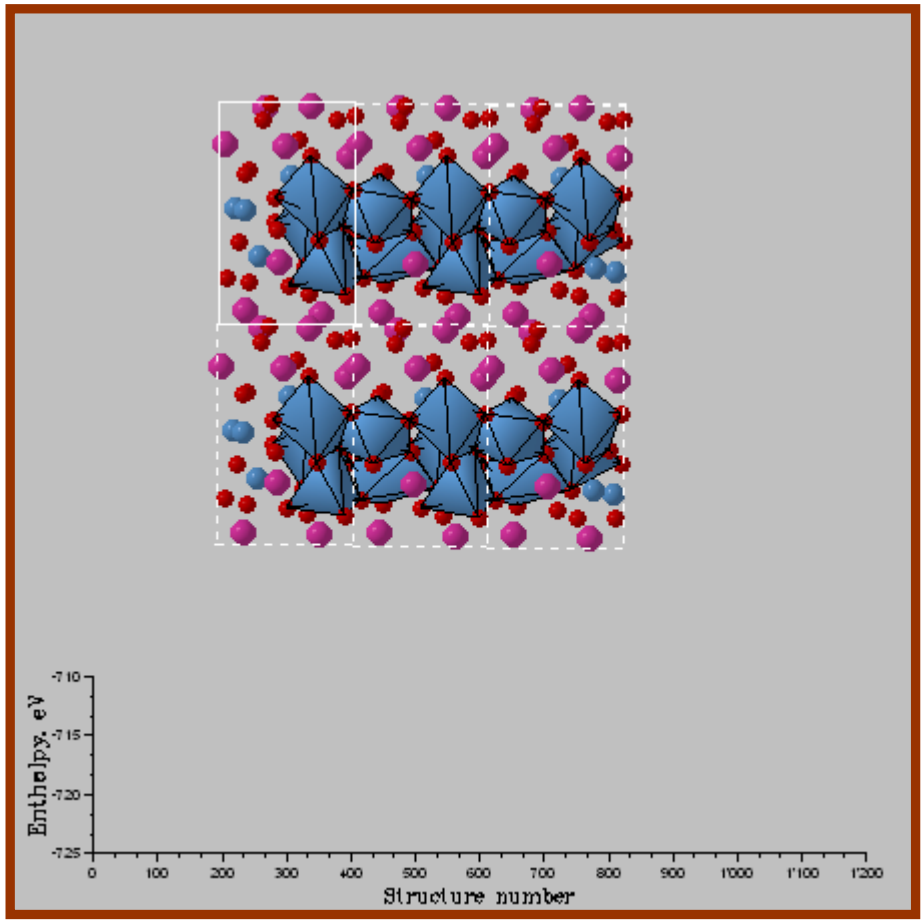
[ARO & Glass, J.Chem.Phys. (2006)]

Test 3: USPEX vs random sampling

Test case: 40-atom cell of $MgSiO_3$ with fixed lattice parameters of post-perovskite



Random structures, all locally optimised
Did NOT find PPV after 120000 steps

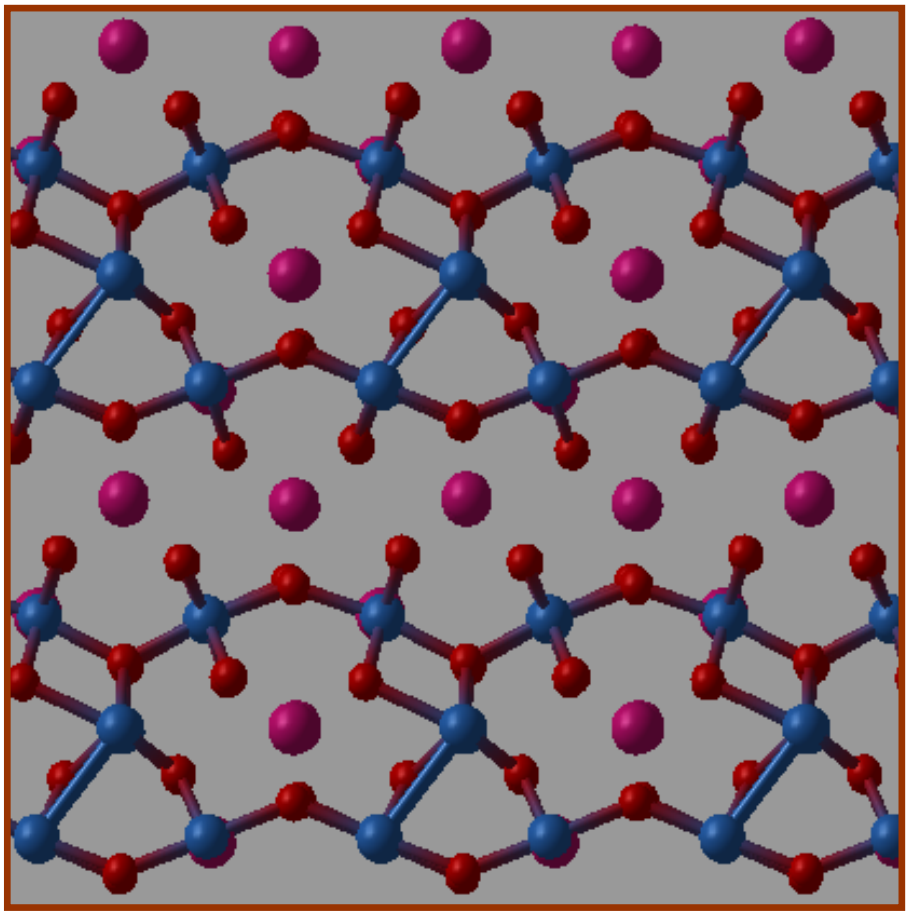


Search with USPEX
Found PPV after 600-950 steps

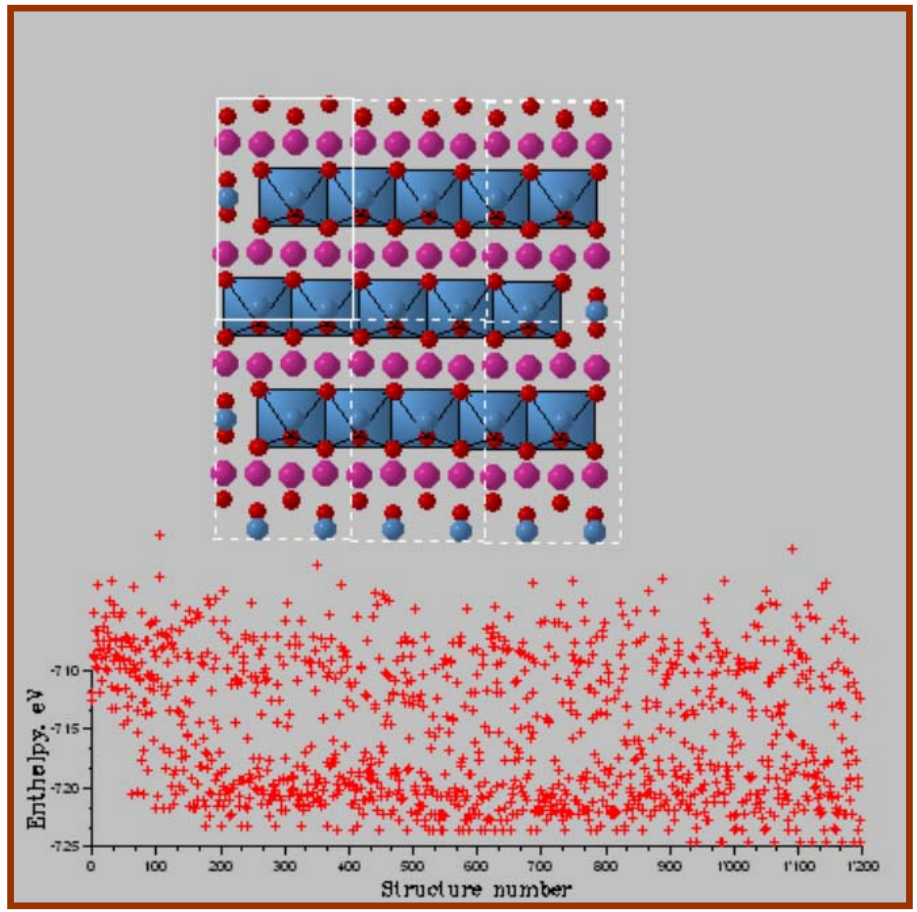
[Martonak, ARO & Glass, Phase Transitions (2007)]

Test 3: USPEX is self-learning, self-improving

Test case: 40-atom cell of $MgSiO_3$ with fixed lattice parameters of post-perovskite



Best structure obtained after 120000 steps Is *not* PPV



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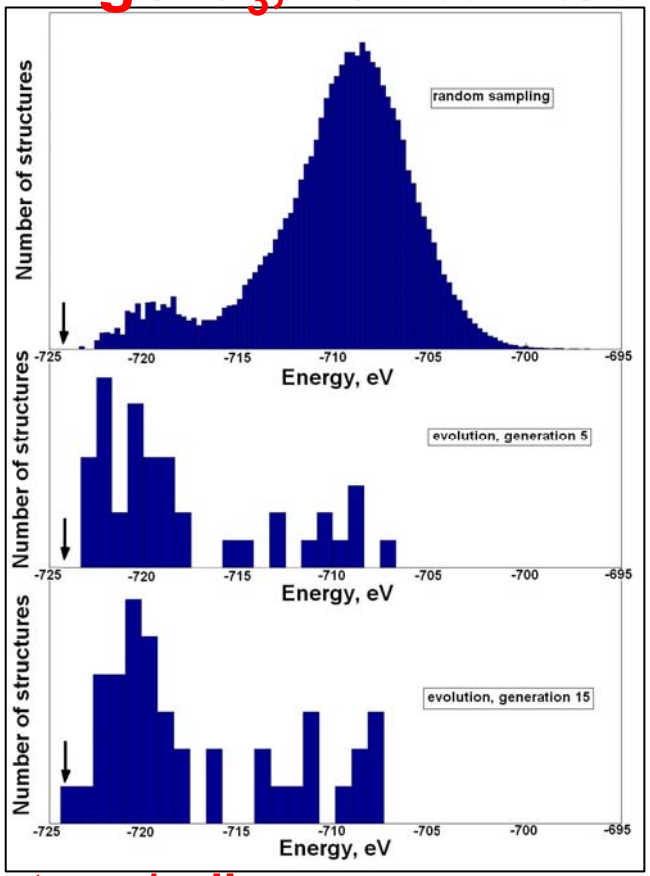
[Martonak, ARO & Glass, Phase Transitions (2007)]

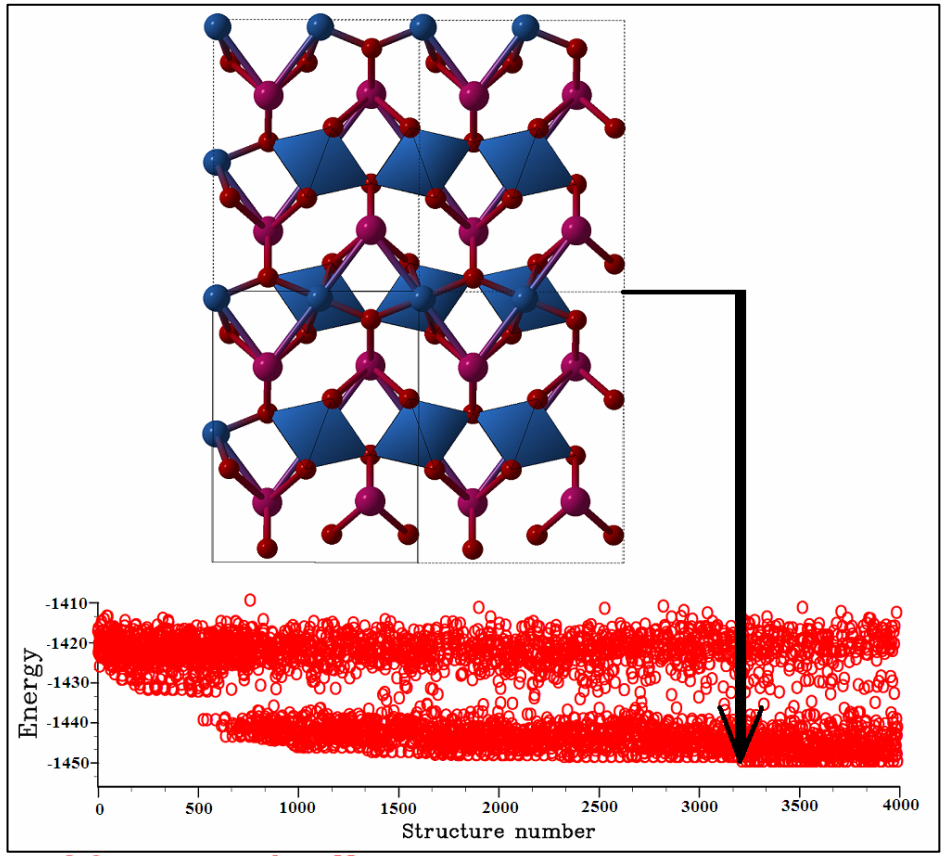
Test 3: USPEX is self-learning, self-improving

$MgSiO_3$, 40 atoms/cell



40 atoms/cell. Ground state not found among 120‘000 random structures, but takes 600-950 structures with USPEX

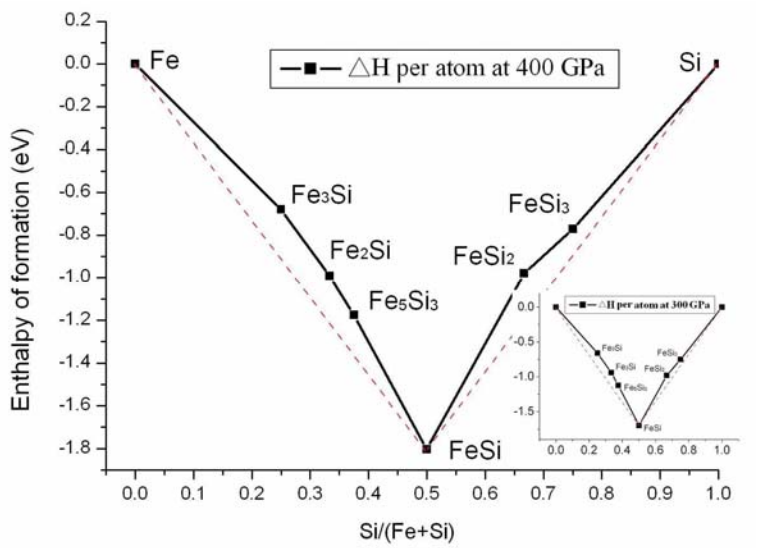
$MgSiO_3$, 80 atoms/cell

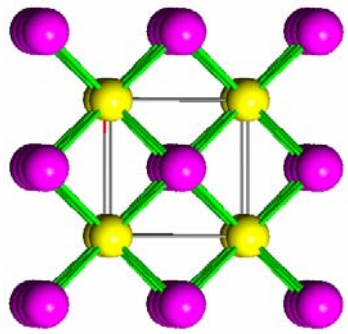


80 atoms/cell. Evolutionary runs take only ~3200 structures to find the ground state

[ARO & Glass, J. Phys. C (2008)]

Multicomponent systems: B2-FeSi is the only stable compound in the Fe-Si system at inner core pressures



