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Predicting Variable Stoichiometric Compounds

Qiang Zhu

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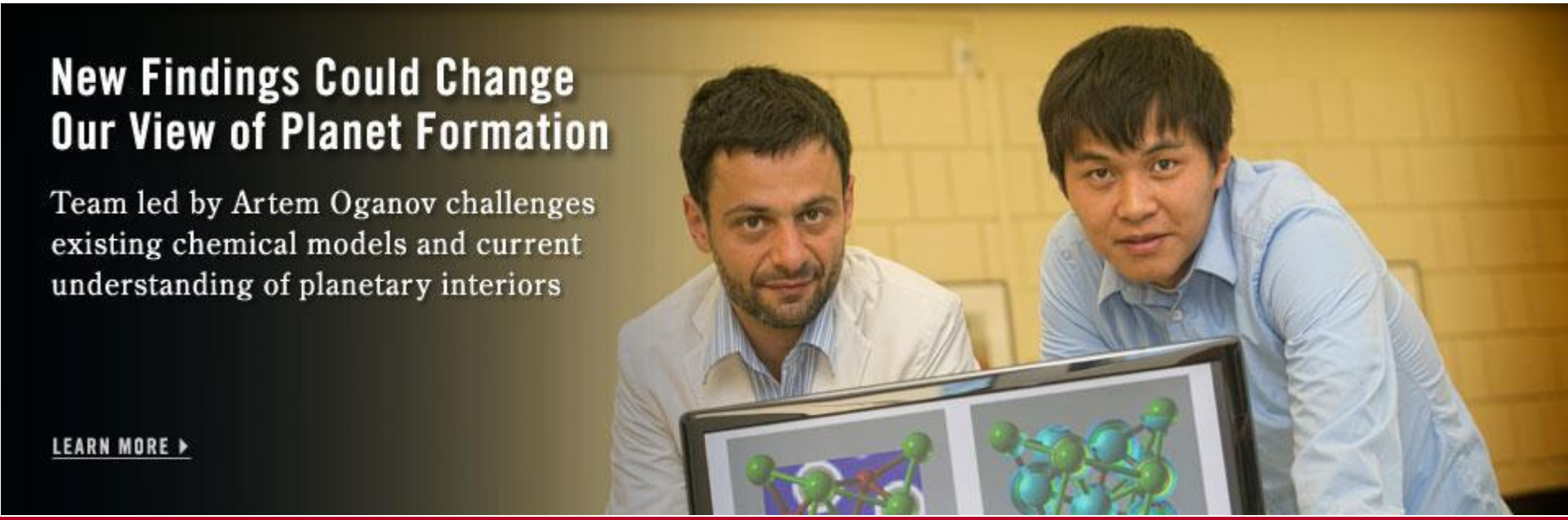

USPEX: Computational Materials Design

Crystal Structure Prediction

System

- **Dimension**
  - 0: Nano-particle;
  - 1: polymers;
  - 2: surfaces/crystals;
  - 3: Bulk
- **Stoichiometry**
  - 0: fixed; 1: variable
- **Building block**
  - 0: atom; 1: molecule

Target

- Density
- Hardness
- Dielectric constants
- Band gap
- Magnetic moment
- ….

Crystal Structure:

300: yesterday talk by ARO

301: yesterday talk by Zhu

310: This talk

311: This talk

Materials Discovery:

Next talk by ARO

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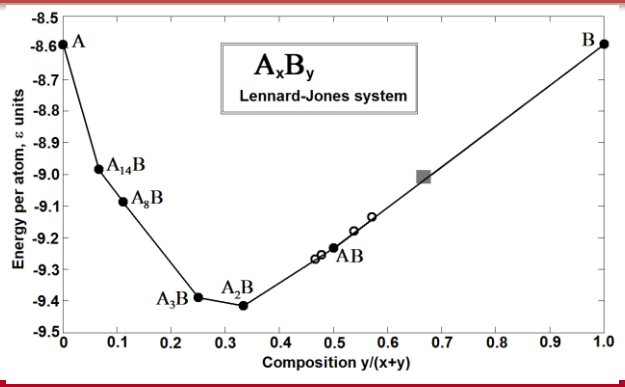
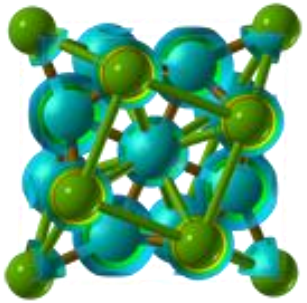
Crystal Structure Prediction in USPEX:

The variable composition systems

I: Xe-O at high P	II: Variable composition Predictions	III: Some apps





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USPEX

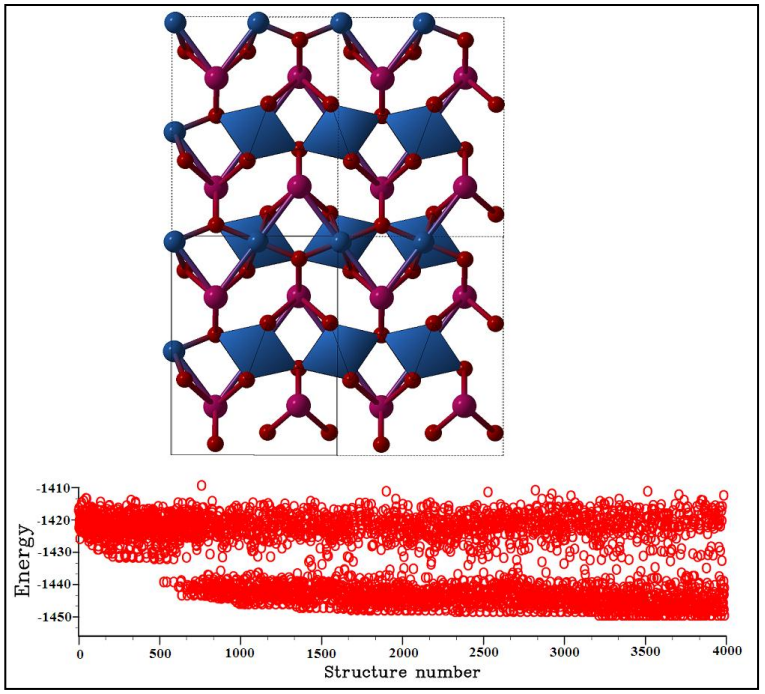
Universal Structure Predictor: Evolutionary Xtallography

- ***Evolutionary Algorithm***
- ***Ab initio* determination**

  Given information as least as possible
- ***Powerful Searching***

  invariant with the system

  Self-improved learning process



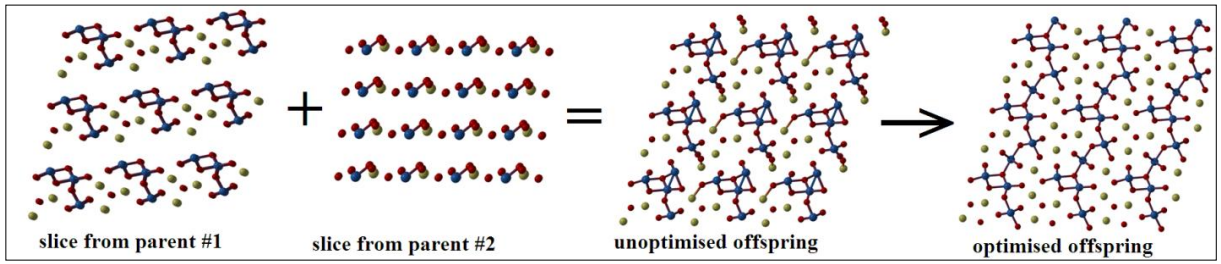
Website: http://uspex.stonybrook.edu

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

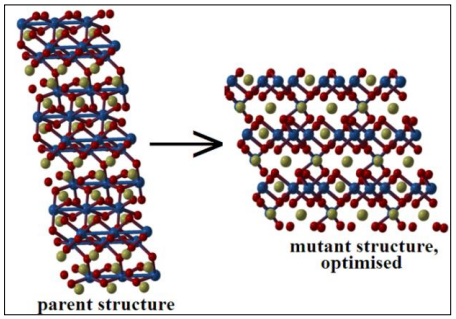
USPEX

- **(Random) initialization:** from INPUTs : chemical formula, P/T, etc
- **Relaxation**: (free) energy (done by VASP, .etc)
- **Selection**: lowest-energy structures as parents
- **New population**: Standard variation operations

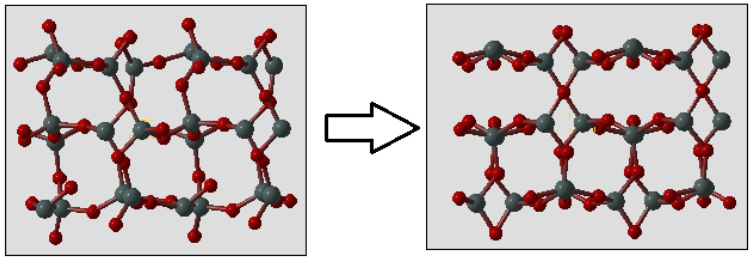
(1) Heredity (crossover)