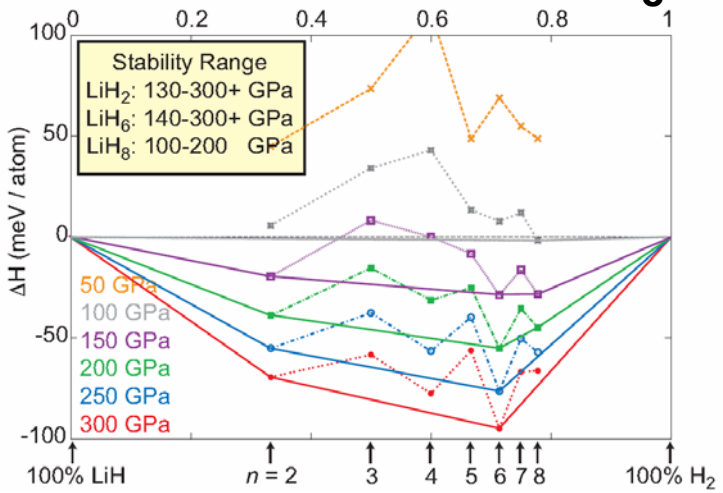


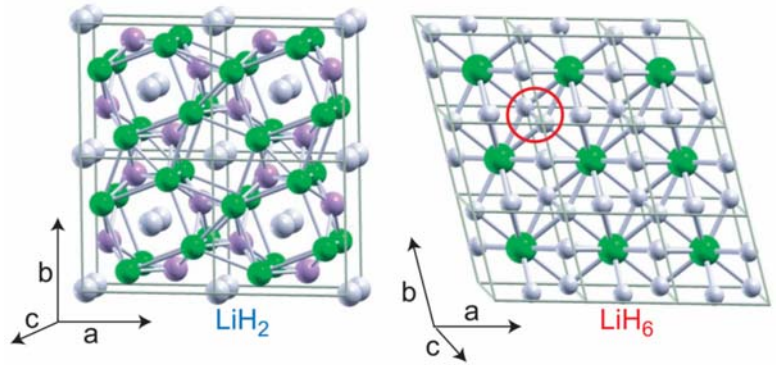
Fe-Si

[Zhang & ARO, in press (2009)]

Surprise: LiH is unstable above 100 GPa. LiH_8, LiH_6 and LiH_2 are

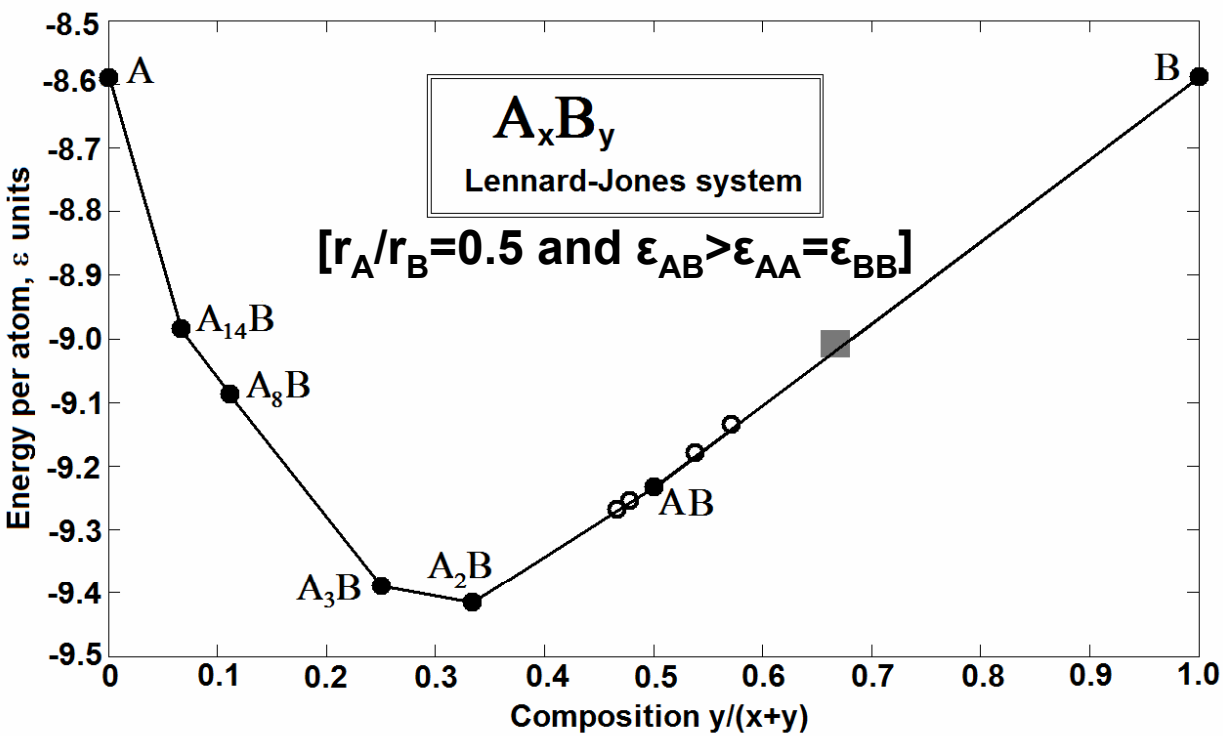
Li-H

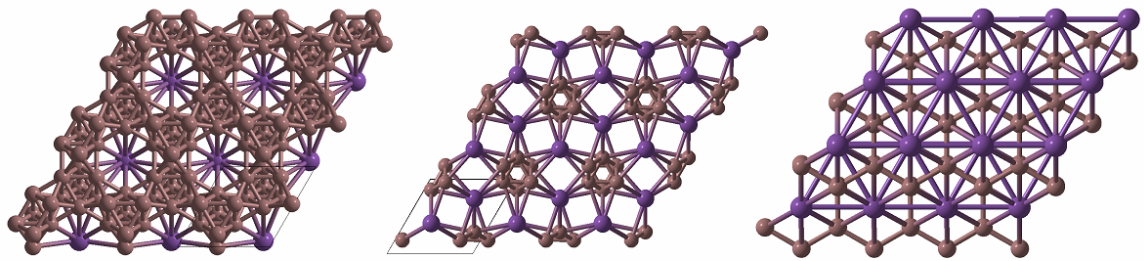




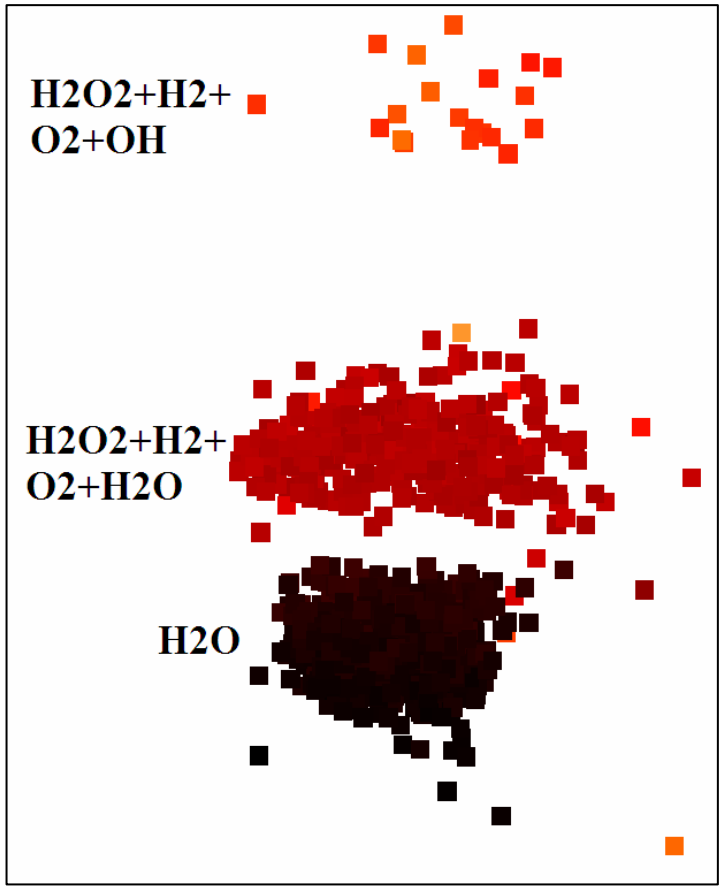
[Zurek, Hoffmann, Ashcroft, ARO, Lyakhov, PNAS 106, 17640-17643 (2009)]

Extension: Simultaneous "single-shot" prediction of structures and compositions is possible





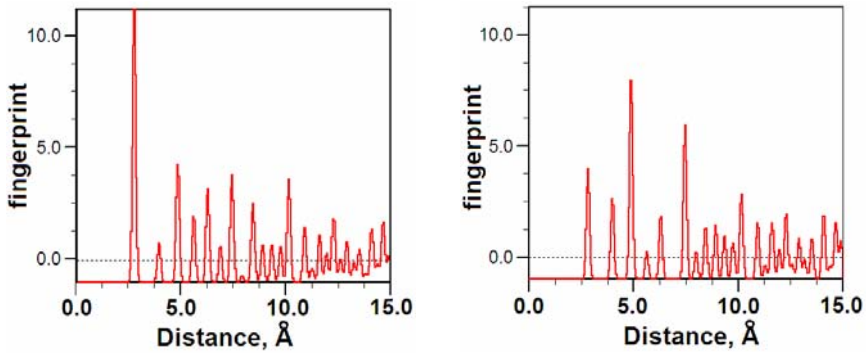
2. Analysing the method and its results



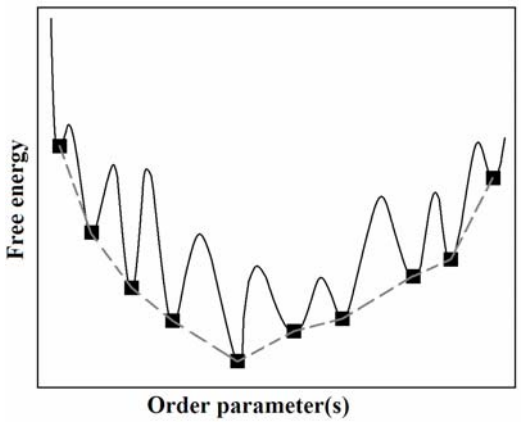
ARO & Valle, J.Chem.Phys. (2009)

Fingerprinting method is the basis of our analysis

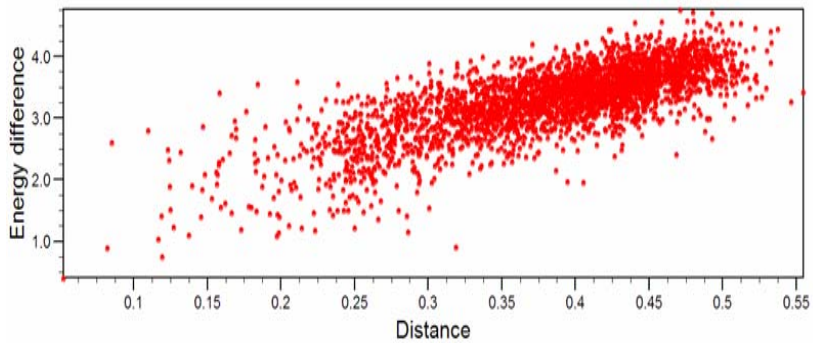
Fingerprint function is a 1D-descriptor of the structure: diffraction spectrum, PCF, ...



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

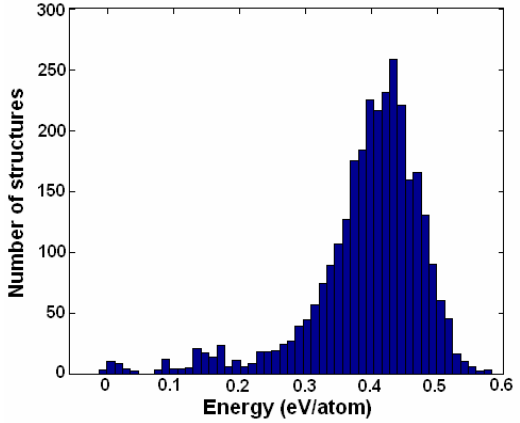


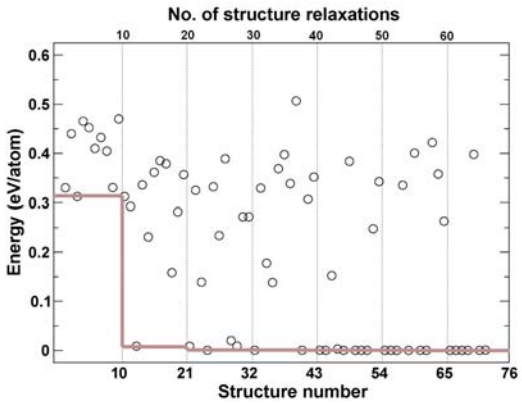
Real system (GaAs): correlation of energy and the distance from the ground-state structure

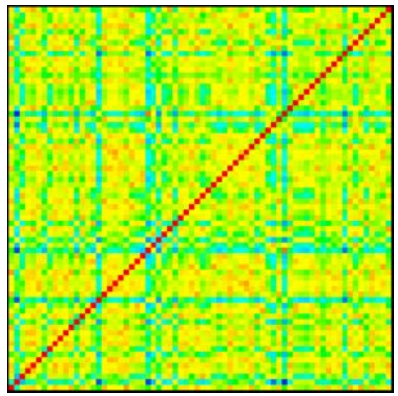
[ARO & Valle, J. Chem. Phys. 130, 104504 (2009)]

The power of learning

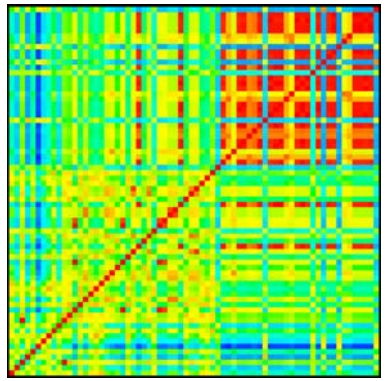
GaAs, 8 atoms/cell







Random sampling



Evolutionary run

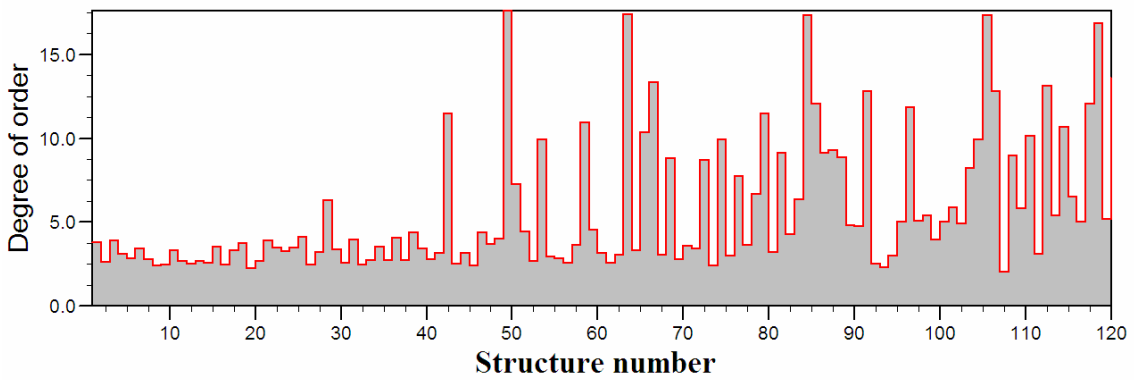
Similarity matrix (Valle'07):

Measure of structural diversity
Symmetric, values in [0;1]
Colour coding: 0-blue, 1-red.

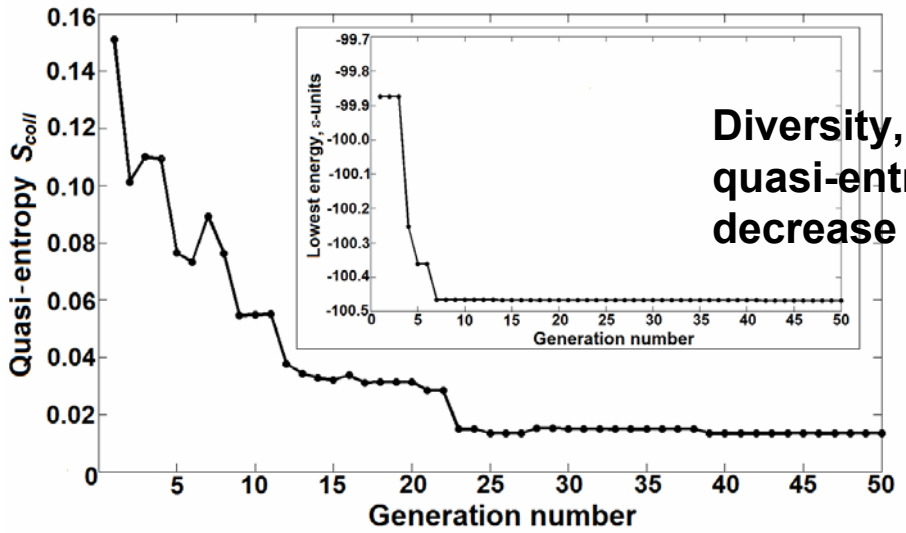
Finding ground state takes ~500 random structures, or 30 structures with USPEX

[ARO et al., Psi-k Highlight (2007)]

Fingerprinting allows to monitor diversity and emergence of order from chaos in simulations



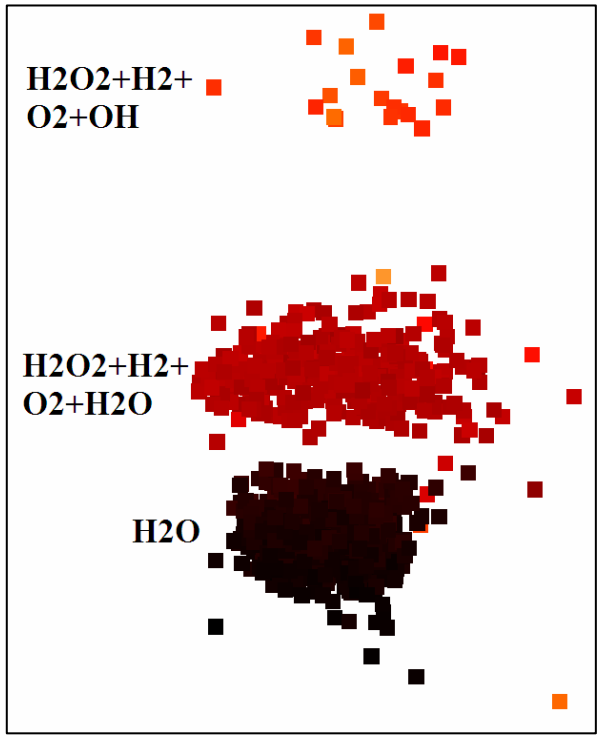
Increase of order during evolutionary simulation of GaAs



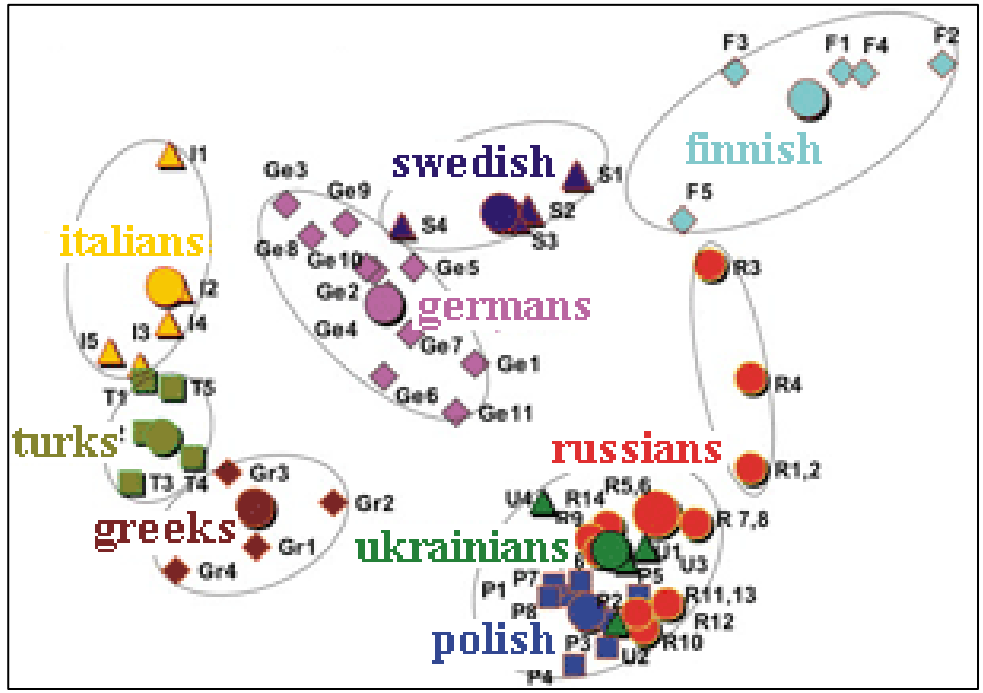
Diversity, measured by collective quasi-entropy S_{coll}, should not decrease too fast

[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* – lowest E, *lighter* – higher E).

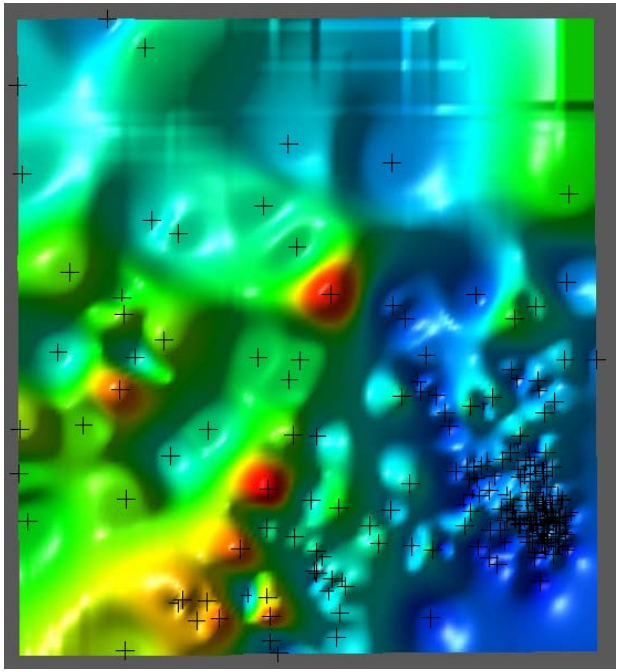


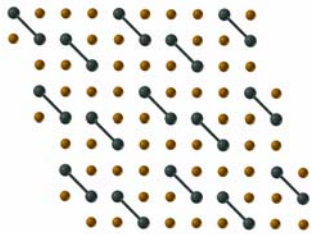
DNA grouping in Europe

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

Visualizing energy landscapes

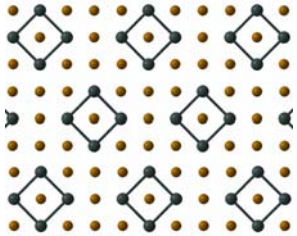
Au_8Pd_4 - simple





-61.960 eV

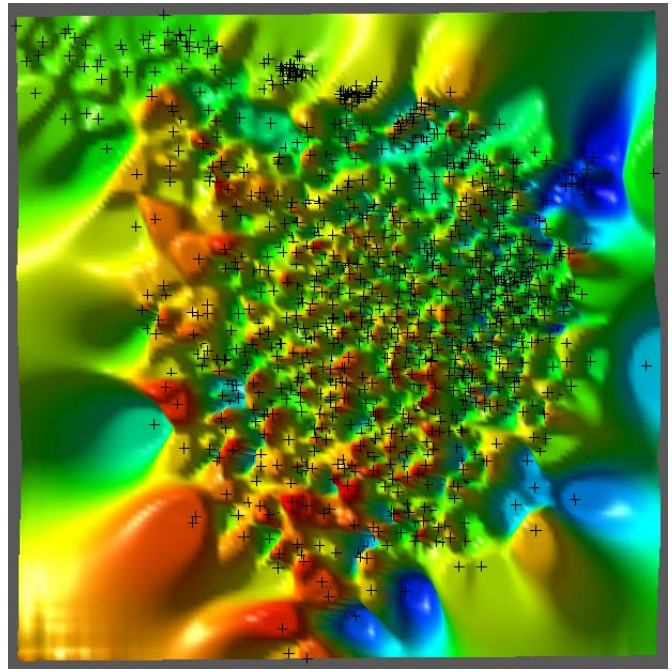
From USPEX

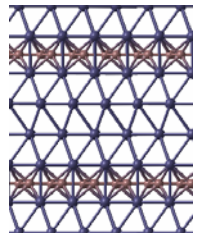


-61.957 eV

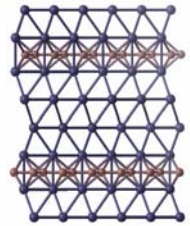
Cluster expansion

L_4J_8 - complex





-99.12ε



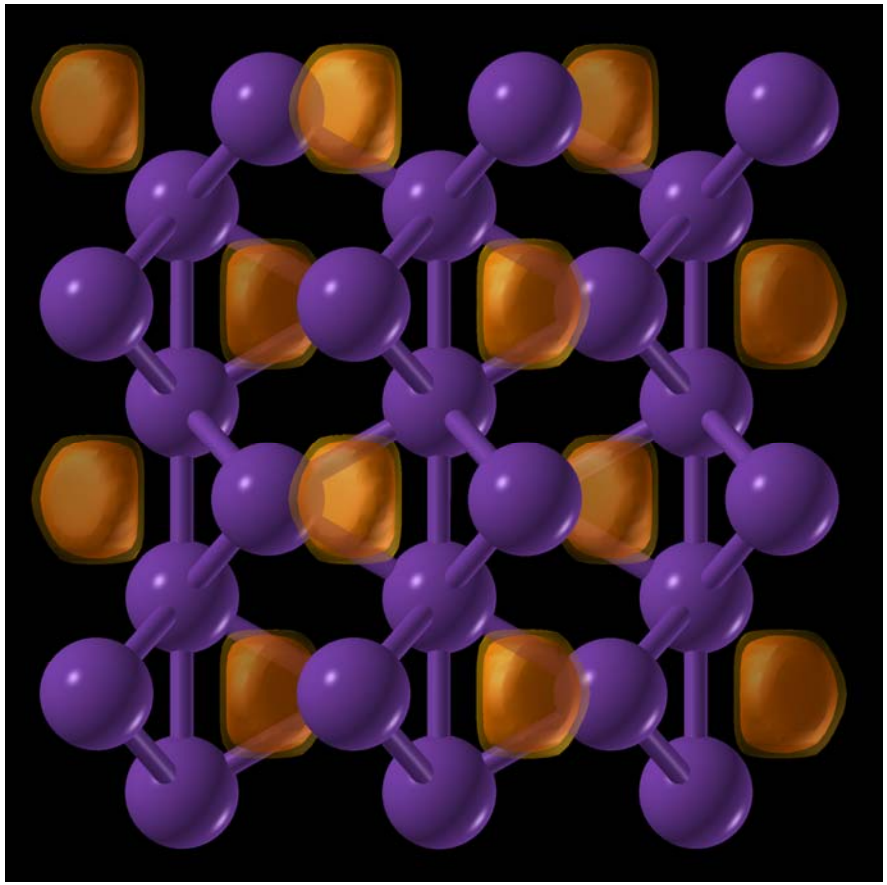
-99.05ε

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

USPEX finds ground state in 250 attempts, random sampling – in 5000 attempts

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

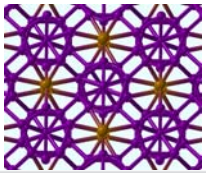
3. Some applications



Illustrations of structure predictions at the GGA-PAW level of theory

- Search for new materials
- Exploration of matter at extreme conditions

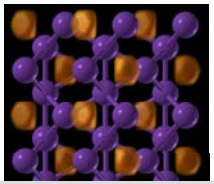
Some of the applications done so far:



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

Ionic high-pressure form of elemental boron

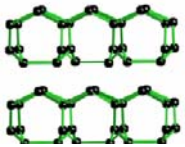
Artem R. Oganov[1,2]†, Jiuhua Chen[3,4], Carlo Gatti[5], Yanzhang Ma[6], Yanming Ma[1,7], Colin W. Glass[1], Zhenxian Liu[8], Tony Yu[3], Oleksandr O. Kurakevych[9] & Vladimir L. Solozhenko[9]



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

Transparent dense sodium

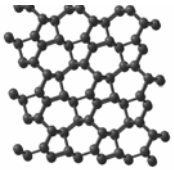
Yanming Ma[1,2], Mikhail Eremets[3], Artem R. Oganov[2,4]†, Yu Xie[1], Ivan Trojan[3], Sergey Medvedev[3], Andriy O. Lyakhov[2]†, Mario Valle[5] & Vitali Prakapenka[4]



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

Novel High Pressure Structures of Polymeric Nitrogen

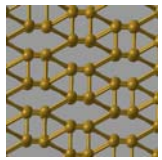
Yanming Ma,[1,2,*] Artem R. Oganov,[2,3] Zhenwei Li,[1] Yu Xie,[1] and Jani Kotakoski[4]



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

Superhard Monoclinic Polymorph of Carbon

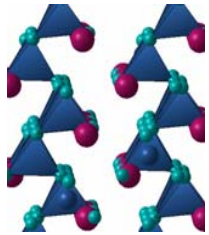
Quan Li,[1] Yanming Ma,[1,*] Artem R. Oganov,[2,3,†] Hongbo Wang,[1] Hui Wang,[1] Ying Xu,[1] Tian Cui,[1] Ho-Kwang Mao,[4,‡] and Guangtian Zou[1]



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

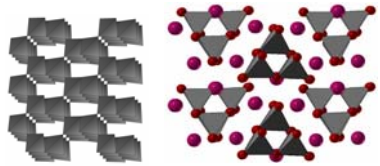
Yanming Ma,[1,2] Artem R. Oganov,[1,3,*] and Colin W. Glass[1]



Earth and Planetary Science Letters 241 (2006) 95–103

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

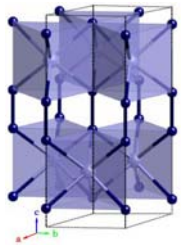
Artem R. Oganov [a,*], Colin W. Glass [a], Shigeaki Ono [b]



Earth and Planetary Science Letters 273 (2008) 38–47

Novel high-pressure structures of $MgCO_3$, $CaCO_3$ and CO_2 and their role in Earth's lower mantle

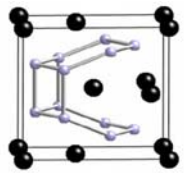
Artem R. Oganov [a,b,*], Shigeaki Ono [c], Yanming Ma [a,d], Colin W. Glass [a], Alberto Garcia [e]



PHYSICAL REVIEW B 79, 132109 (2009)

Ultra-incompressible phases of tungsten dinitride predicted from first principles

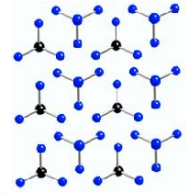
Hui Wang,[1] Quan Li,[1] Yinwei Li,[1] Ying Xu,[1] Tian Cui,[1] Artem R. Oganov,[2,3] and Yanming Ma[1,*]



PHYSICAL REVIEW B 79, 054101 (2009)

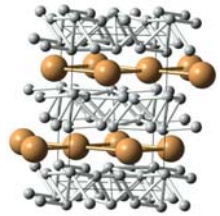
Absence of superconductivity in the high-pressure polymorph of MgB_2

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]

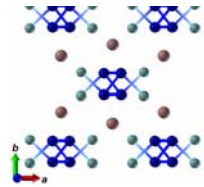


Pbcn

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

Novel Structures and Superconductivity of Silane under Pressure

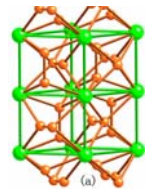
Miguel Martinez-Canales,[1,2] Artem R. Oganov,[3,4] Yanming Ma,[5] Yan Yan,[5] Andriy O. Lyakhov,[3] and Aitor Bergara[1,2,6]



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]