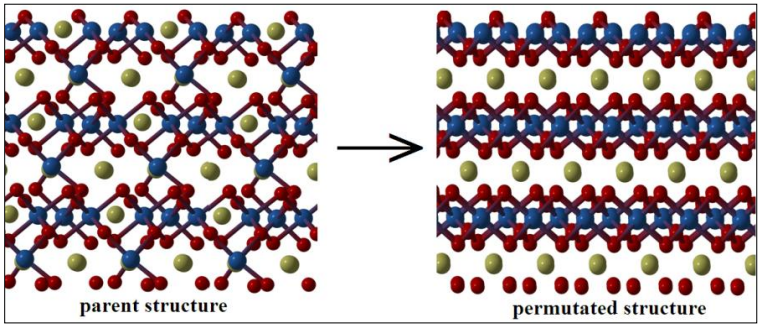
(2) Lattice mutation



(3) Softmutation



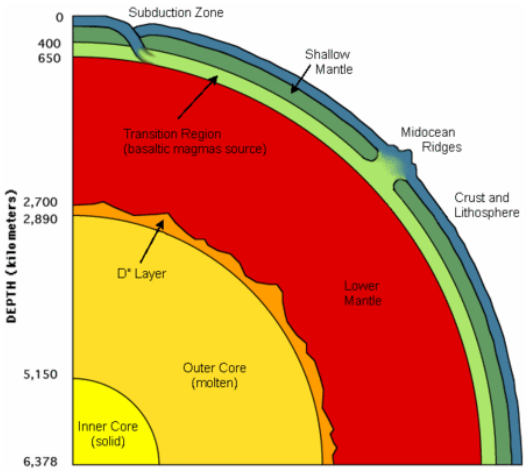
(4) Permutation



Missing Xenon Paradox

" our atmosphere contains far less xenon, relative to the lighter noble gases, than meteorites similar to the rocky material that formed the Earth,"

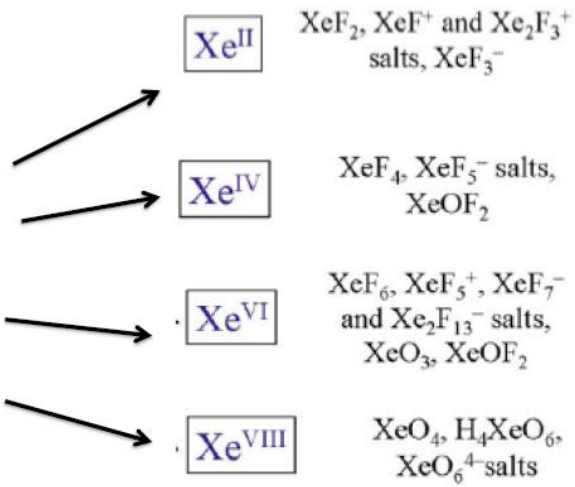
----- Anderson, E, .*Science*, 1977



Hypothesis: Xenon is stored in the Earth's mantle ?
(most likely with perovskite, oxides or silicates, Sanloup, Science, 2005)

Xenon Chemistry

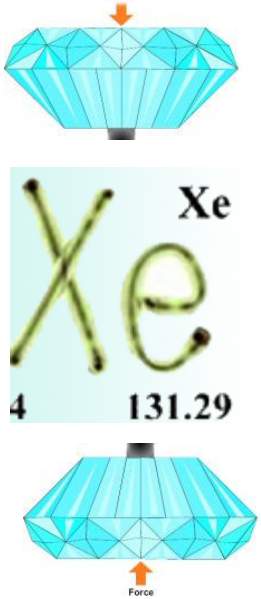
Ambient condition



Xenon does exhibit multiple valence state

Grochala, Chem. Soc. Rev, 2007

Earth's mantle condition



Prediction on Xe-O system

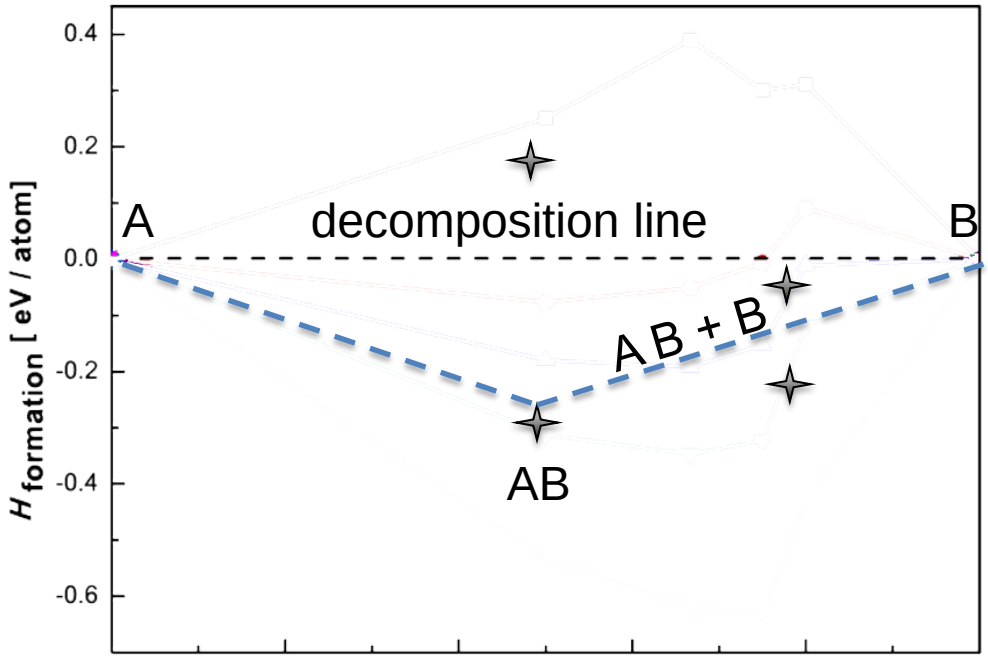
Pressures(GPa):

5, 50, 100, 120, 150, 180, 200 , 220

Stoichiometry:

XeO, XeO_2, XeO_3, XeO_4

How to evaluate the thermodynamical stability

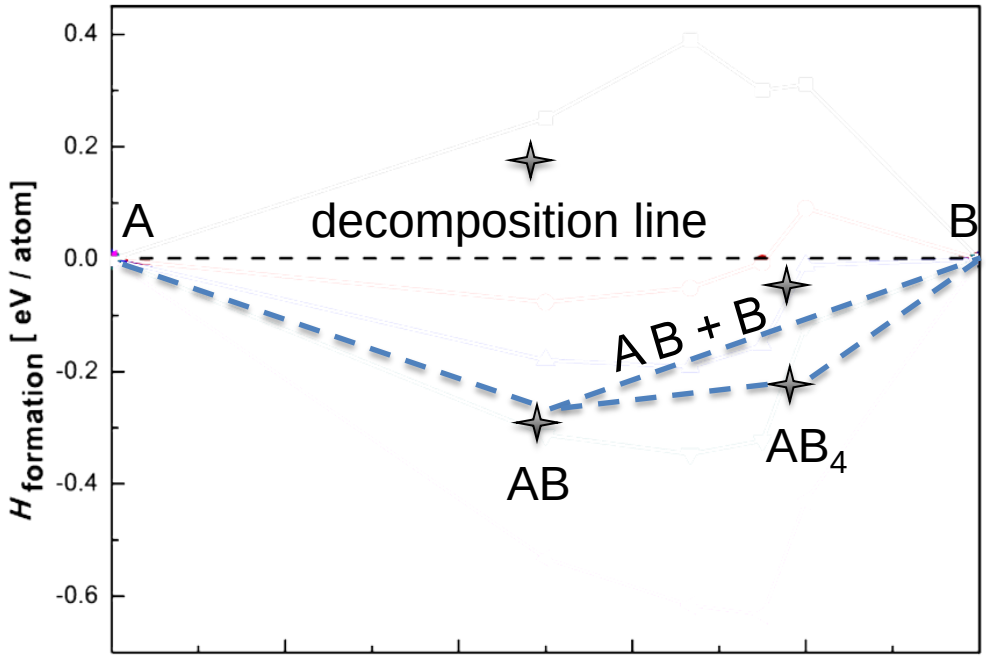


$$A + B \longrightarrow AB$$

$E_{AB} > E_A + E_B$; AB decompose

$E_{AB} < E_A + E_B$; AB is stable

How to evaluate the thermodynamical stability



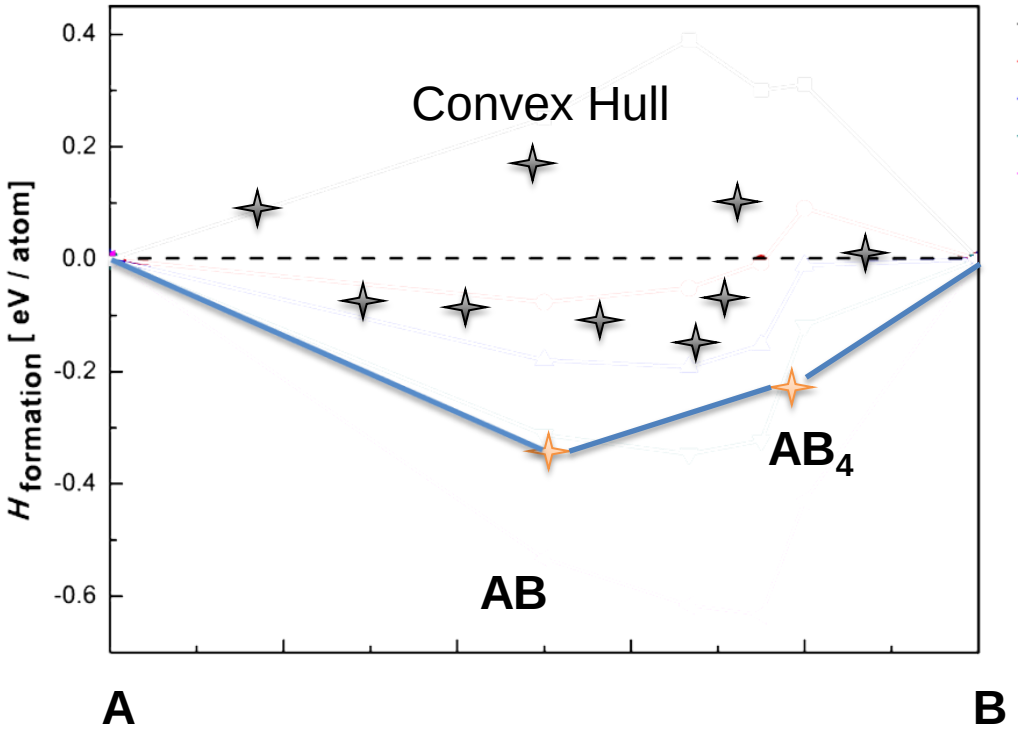
$$A + B \longrightarrow AB$$

$E_A + E_B > E_{AB}$; AB decompose

$E_A + E_B < E_{AB}$; AB is stable

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

How to evaluate the thermodynamical stability



$$A + B \longrightarrow AB$$

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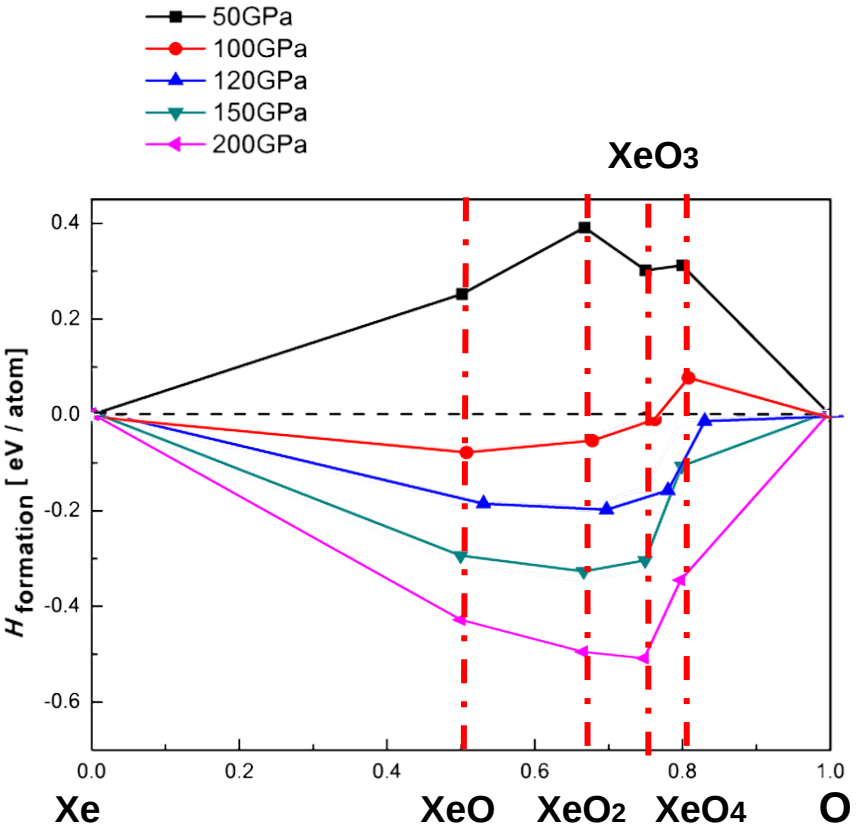
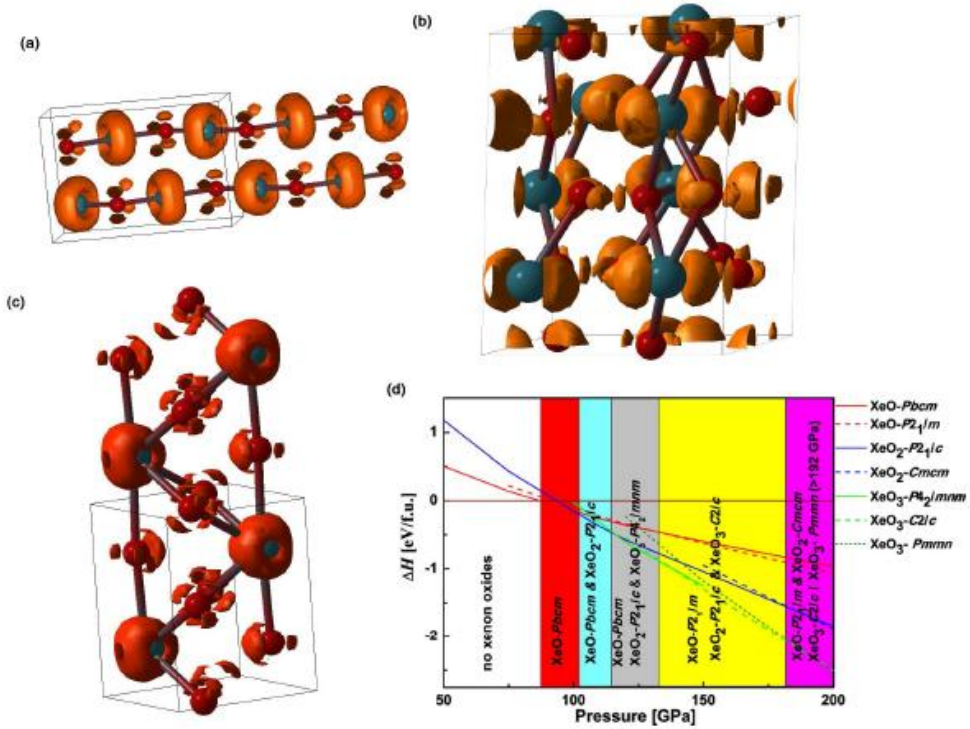
Stable structure must be below all the possible decomposition lines !!