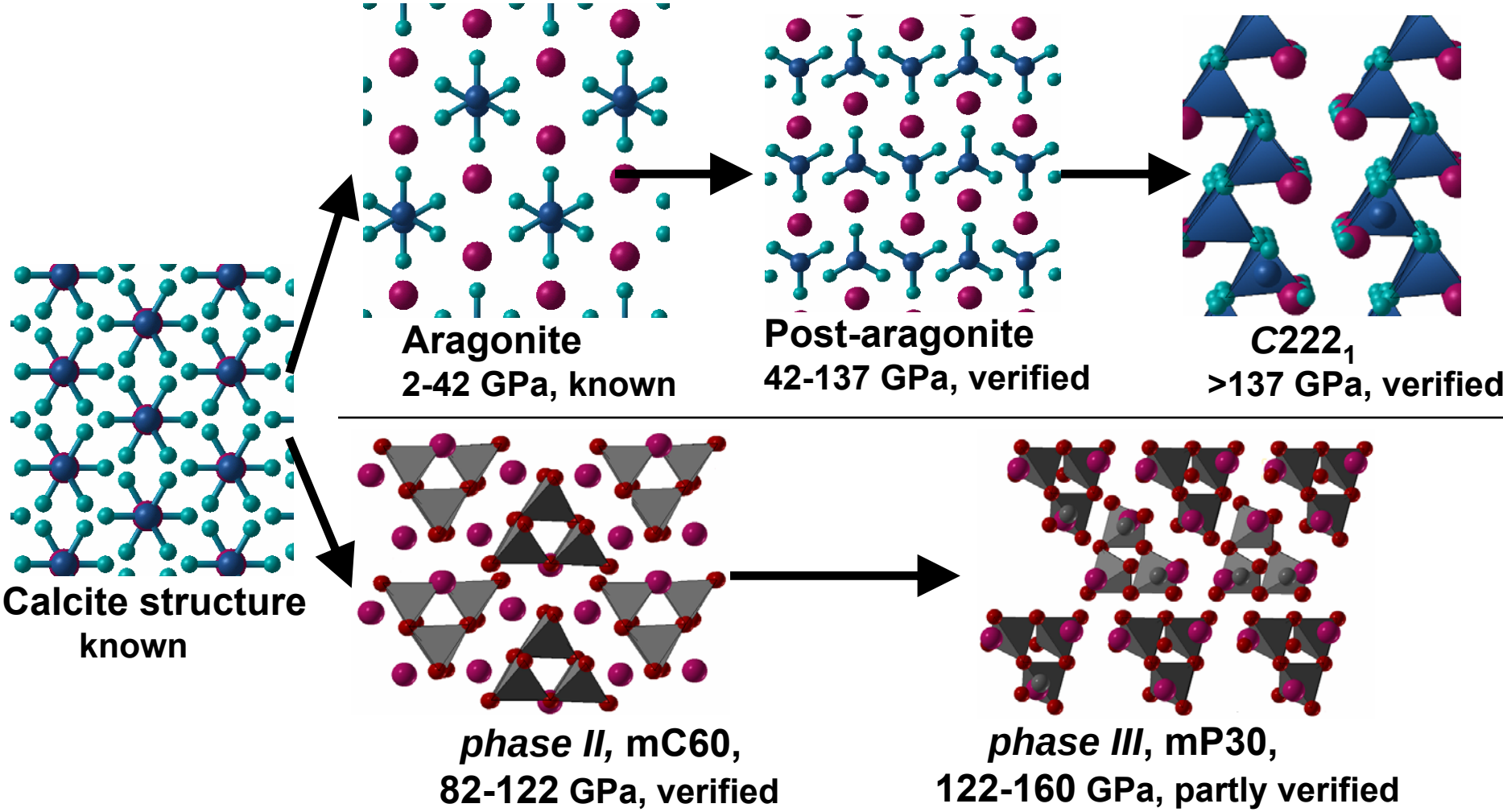


Crystal Structures and Superconductivity of Stannane under High Pressure

Guoying Gao,[1] Artem R. Oganov,[2,3] Zhenwei Li,[1] Peifang Li,[1] Tian Cui,[1] Aitor Bergara,[4,5,6] Yanming Ma,[1,*] Toshiaki Iitaka,[7] Guangtian Zou[1]

New forms of carbonates – main reservoirs of oxidized carbon in the Earth

$CaCO_3$



ARO et al., *EPSL* 241, 95-103 (2006) and *EPSL* 273, 38-47 (2008)

$MgCO_3$

SiH_4 and GeH_4 show unusual behavior

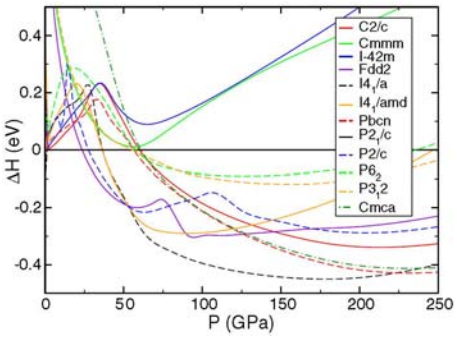
SiH_4

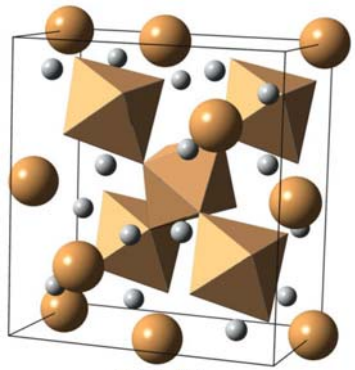
- **Random sampling (Pickard and Needs, PRL 2006):**

*P*2/*c* (~40 GPa) → *I*4$_1$/*a* (50-263 GPa) → *C*2/*c* (>263 GPa)

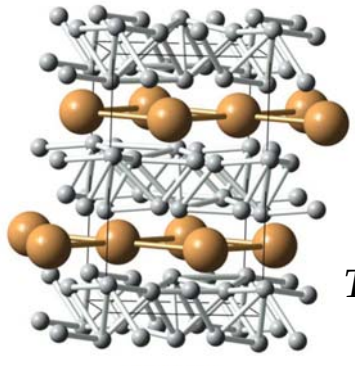
- **USPEX (Martinez, ARO et al., PRL 2009):**

*P*2$_1$/*c* (<25 GPa)→*Fdd*2 (25-55 GPa)→*I*4$_1$/a (55-220 GPa)→*Pbcn* (>220 GPa)





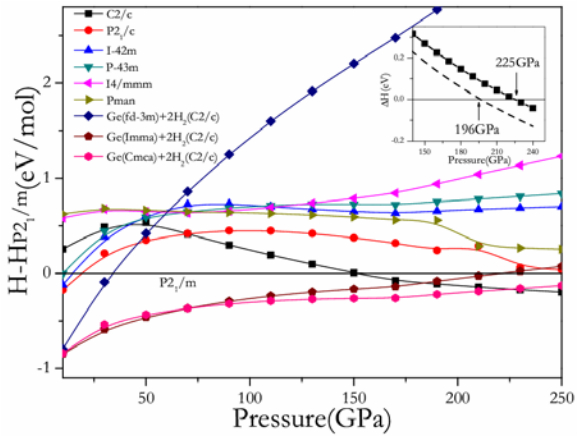
Fdd2



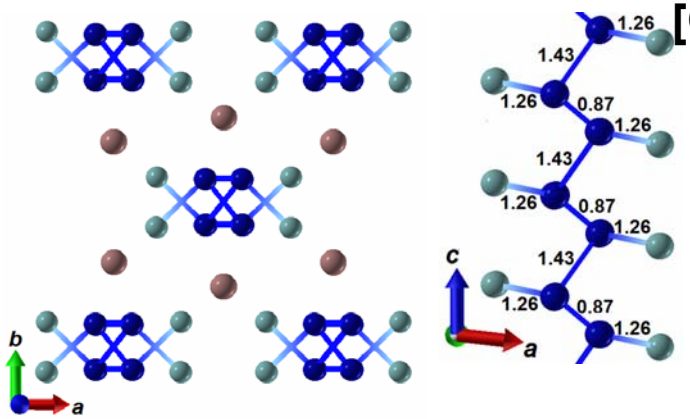
Pbcn

At 190 K: Tc=16.5 K (earlier suggestions: >160 K)

$$T_c = \frac{\omega_{\log}}{1.2}\exp\left[-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1-0.62\lambda)}\right]$$



Germane is stable to decomposition at > 196 GPa



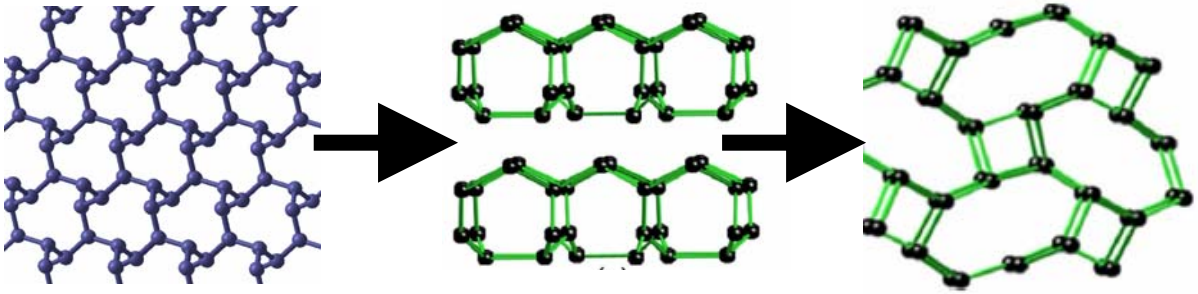
C2/c structure has short H-H distances (0.87 Å) and T_C = 64 K (!!!)

[Gao, ARO, Ma, PRL 2008]

GeH_4

Oscillating dimensionality in polymeric nitrogen (Ma, ARO, et al., PRL 2009)

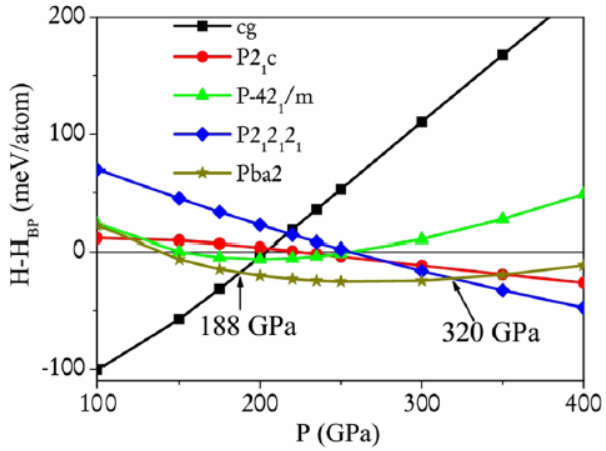
N



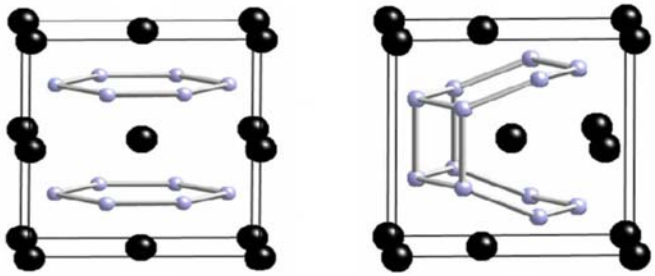
Cubic gauche ($P2_13$)
3D
<188 GPa

*Iba*2 and *Pba*2
2D
188-320 GPa

$P2_12_12_1$
3D
>320 GPa

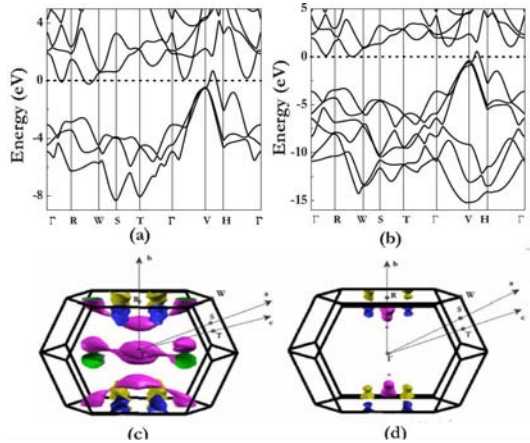


MgB_2 phases: „hole-doped carbons“. High-P „diamond“ phase is not superconducting (Ma, Wang, ARO, PRB 2009)



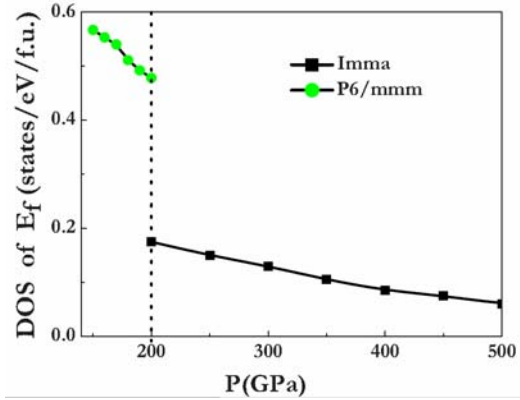
AlB_2-type
<190 GPa
„graphite“

KHg_2-type
>190 GPa
„lonsdaleite“



200 GPa

500 GPa



MgB_2

Boron is the most complex element. Even its discovery was full of troubles.

B

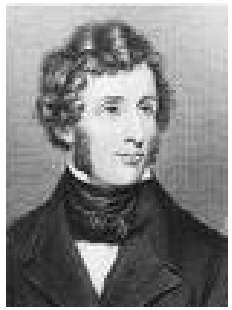
J.L. Gay-Lussac

H. Davy

1808: J.L.Gay-Lussac and H.Davy claim the discovery of a new chemical element - boron.

H. Moissan

1895: H. Moissan proves that the discovered substance was not elemental boron and contained at most 50-60% of boron. Moissan's material was later found to be less than 90% boron.



F. Wöhler

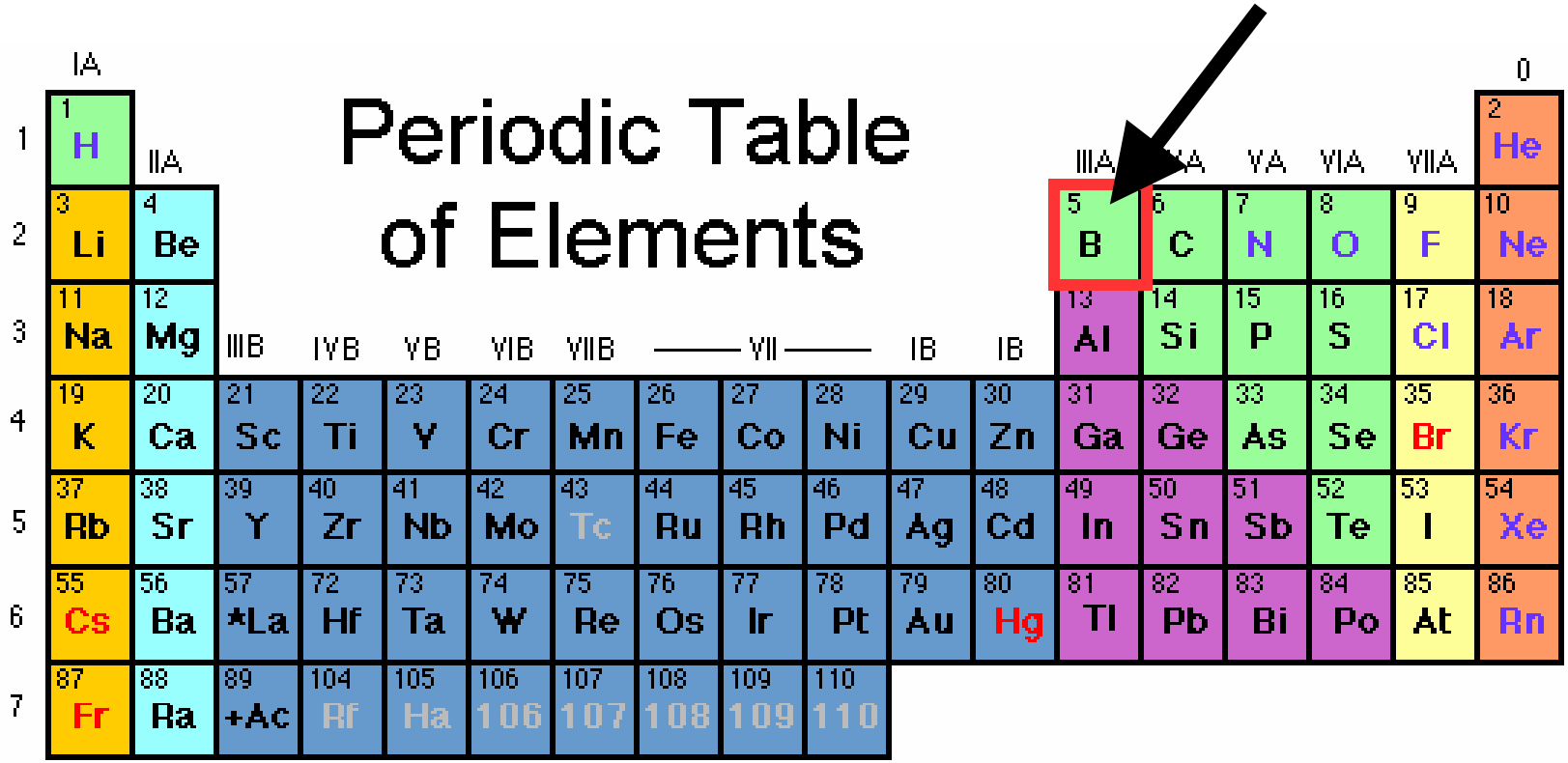
1858: F. Wöhler concludes that boron exists in two forms - "diamond-like" and "graphite-like"; both were later found to be compounds - AlB_{12} and $B_{48}C_2Al$, respectively.