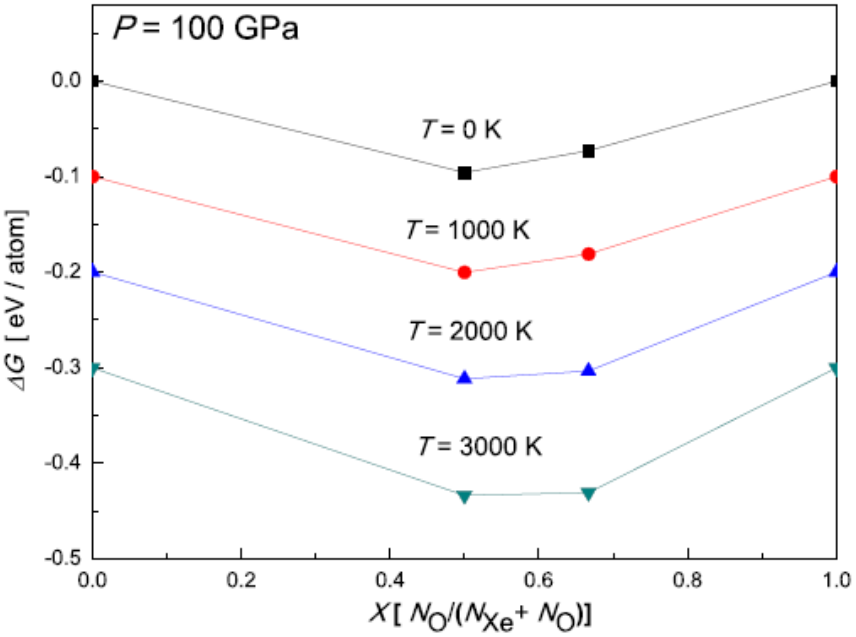
Xenon oxides at high pressure

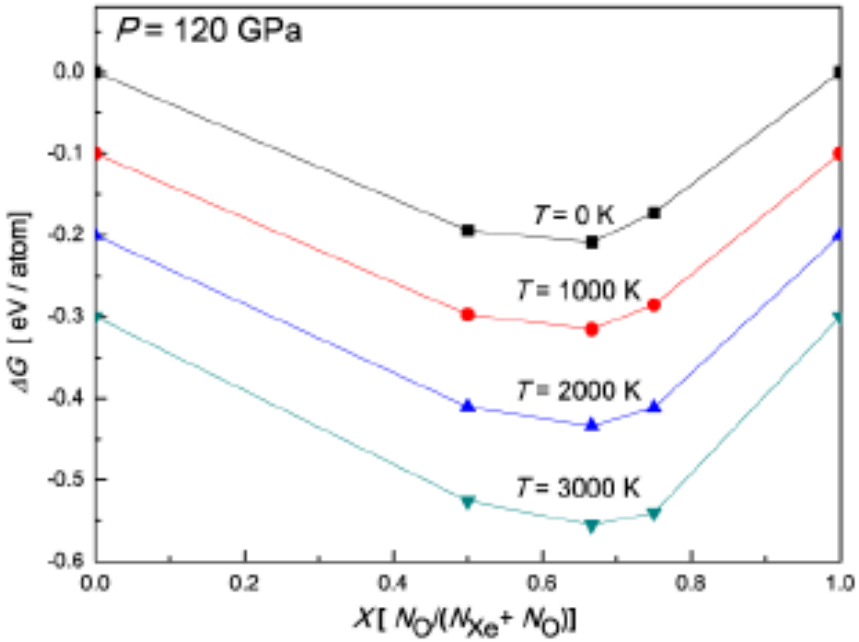




Q. Zhu, et al, Nature Chemistry, 2013

Stability of Xenon Oxides at high T





Q. Zhu, et al, Nature Chemistry, 2013

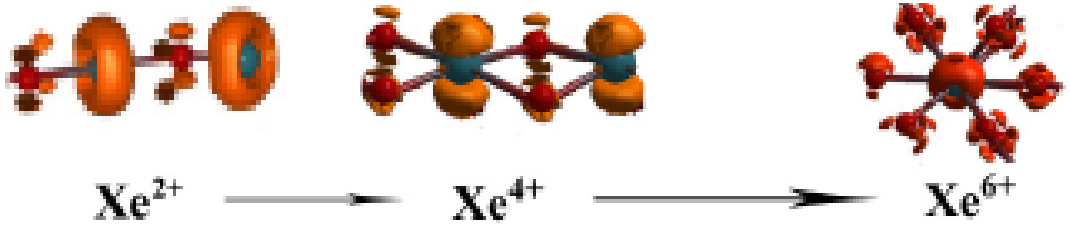
nature chemistry

ARTICLES

PUBLISHED ONLINE: XX XX 2012 | DOI: 10.1038/NCHEM.1497

Stability of xenon oxides at high pressures

Qiang Zhu[1]*, Daniel Y. Jung[2], Artem R. Oganov[1,3]*, Colin W. Glass[4], Carlo Gatti[5] and Andriy O. Lyakhov[1]



General Rule:

New stoichiometric compounds might exist under high pressures ! -- can we predict them automatically?

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To *predict* all stable stoichiometries and structures simultaneously?

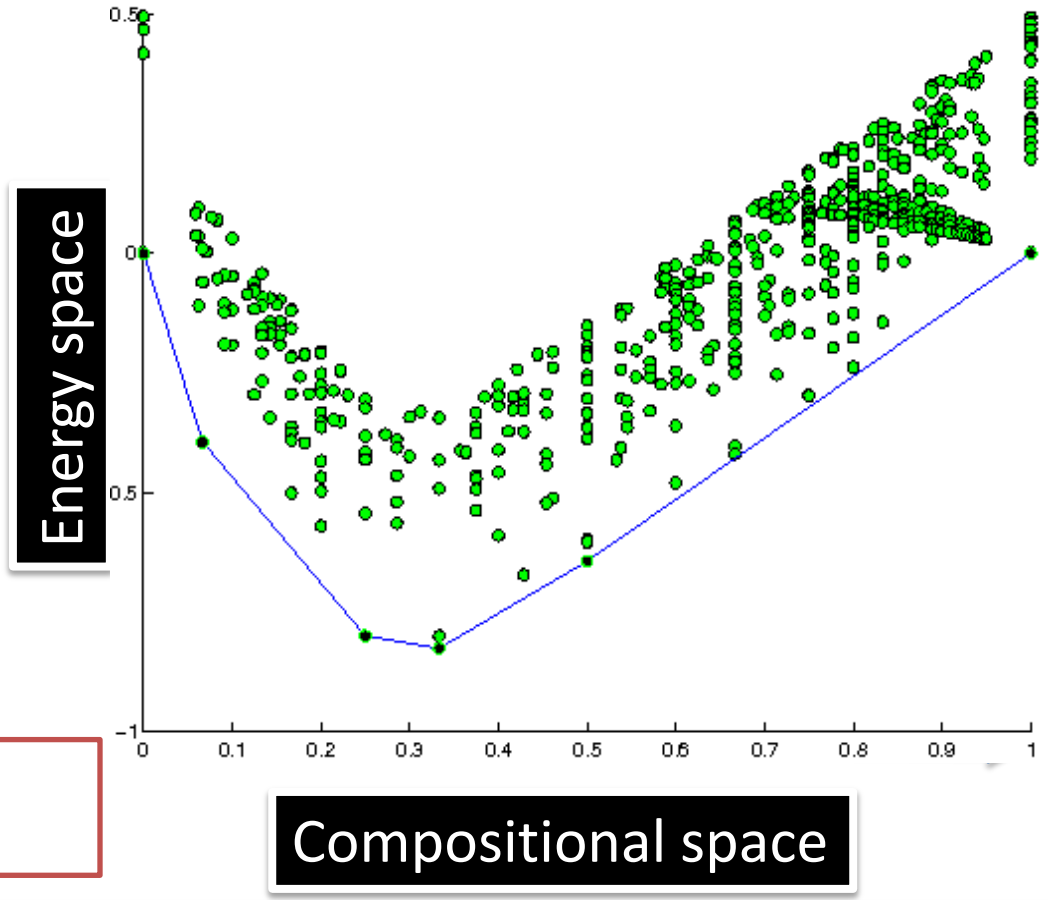
Q1: How to evaluate the quality of each structure with different compositions?

A1: Optimization target: convex hull

Discrete

↓

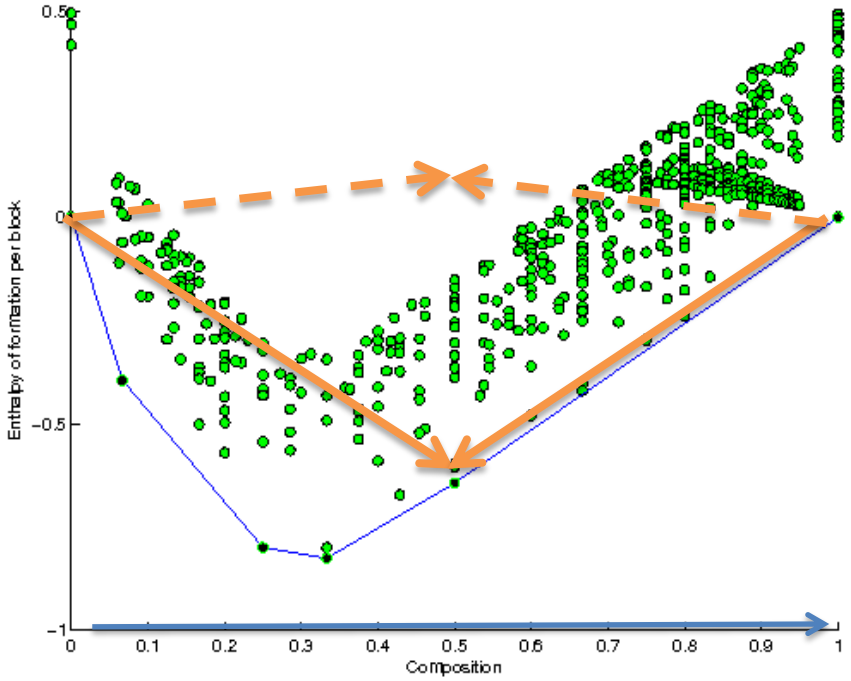
Continuous

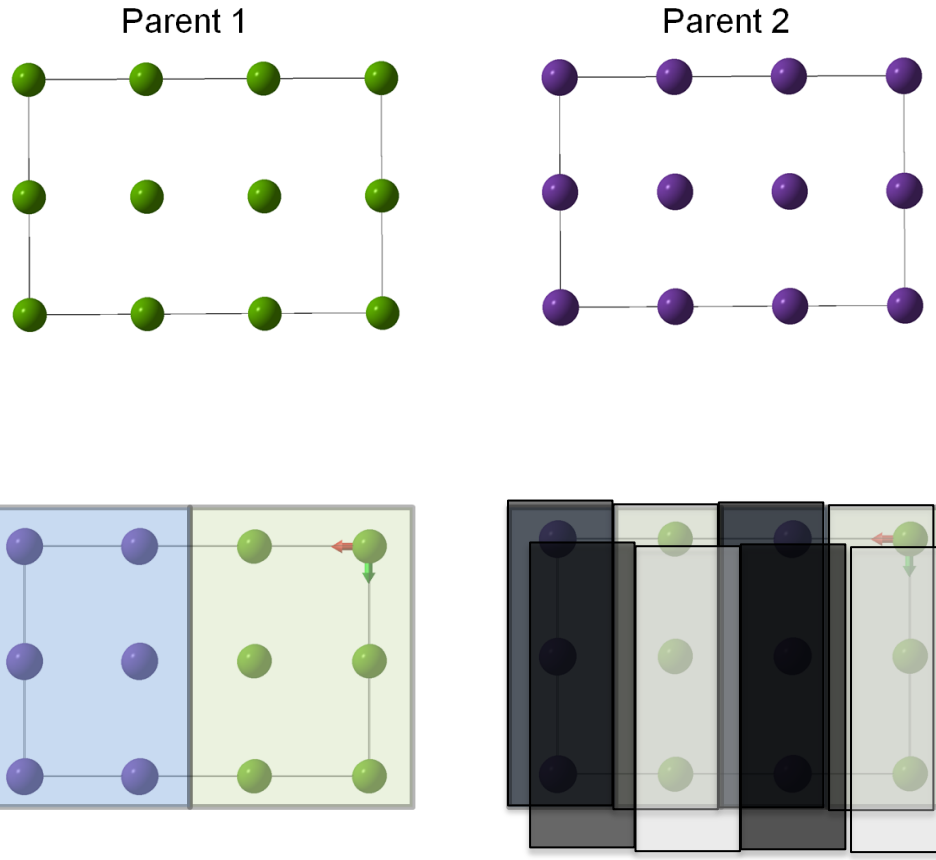


Q2: Allow the compositional variation?

A3: Smart variation operators

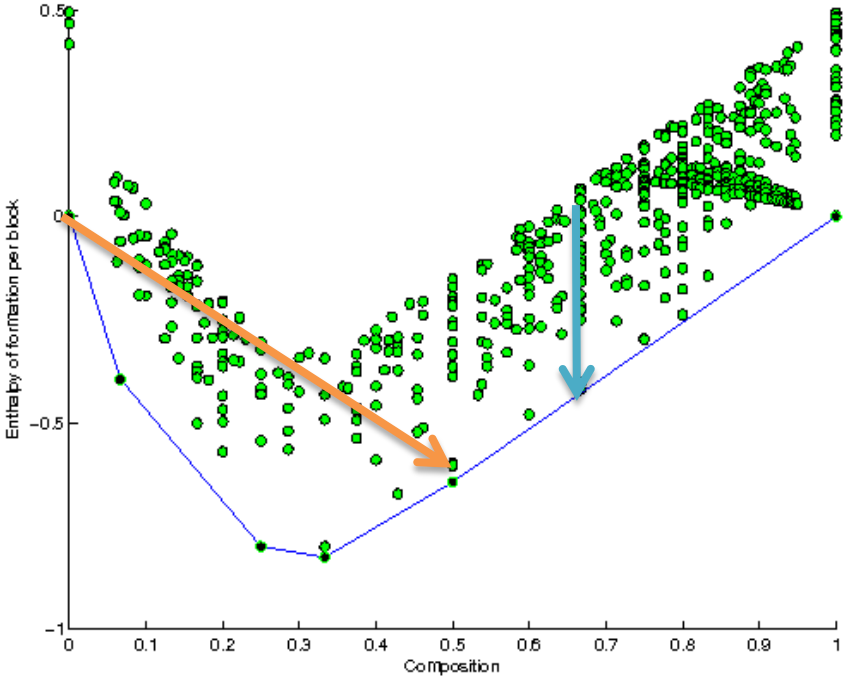
Heredity

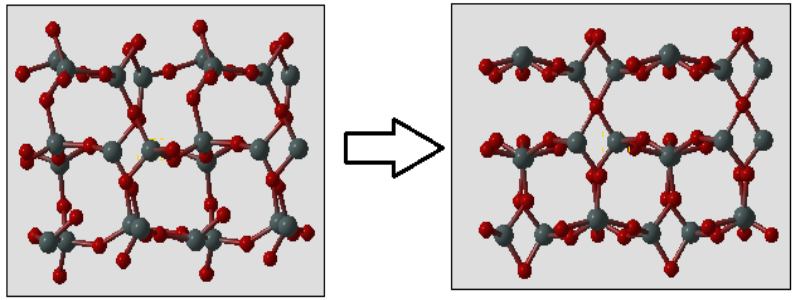

0.5
0
−0.5
−1
Enthalpy of formation per block
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Composition


Parent 1
Parent 2

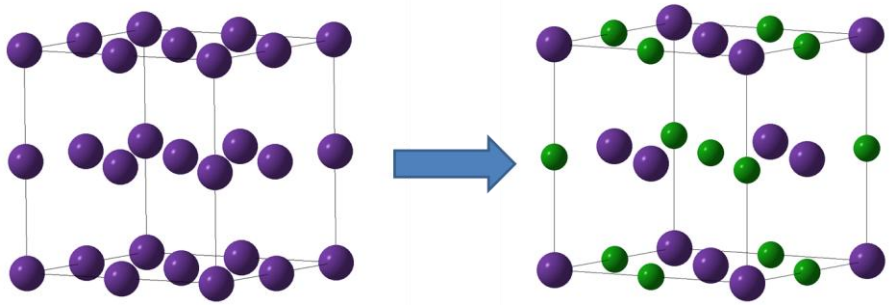
Mutations

On-the-fly optimization:
take the advantage of all the instantly learned knowledge