2004: 16 crystalline forms of boron are known (most believed to be compounds!). Stable forms still unknown.

[ARO & Solozhenko, J. Superhard Mat. 31, 285-291 (2009)]

Located between metals and non-metals, boron is a frustrated element. As a compromise, it forms complex and unusual crystal structures.

B

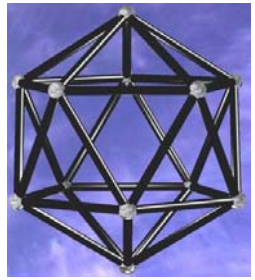


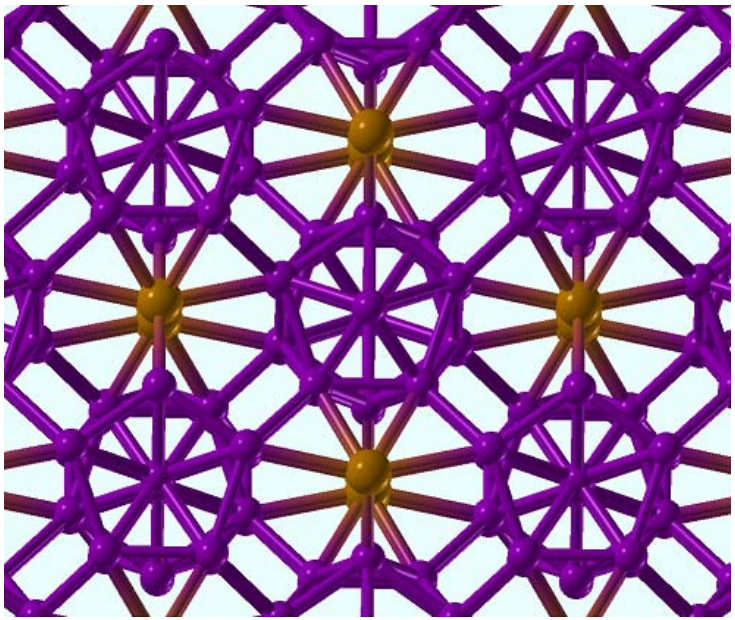
Boron forms a partially *ionic* phase above 10 GPa

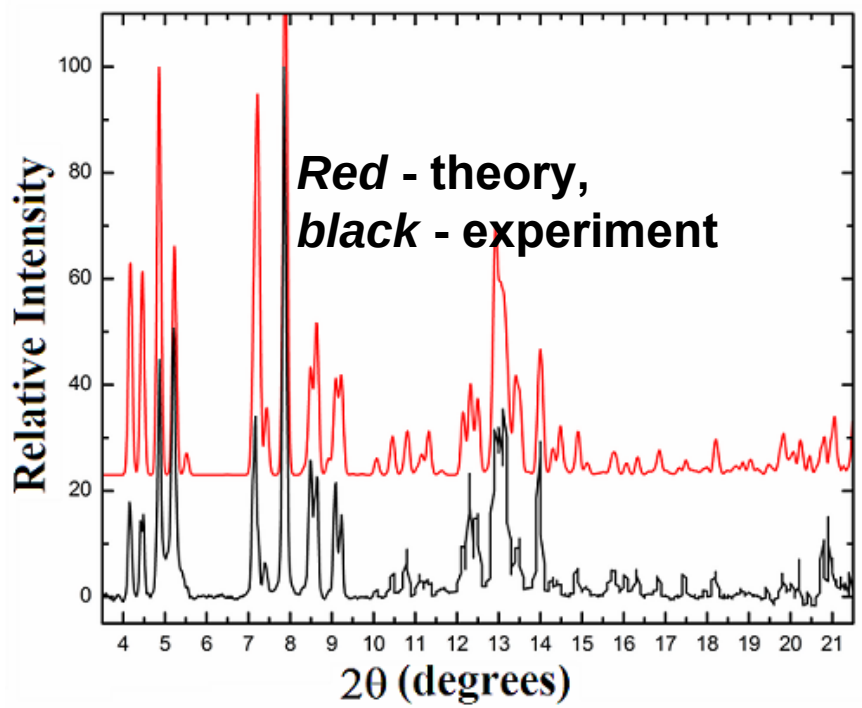
B

The concept of electron-deficiency was devised to explain boron chemistry. "*it is the ideas that are deficient, not the electrons*" (J.Burdett).

2004: Chen & Solozhenko: synthesised new phase, structure could not be solved.
2006: ARO: found the structure, demonstrated that it is stable.
2008: Solozhenko, Kurakevych & ARO – its hardness is 50 GPa.

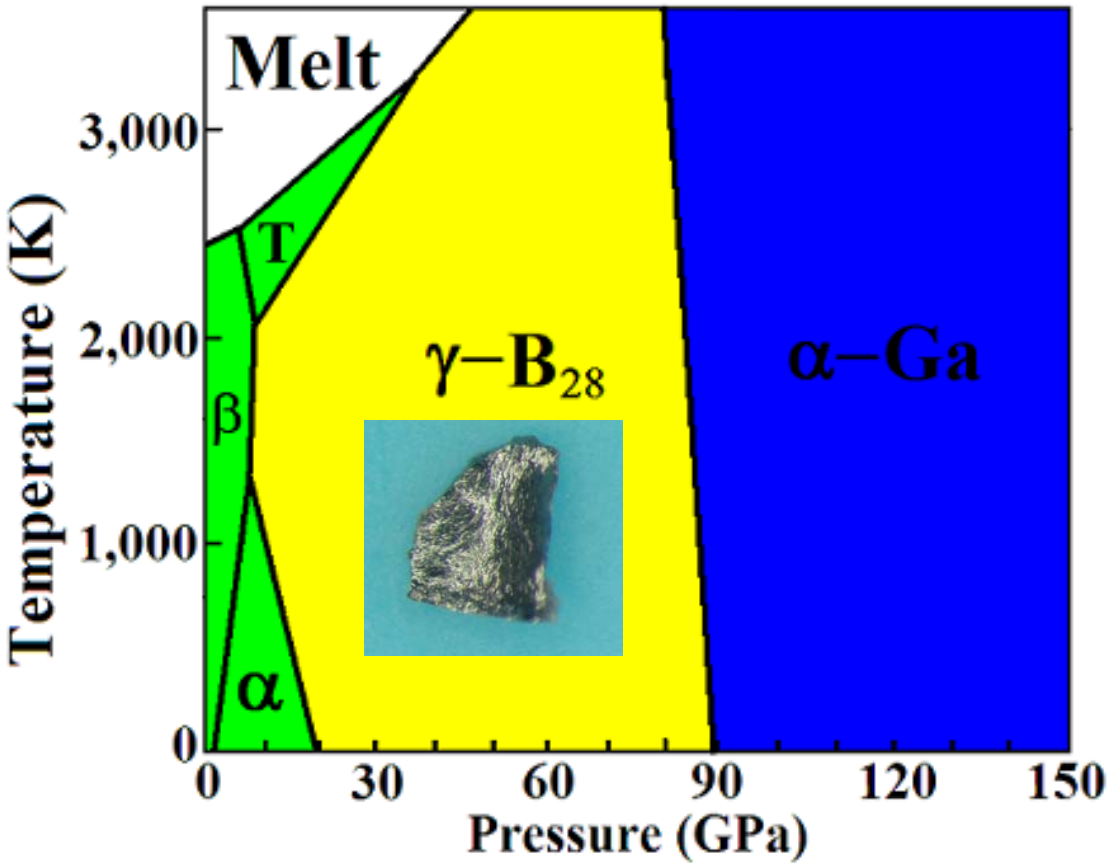






Structure of partially ionic phase of boron: $(B_2)^{\delta+}(B_{12})^{\delta-}$, δ=+0.5 (Bader partitioning), +2.2 (Born dynamical charges).

Phase diagram of boron seems to be clear – at last

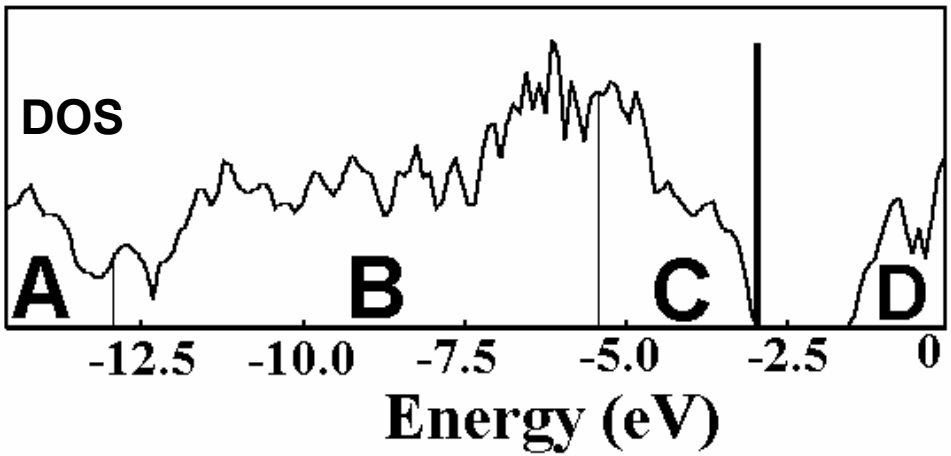


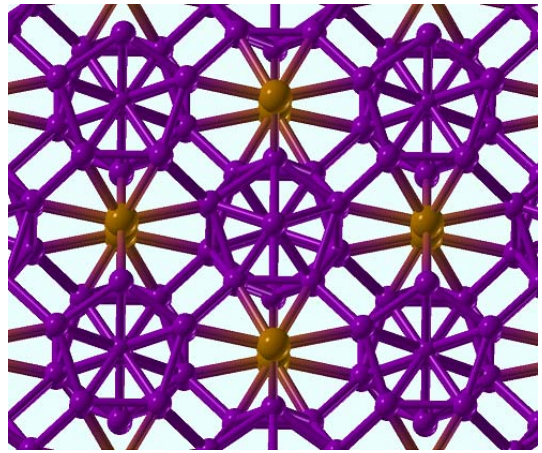
Phase diagram of boron
(ARO et al, Nature 2009)

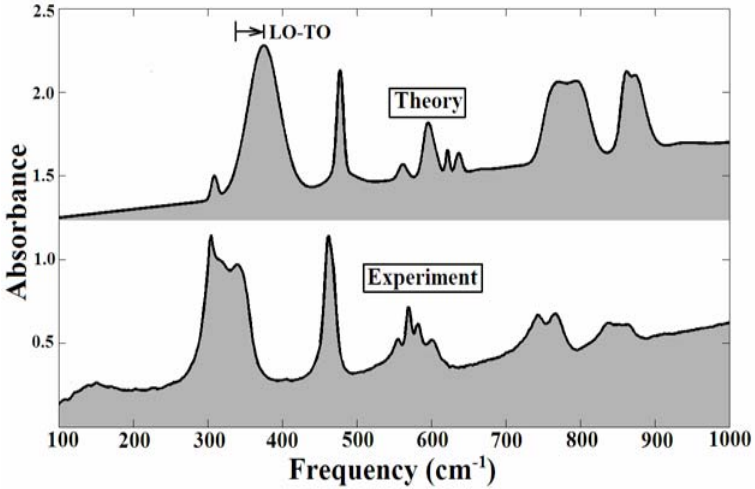
γ-B_{28} was probably observed in a largely discarded 1965 paper by R. Wentorf

Superconducting α-Ga-type phase is purely theoretical and has yet to be synthesized

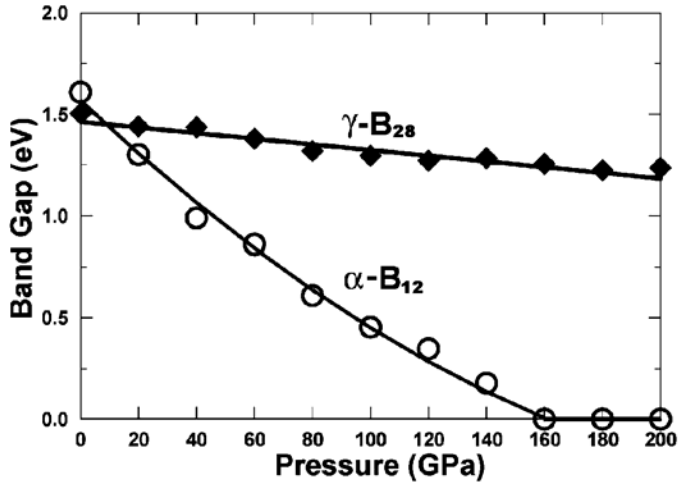
Charge transfer is clear from the electronic structure







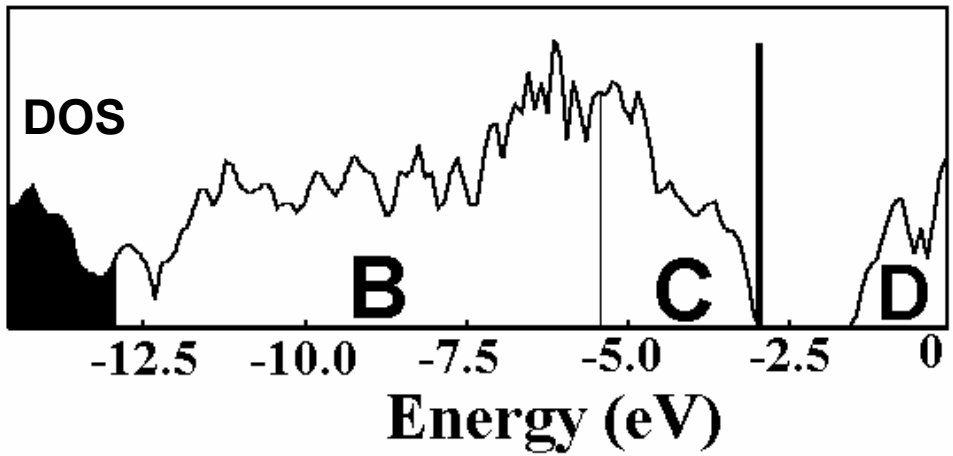
Infrared spectra are entirely due to large dynamical charges on atoms

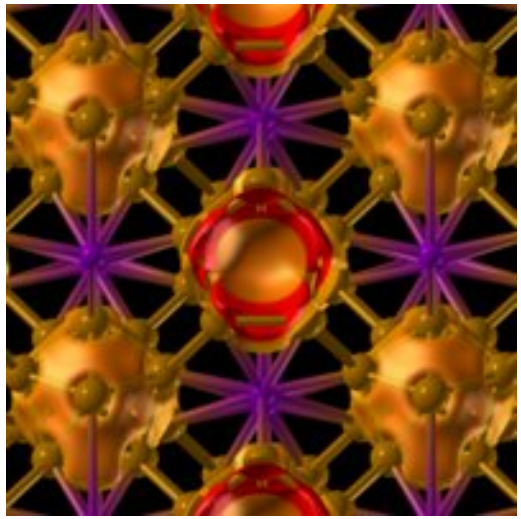


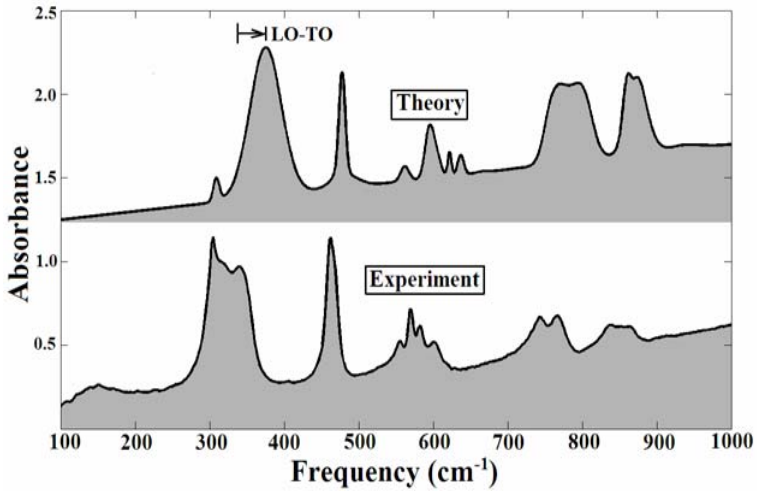
Unlike other forms of boron, ionic γ-B does not metallize even at very high pressure

Charge transfer is clear from the electronic structure

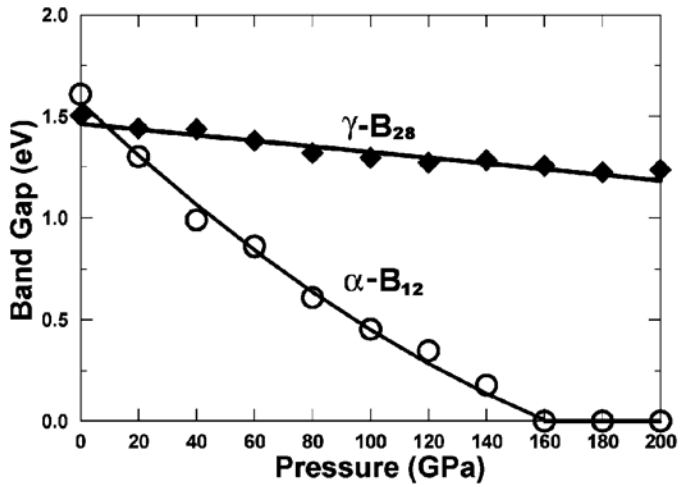
B





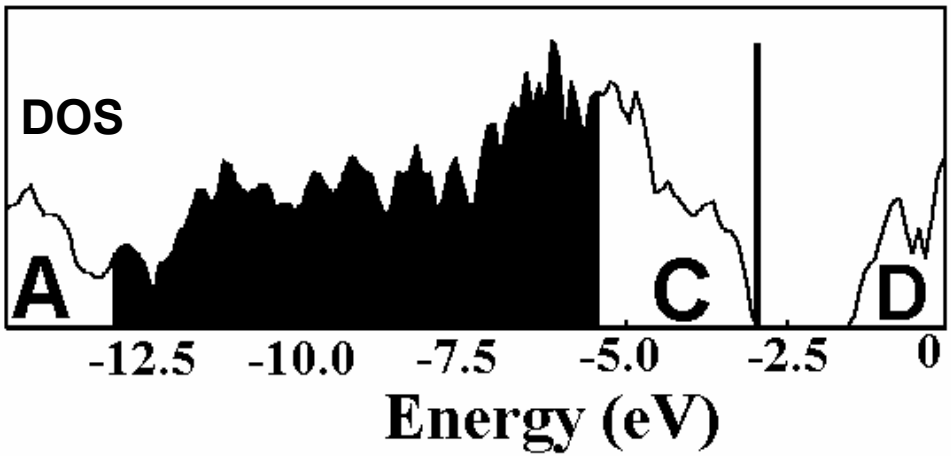


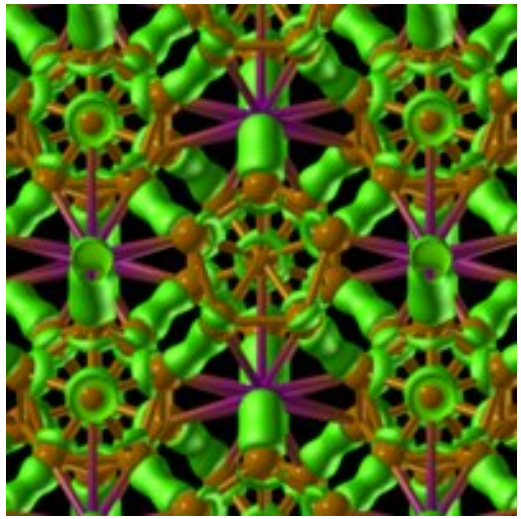
Infrared spectra are entirely due to large dynamical charges on atoms

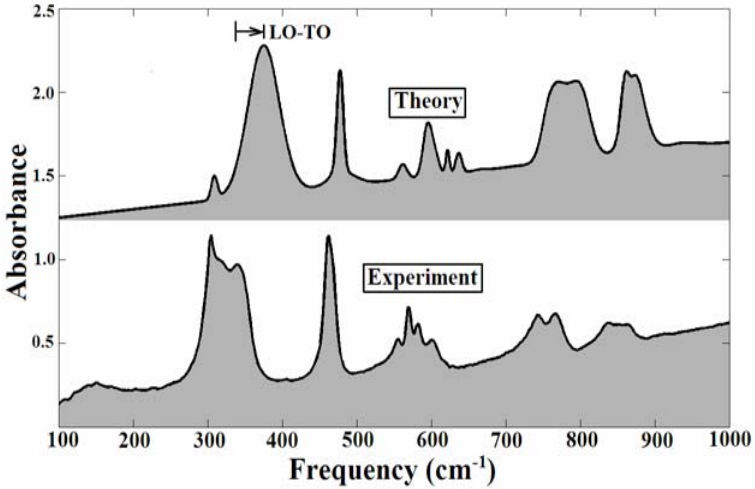


Unlike other forms of boron, ionic γ-B does not metallize even at very high pressure

Charge transfer is clear from the electronic structure







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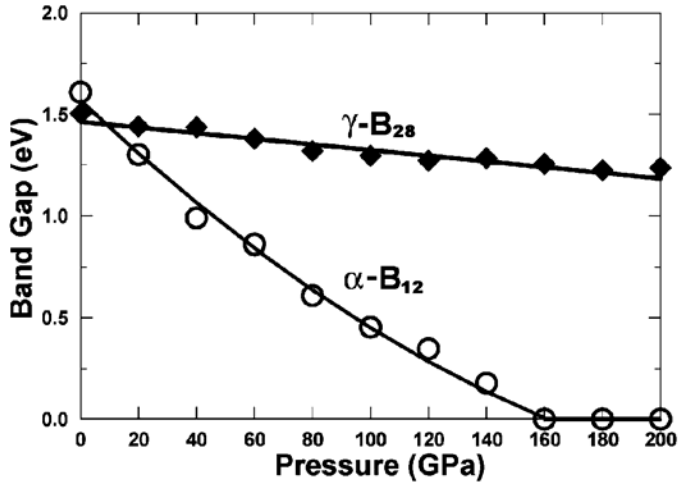

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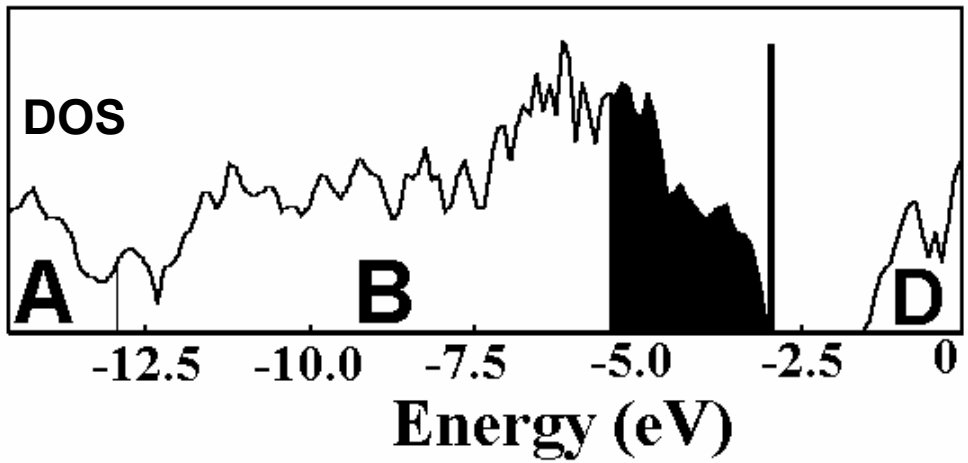
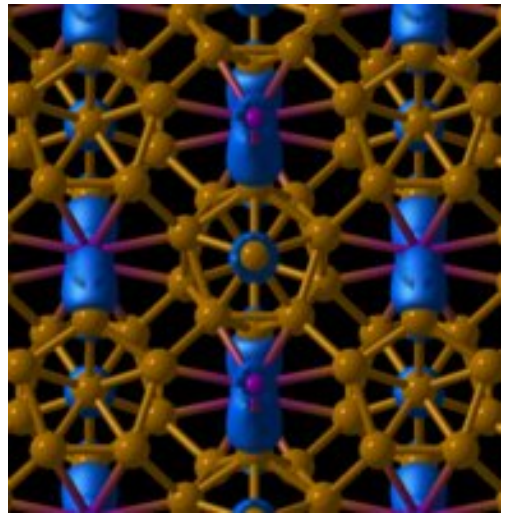
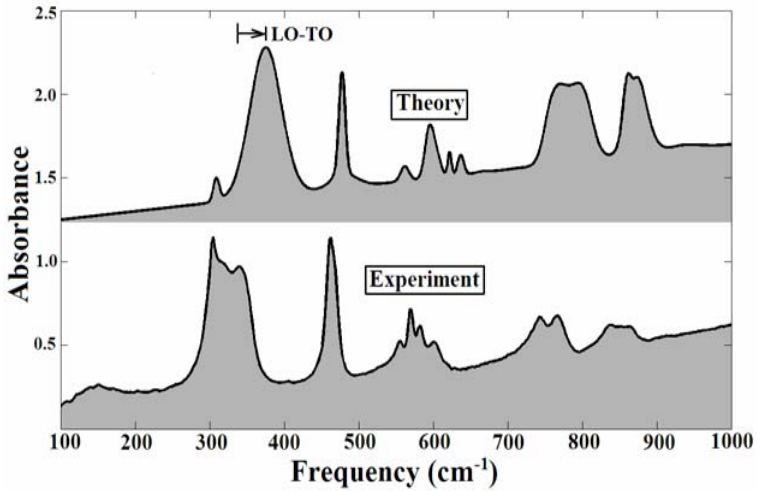
B







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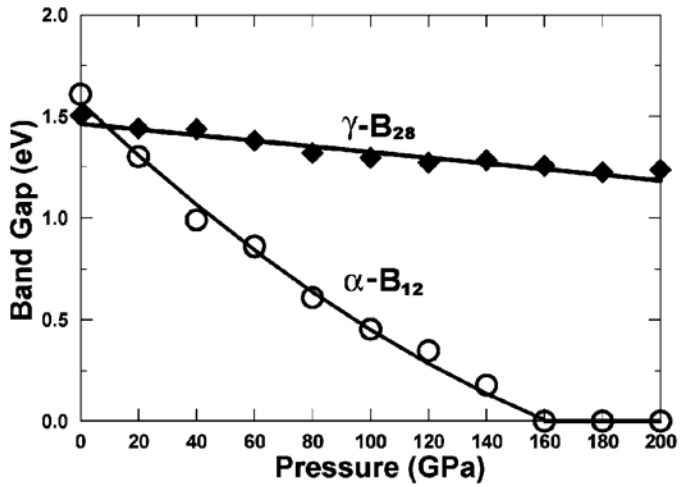

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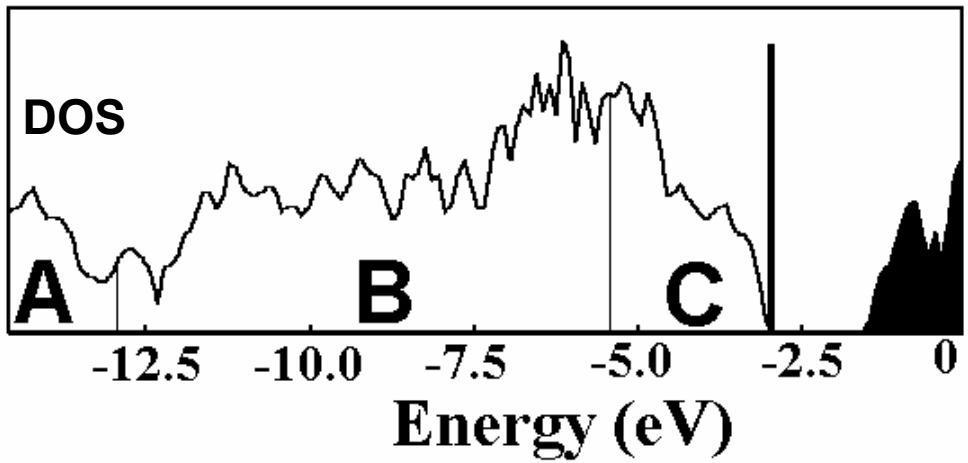

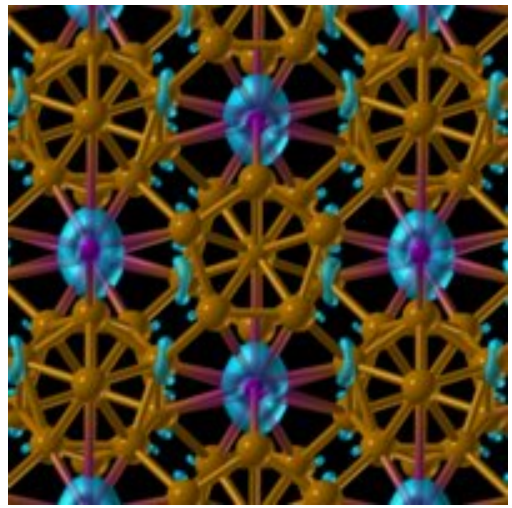

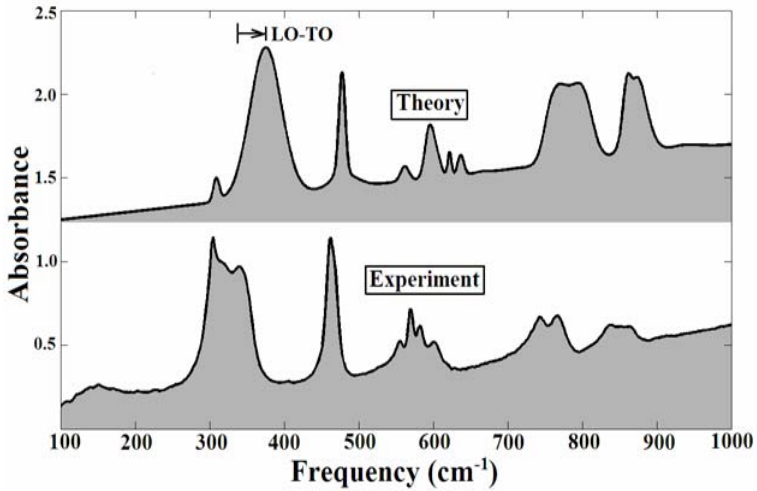

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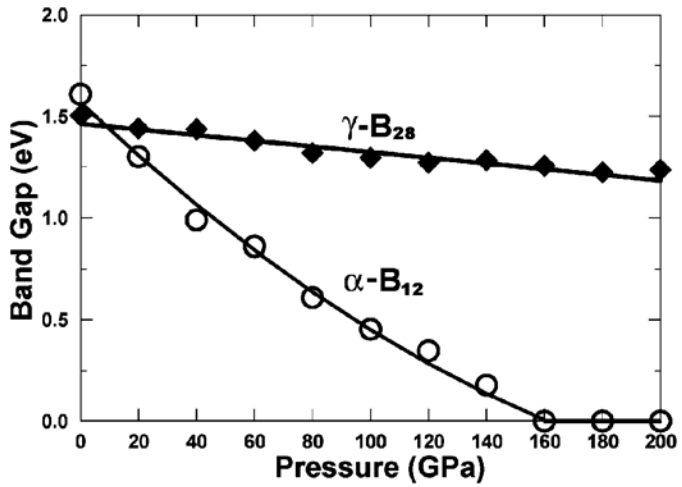