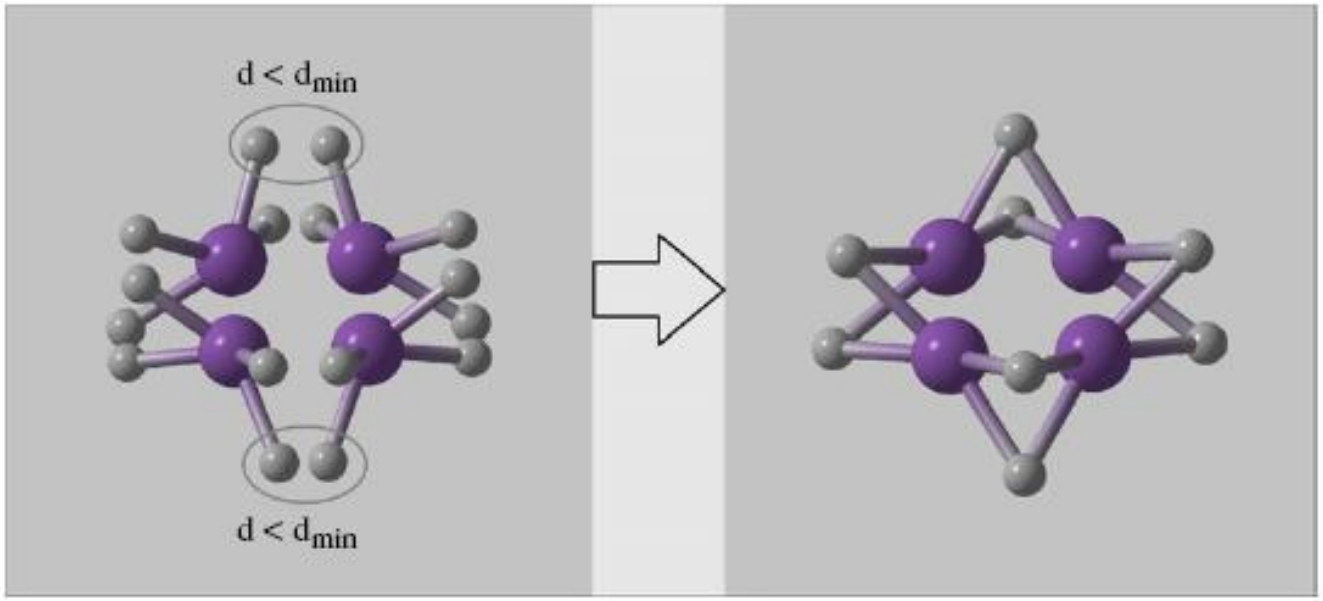
Softmutation/Permutation



Transmutation

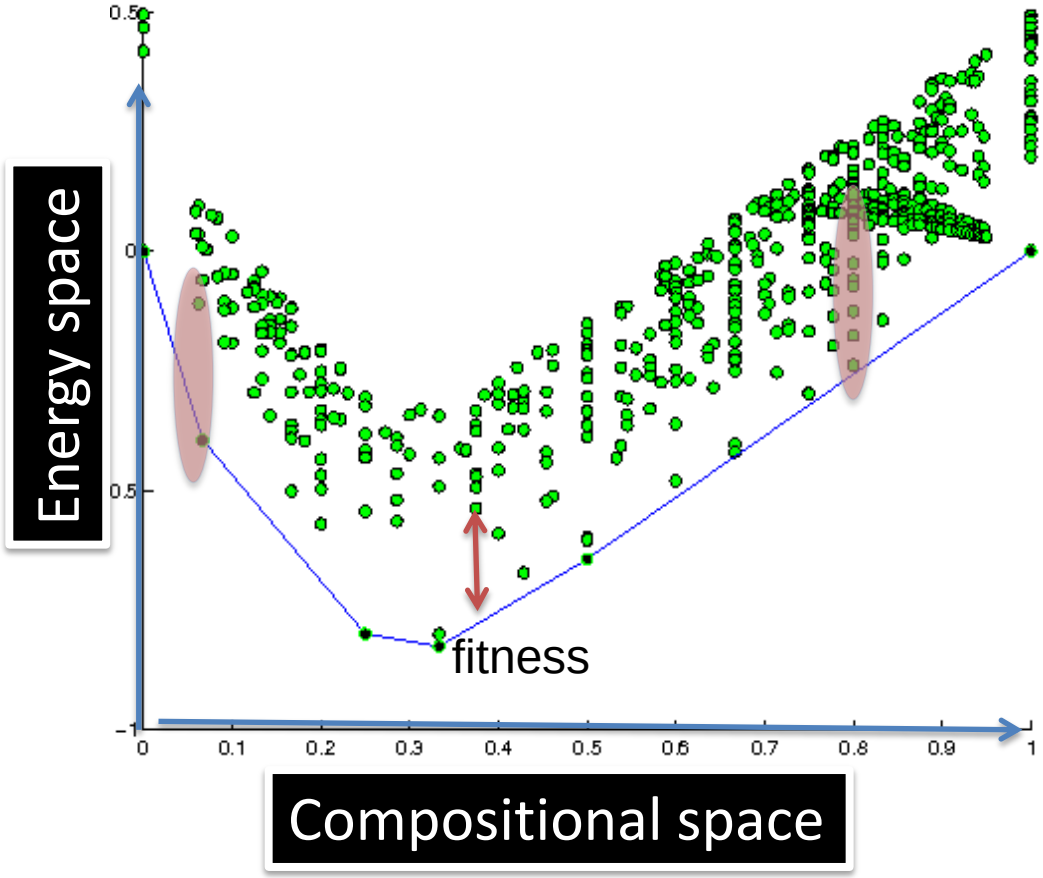
Initialization

To generate structures with random space groups



Selection

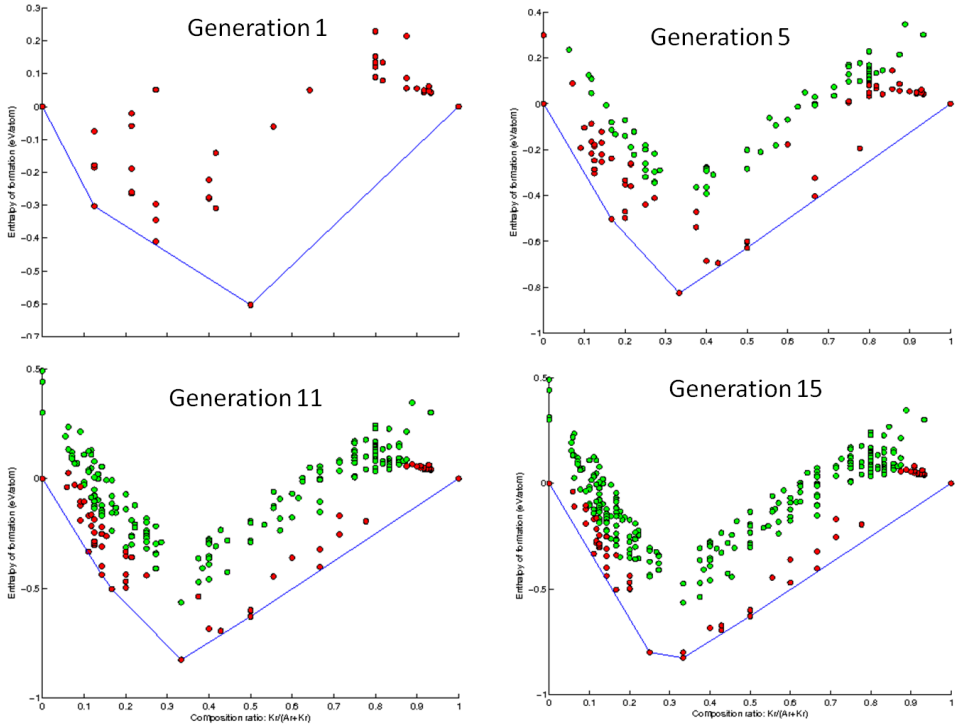
Variable energy window widths

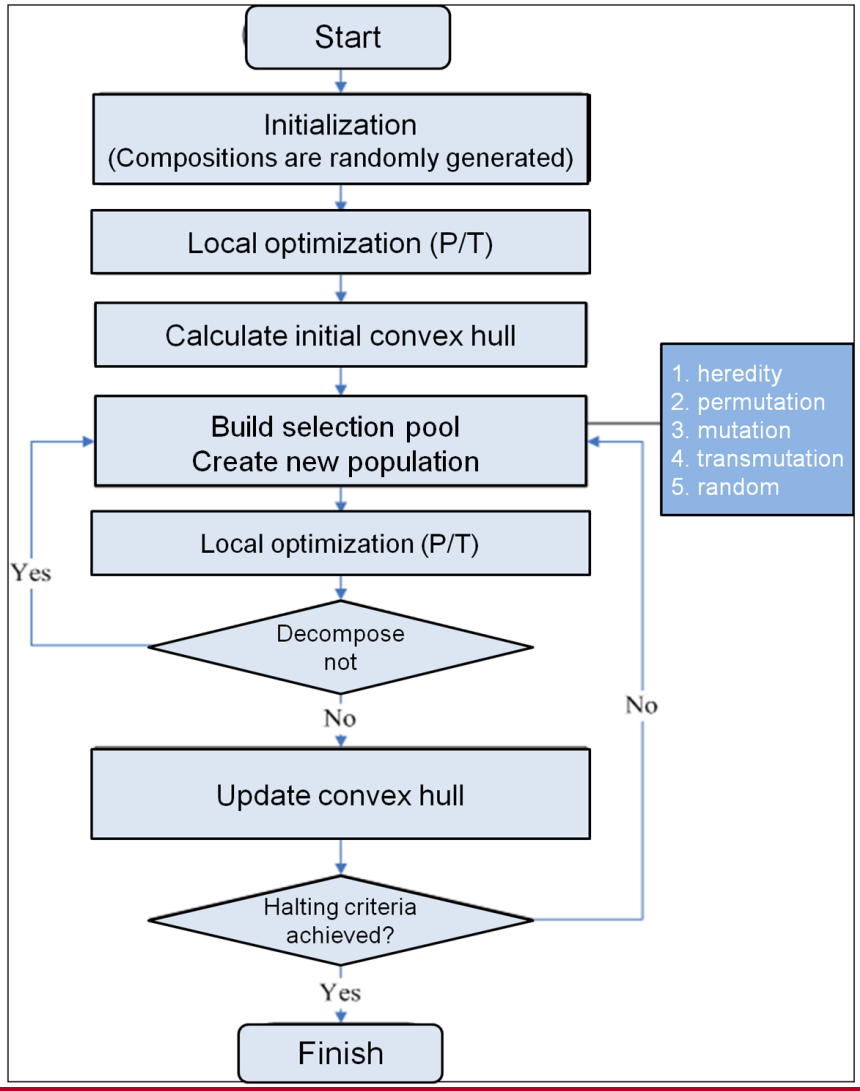


Algorithm and examples

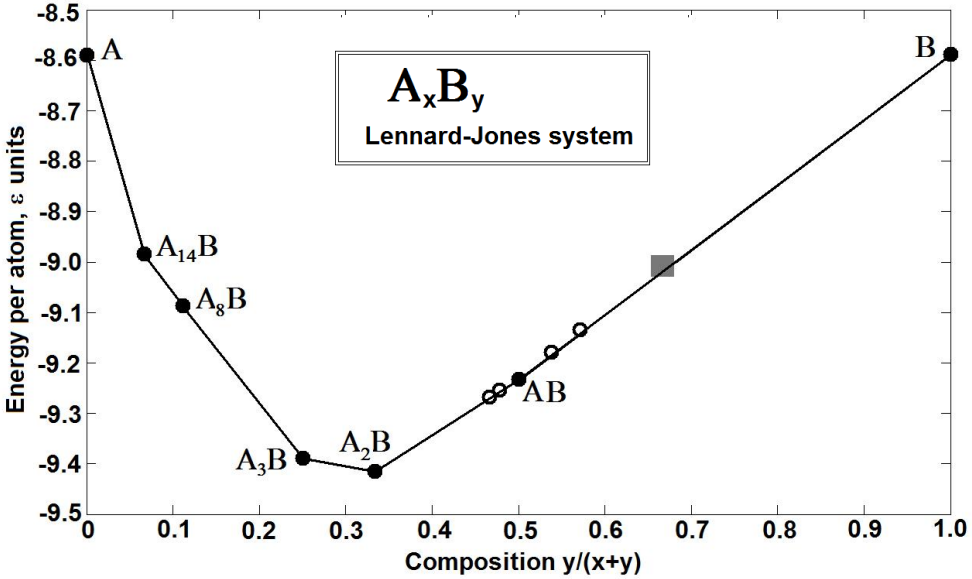
A_xB_y

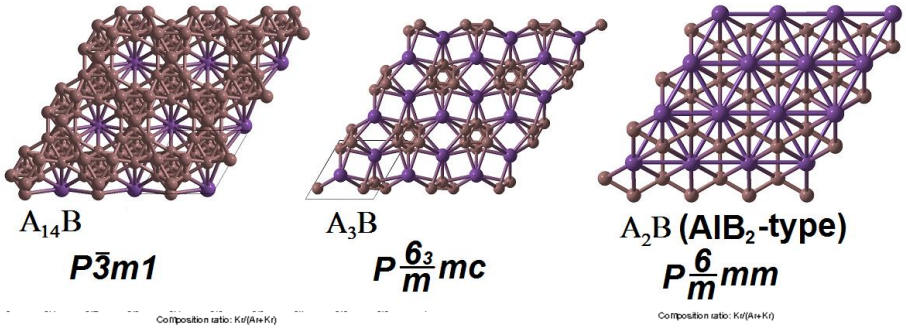
Lennard-Jones system

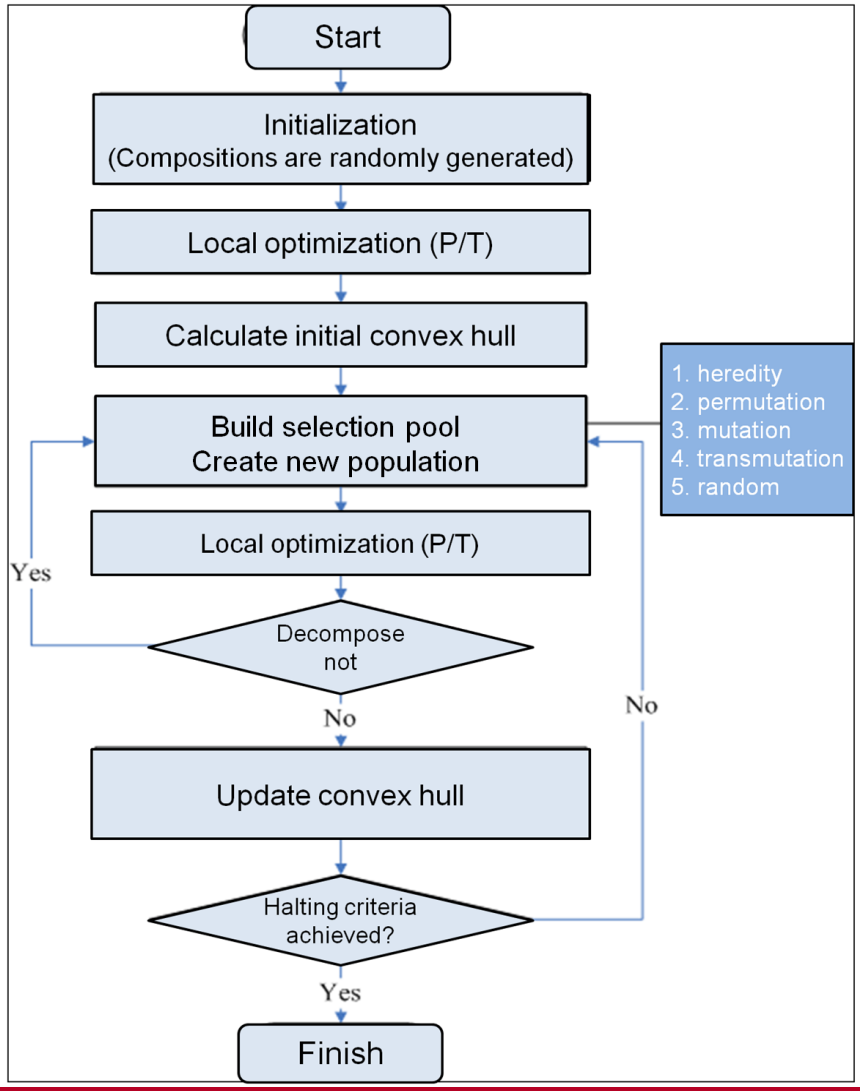




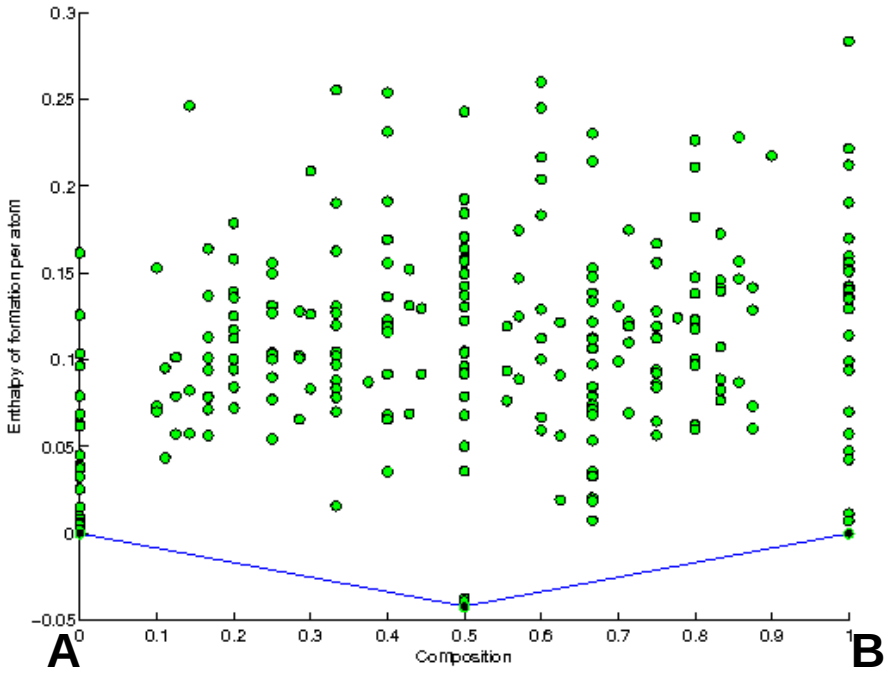
Algorithm and examples







Applicable systems



A	B
Ni	Cu
Na	Cl
NaCl	Cl
MgO	SiO_2/Al_2O_3
H_2	H_2O
$CaCl_2/CaSO_4$	H_2O

Even ternary systems: C-H-O, C-N-O