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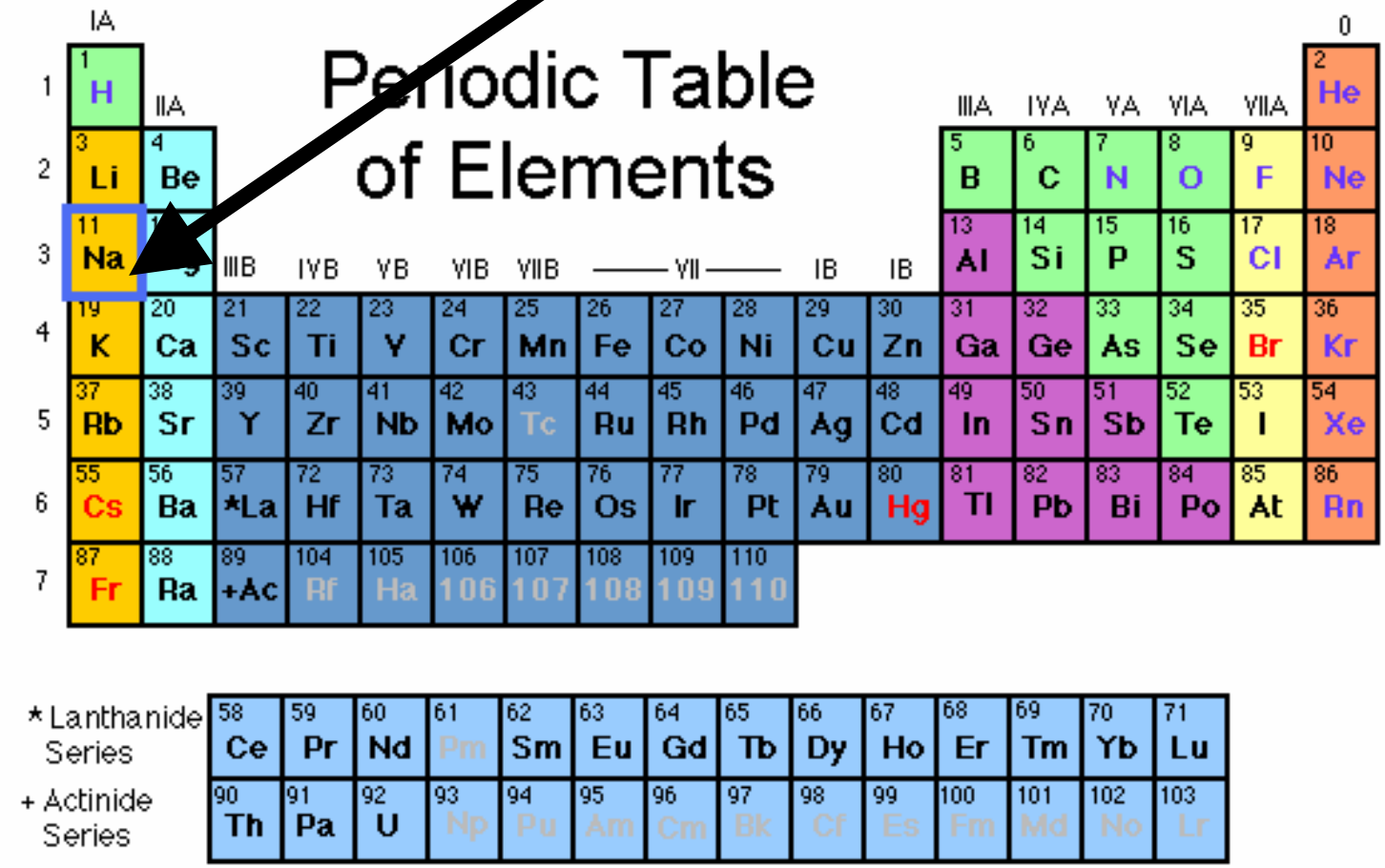
Sodium is an alkali metal, at normal conditions well described by the nearly free electron model



Sodium is an alkali metal, at normal conditions well described by the nearly free electron model

Periodic Table of Elements

	IA	IIA	IIIB	IVB	VB	VIB	VIIB	—— VII ——	IB	IB	IIIA	IVA	VA	VIA	VIIA	0
1	1 H															2 He
											5 B	6 C	7 N	8 O	9 F	10 Ne
											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
				22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 *La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 +Ac	104 Rf	105 Ha	106 106	107 107	108 108	109 109	110 110								

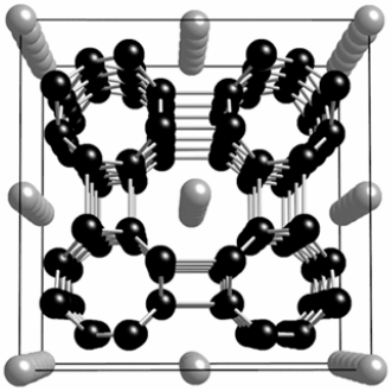
* Lanthanide Series	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
+ Actinide Series	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

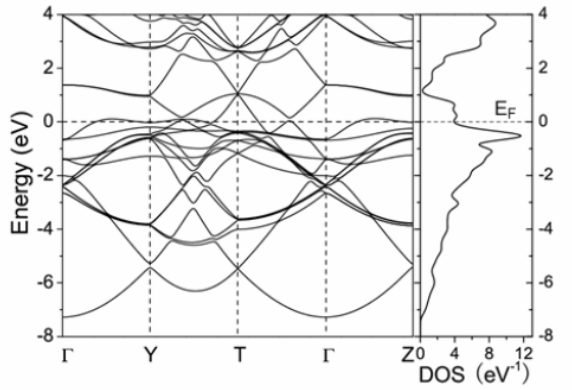
Sodium shows unexpectedly complex behavior under pressure

H. Davy

1807: Discovered by Sir Humphrey Davy.

2002: Hanfland, Syassen, Novikov, Christensen found remarkably complex structures above 1 Mbar.

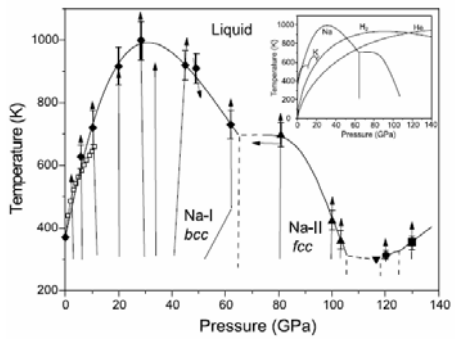




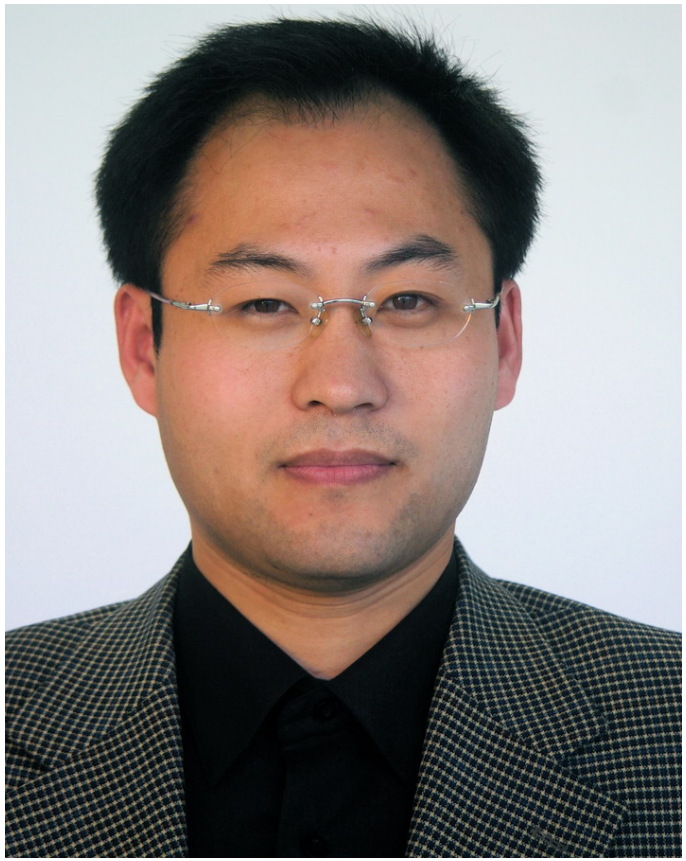
This phase is a 1D-metal (Lazicki, PNAS 2009)

2005: Gregoryanz et al. find melting curve minimum at ~1.2 Mbar

Does sodium become a d-metal?



A new phase was predicted in 2007 and subsequently synthesized at high pressure



Yanming Ma (Jilin University, China)

Mikhail Eremets (MPI Mainz, Germany)

Theory predicts a new structure that is insulating and … transparent!


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

LETTERS

Transparent dense sodium

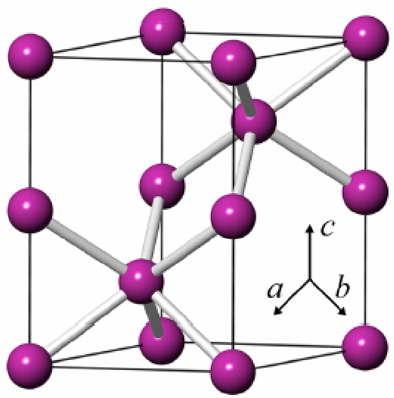
Yanming Ma[1,2], Mikhail Eremets[3], Artem R. Oganov[2,4]†, Yu Xie[1], Ivan Trojan[3], Sergey Medvedev[3], Andriy O. Lyakhov[2]†, Mario Valle[5] & Vitali Prakapenka[6]

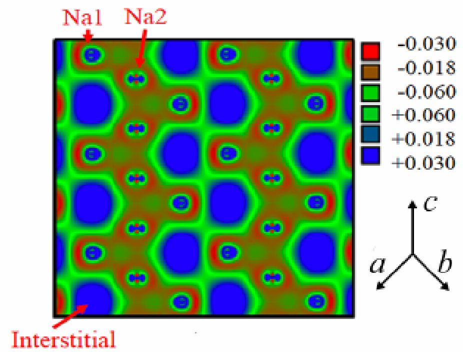
Under pressure, metals exhibit increasingly shorter interatomic distances. Intuitively, this response is expected to be accompanied by an increase in the widths of the valence and conduction bands and hence a more pronounced free-electron-like behaviour. But at the densities that can now be achieved experimentally, compression can be so substantial that core electrons overlap. This effect dramatically alters electronic properties from those typically associated with simple free-electron metals such as lithium (Li; refs 1–3) and sodium (Na; refs 4, 5), leading in turn to structurally complex phases[6–8] and superconductivity with a high critical temperature[9–11]. But the most intriguing prediction—that the seemingly simple metals Li (ref. 1) and Na (ref. 4) will transform under pressure into insulating states, owing to pairing of alkali atoms—has yet to be experimentally confirmed. Here we report experimental observations of a pressure-induced transformation of Na into an optically transparent phase at ~200 GPa (corresponding to ~5.0-fold compression). Experimental and computational data identify the new phase as a wide bandgap dielectric with a six-coordinated, highly distorted double-hexagonal close-

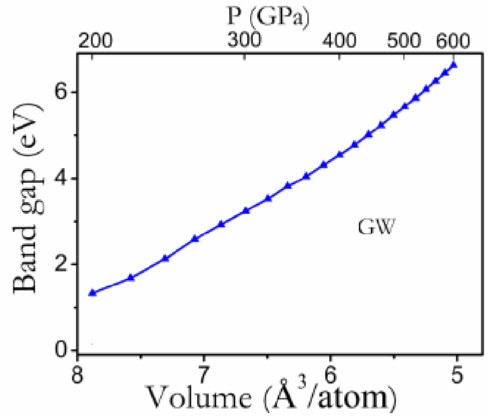
pressures (Fig. 1a), indicating a major phase transformation that according to visual observation is associated with a gradual decrease in the reflection of visible light from the sample. The Raman spectra appearing around 130 GPa are in good accordance with the theoretical spectra calculated for the experimentally observed[14] oP8 (*Pnma*) phase (Supplementary Fig. 1d). Above 150 GPa, the Raman spectra again show marked changes, including a strong decrease in intensity, that signify another phase transition (Fig. 1a). The X-ray diffraction pattern of this phase is consistent with the tI19 structure[14].

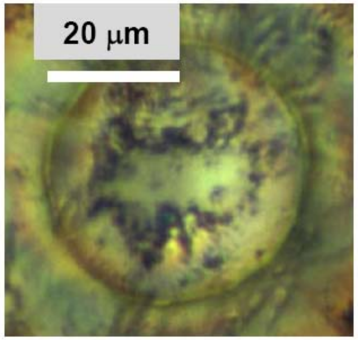
Na becomes optically transparent at pressures of ~200 GPa. (The onset of transparency occurred at 208 GPa in the run shown in Fig. 2a, and at 194 GPa in the run shown in Supplementary Fig. 1a.) The edge in the absorption spectrum (Supplementary Fig. 1c) gives for transparent Na a bandgap of at least ~1.3 eV. The onset of transparency coincides with dramatic changes in the Raman spectra (Fig. 1a), particularly the appearance of a single intense line centred at ~340 cm^{-1}. On releasing the pressure, the transparent phase persists to 182 GPa; at that point, the sample reverts to opaque and exhibits

Sodium becomes transparent at ~200 GPa
(Ma, Eremets, Oganov et al., *Nature* 2009)









110 GPa

Localized interestitial electron pairs make Na insulating.
Structure – close packing of interstitial electron pairs!

hP4-Na structure: elemental analog of the NiAs structure.

Theory predicts a new structure that is insulating and … transparent!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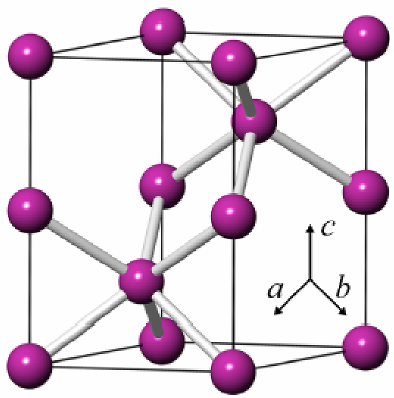

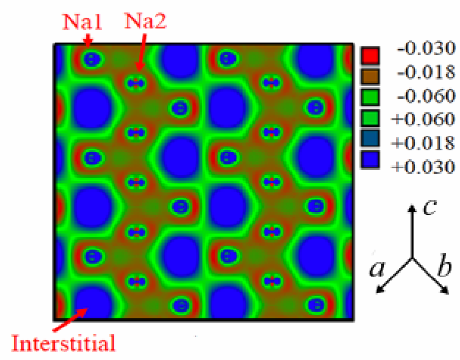

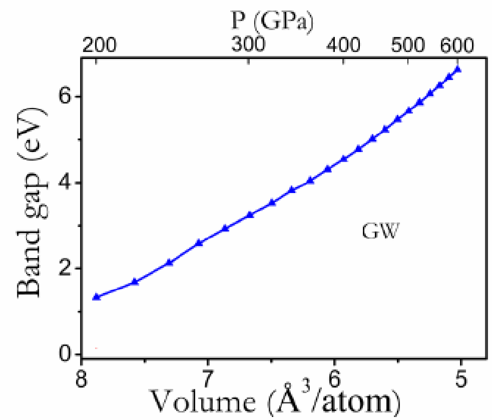

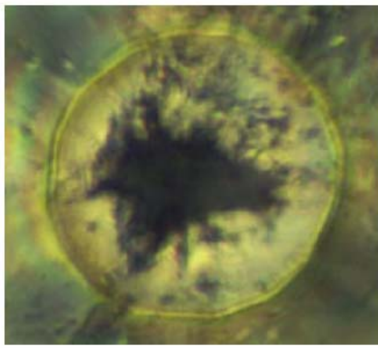

156 GPa

Localized interestitial electron pairs make Na insulating.
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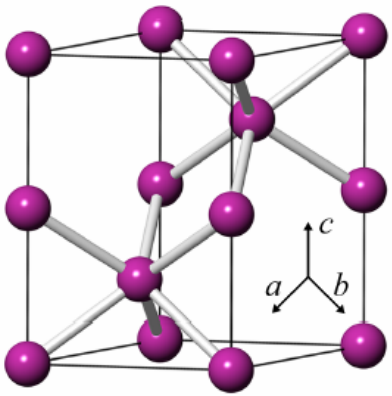
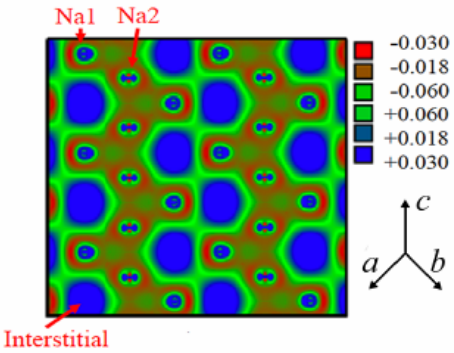
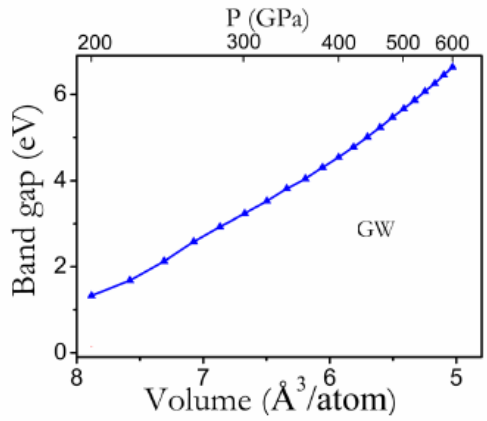
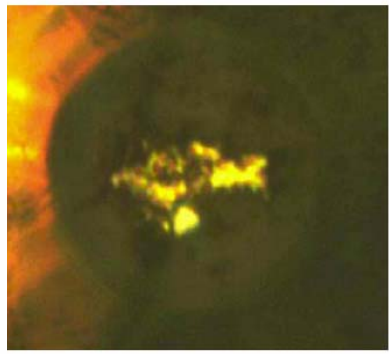






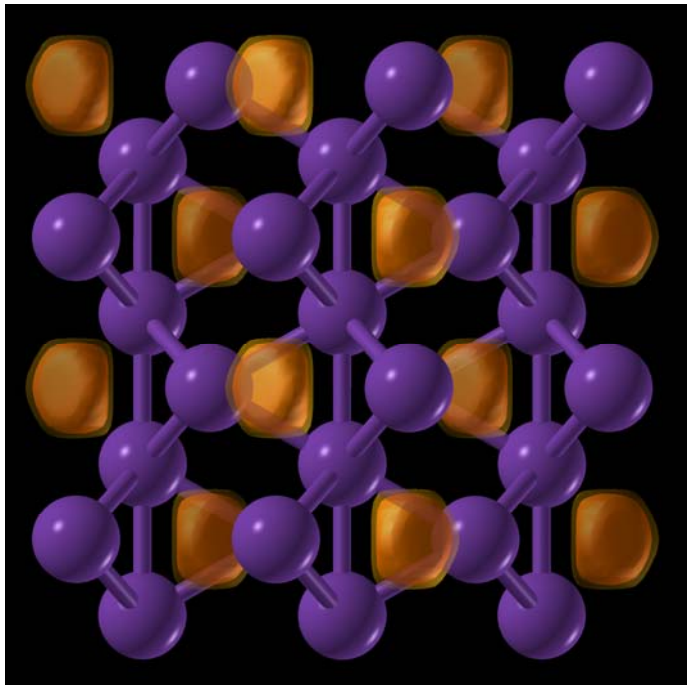


199 GPa

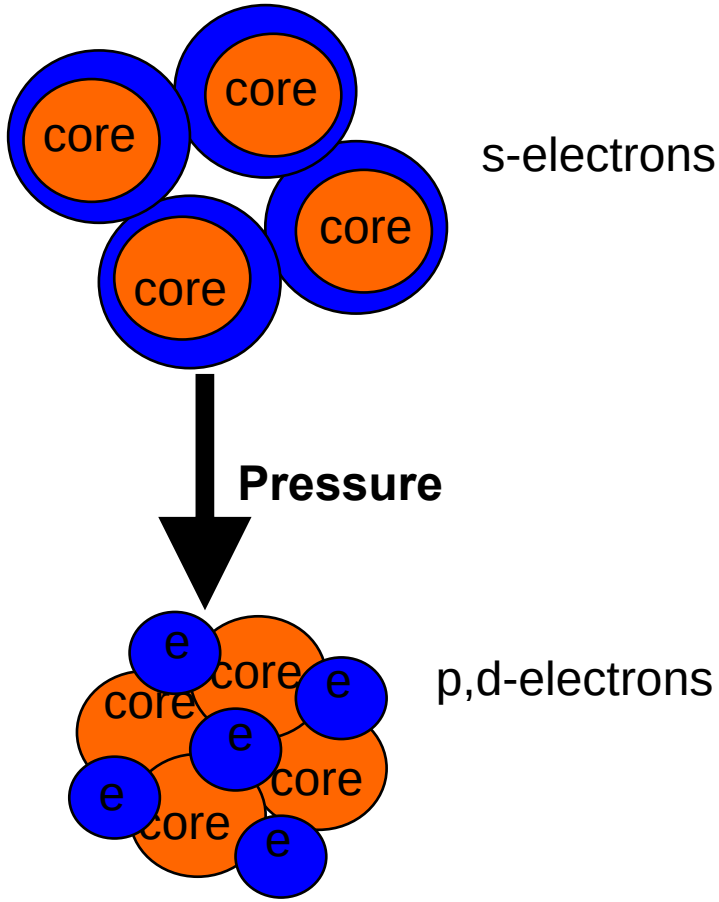
Localized interestitial electron pairs make Na insulating.
Structure – close packing of interstitial electron pairs!

hP4-Na structure: elemental analog of the NiAs structure.

The new structure is a strongly squeezed close packing with valence electron pairs occupying interstitials



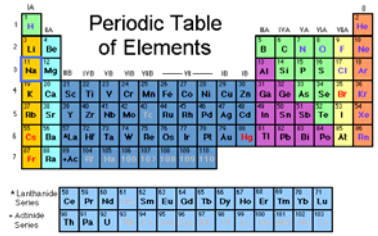
Electron localization function shows strongly localized behavior of electrons in the „empty space“ in Na

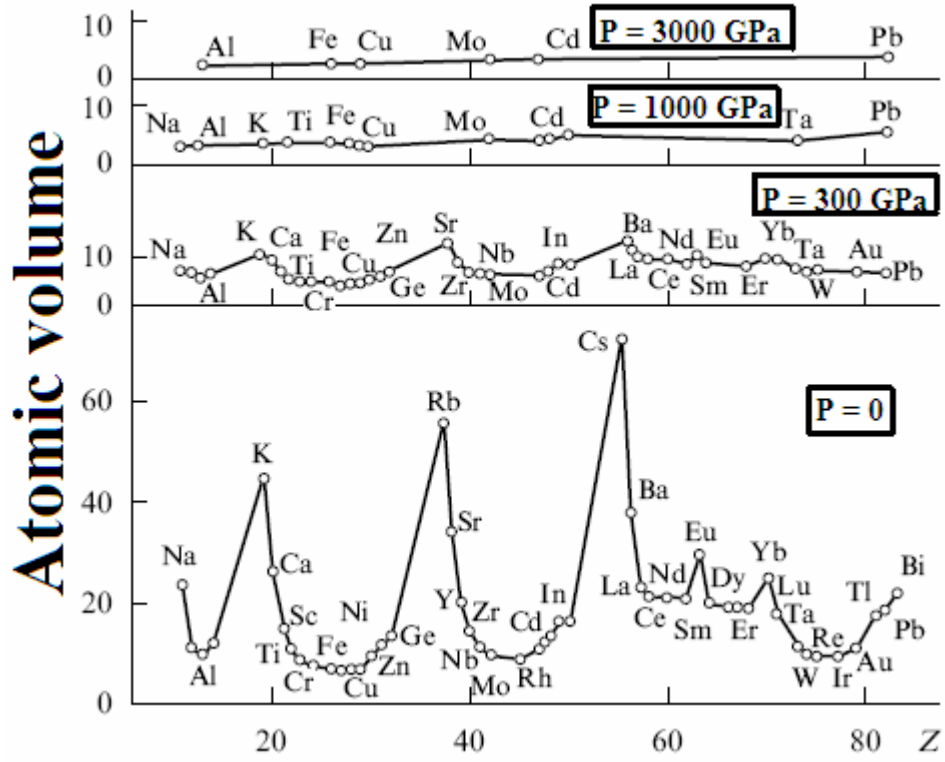


An „electride“, a compound made of ionic cores and strongly localized interstitial electrons. What type of chemical bonding is this?

Similar model was first proposed for Li by Neaton & Ashcroft (1999)

Food for thought…





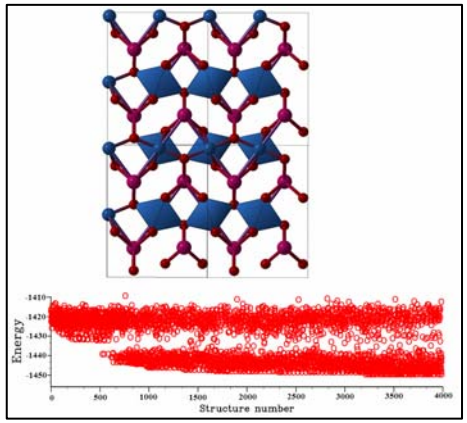
How common are electride states inside giant planets and stars?

Their poor electrical conductivity can affect planetary magnetic fields

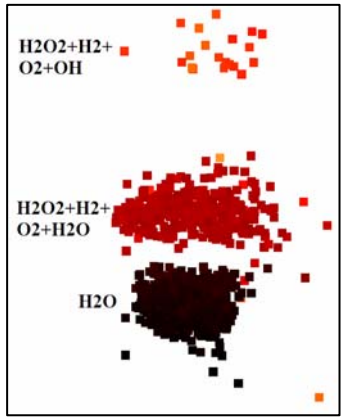
Becoming an insulator, sodium breaks traditional view of the periodic table.

Generally, the Periodic Law becomes invalid at ultrahigh pressures

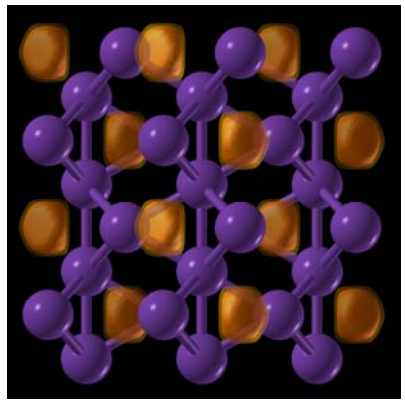
USPEX is a powerful method for structure prediction



Novel analysis tools give further insight



New interesting structures predicted



New users/developers are welcome:

1. Rapidly growing user/developers community. Now ~80 people.
2. Major ideas being developed/implemented right now.
3. It is interfaced to VASP, SIESTA, GULP and scales on 10^3-10^5 CPUs.
4. State-of-the-art analytic tools.

Dedicated to Jeanne

Acknowledgments:

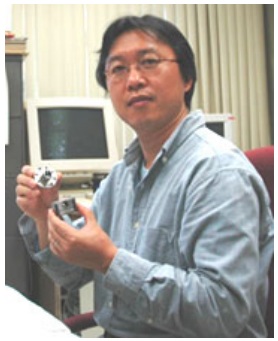

A. Lyakhov


C. Glass

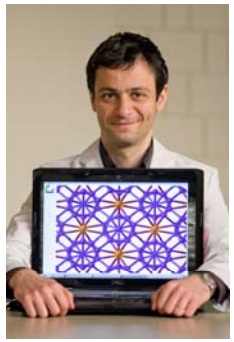

M. Valle


M. Eremets


V. Solozhenko


J. Chen

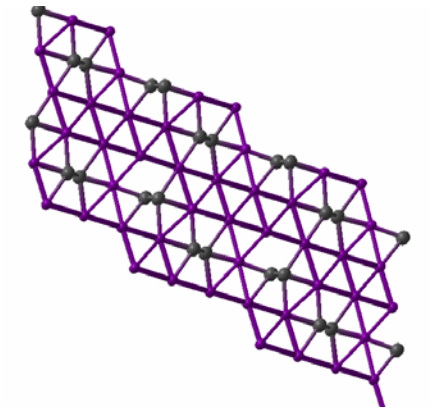

Y. Ma


ARO

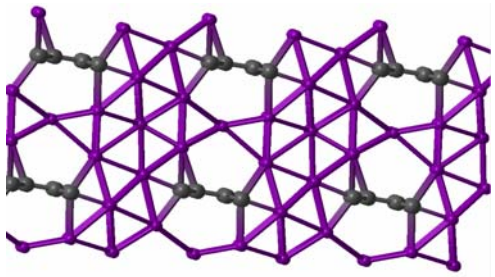
- Y. Xie (Stony Brook)
- Q. Zhu (Stony Brook)
- M. Thompson (Stony Brook)
- F. Zhang (Perth, Australia)
- M. Parrinello (ETH Zurich)
- S. Ono (JAMSTEC, Japan)
- Y. Wang (Jilin University, China)
- G. Gao (Jilin University, China)
- R. Martonak (U. Bratislava, Slovakia)
- C. Gatti (U. Milano, Italy)
- M. Martinez (U. Basque Country, Spain)
- A. Bergara (U. Basque Country, Spain)
- R. Hoffmann (Cornell University)
- C. Hu (Guilin, China)
- USPEX Users and Developers Community (~80 people)

USPEX can detect unmixing, when system is large enough and/or the tendency to unmixing is strong

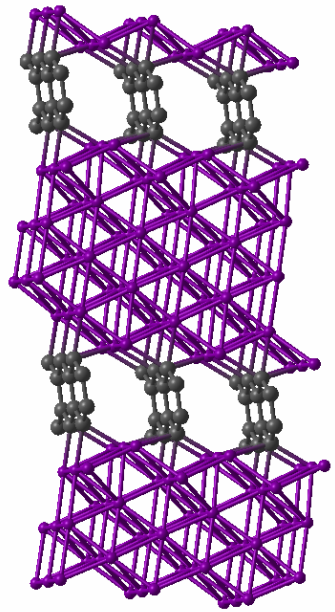
No compounds are known in the Cu-C system.
Example of Cu_2C with 12 atoms/cell:



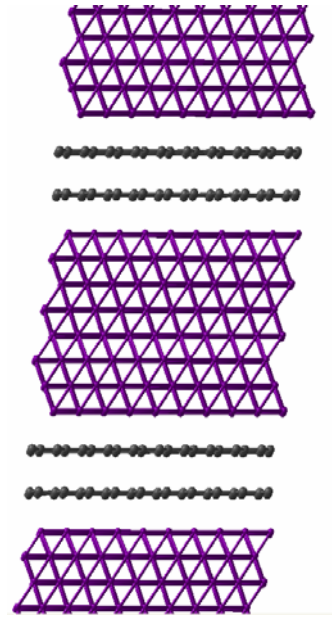
Generation 1
4.68 eV



Generation 6
3.54 eV



Generation 10
2.65 eV



Generation 14
0 eV

[ARO et al., Psi-k Highlight (2007)]