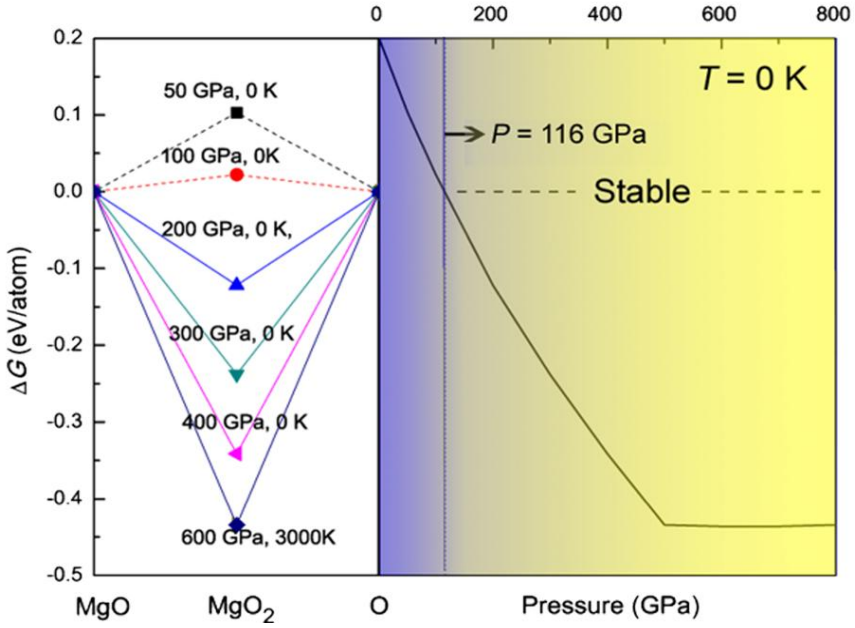
A always good strategy:
to split the compositional space based on the previous calculations

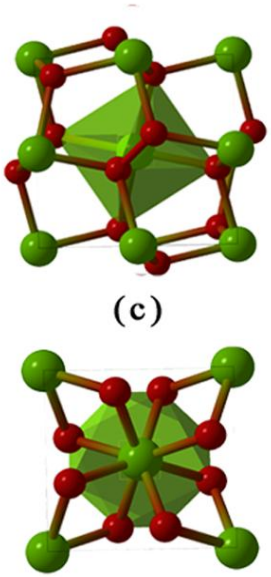
New Findings Could Change Our View of Planet Formation

Team led by Artem Oganov challenges existing chemical models and current understanding of planetary interiors

MgO-O

MgO_2





Zhu, et al, PCCP, 2013

New Findings Could Change Our View of Planet Formation

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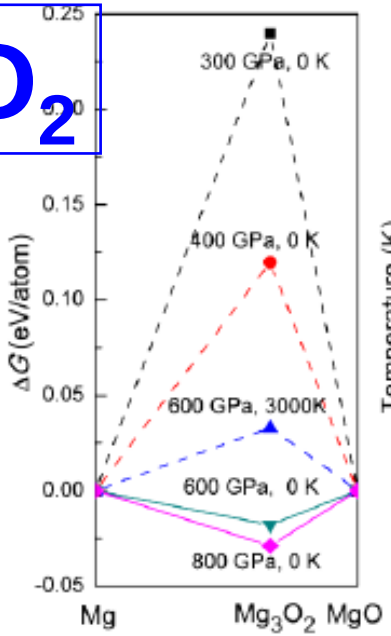
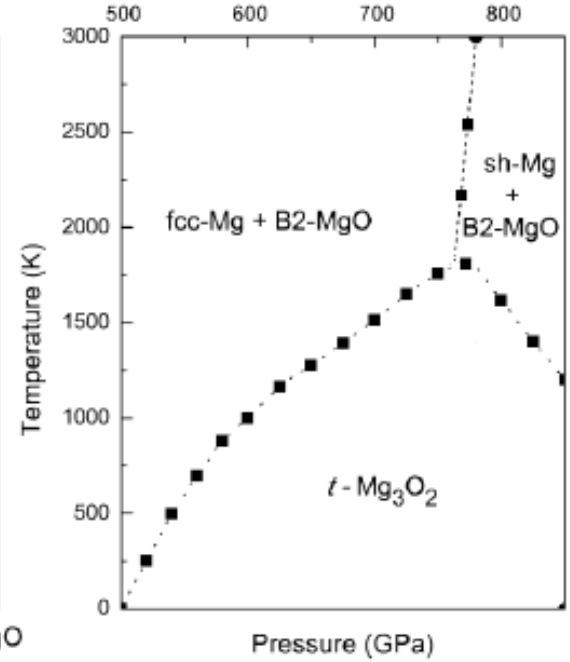
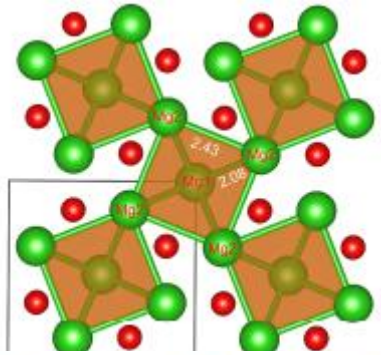
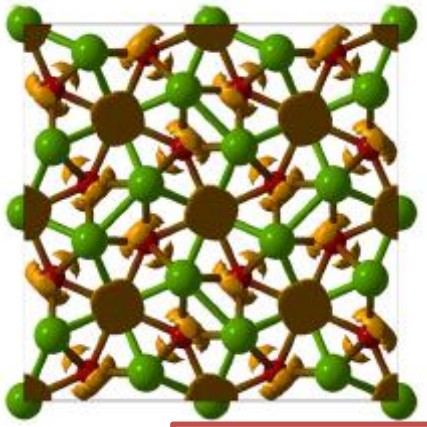
Mg_3O_2





Mg-MgO

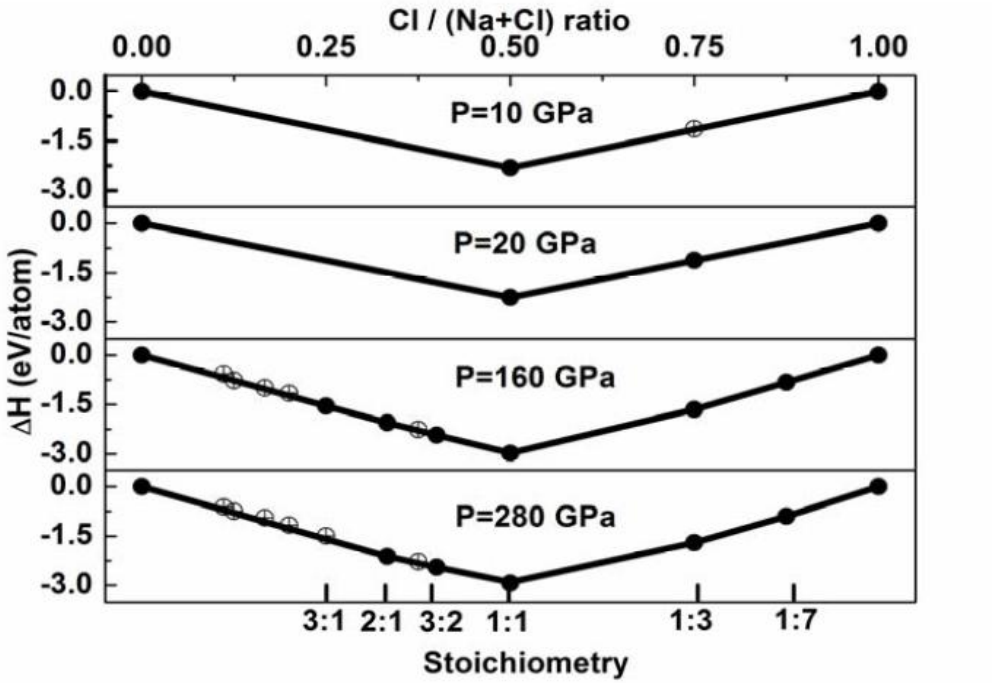


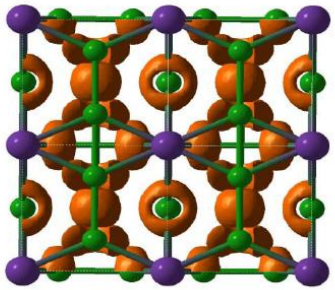


Zhu, et al, PCCP, 2013

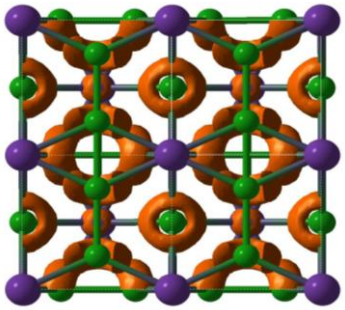
Talk by W. W. Zhang on Wednesday

Na-Cl





$NaCl_3$, stable from ~20 GPa



$NaCl_7$, stable from ~147 GPa

Zhang, ARO, et al, unexpected stable stoichoimetries of sodium chlorides, arxiv

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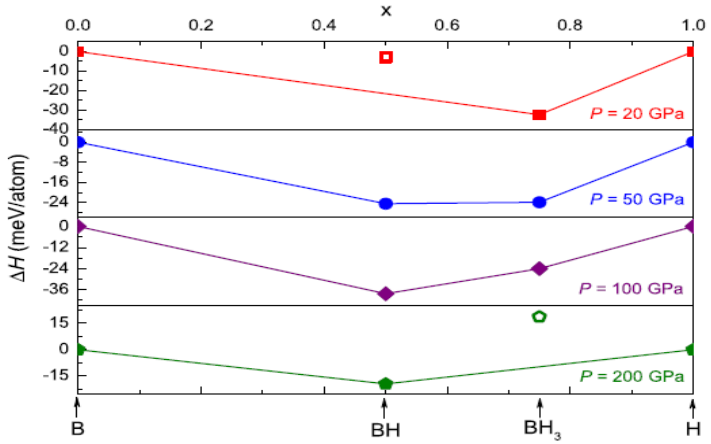
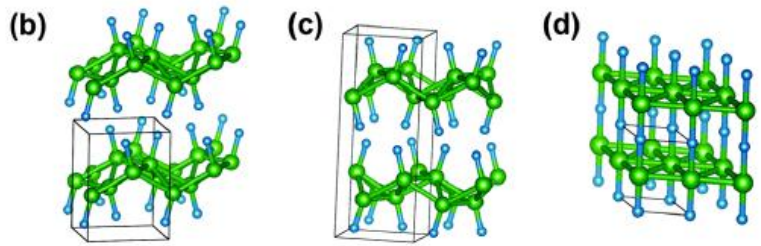
, 165504 (2013) PHYSICAL REVIEW LETTERS 19

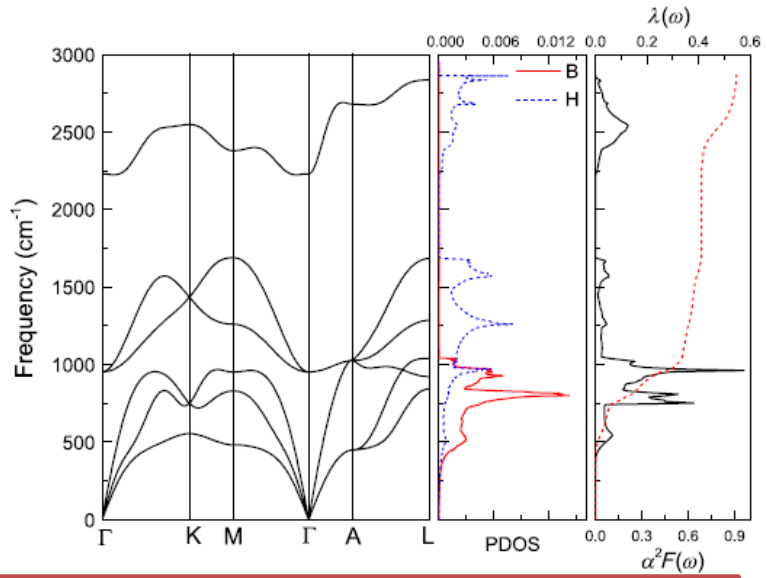
B-H

Pressure-Induced Stabilization and Insulator-Superconductor Transition of BH

Chao-Hao Hu,[1,2,*] Artem R. Oganov,[2,3] Qiang Zhu,[2] Guang-Rui Qian,[2] Gilles Frapper,[4] Andriy O. Lyakhov,[2] and Huai-Ying Zhou[1]

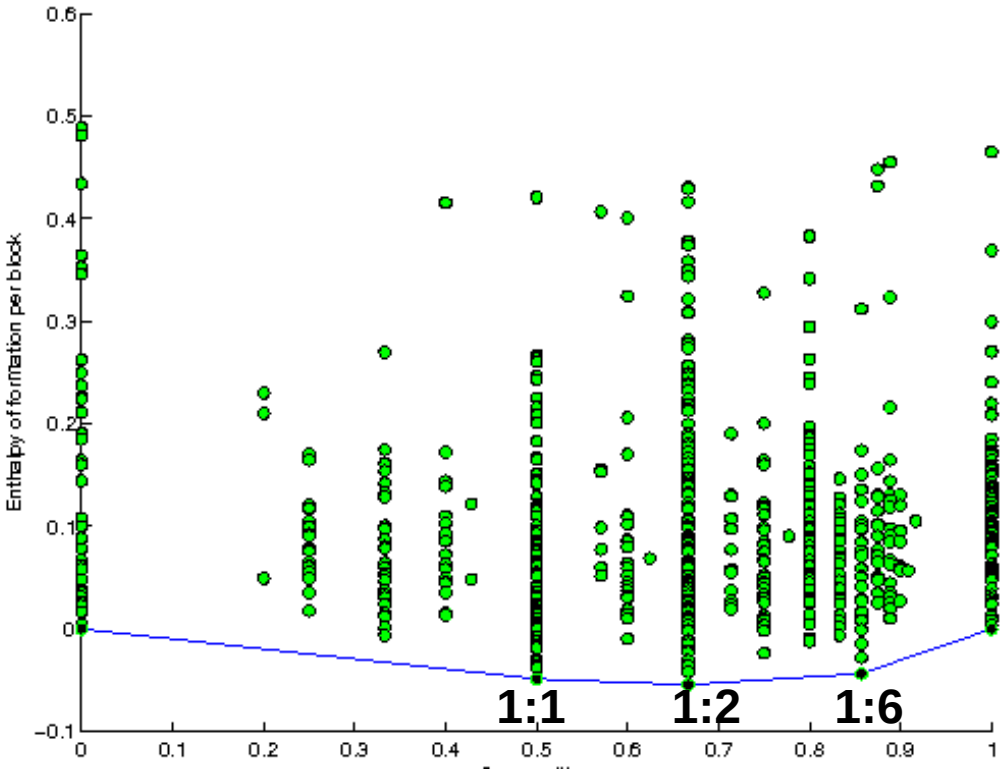




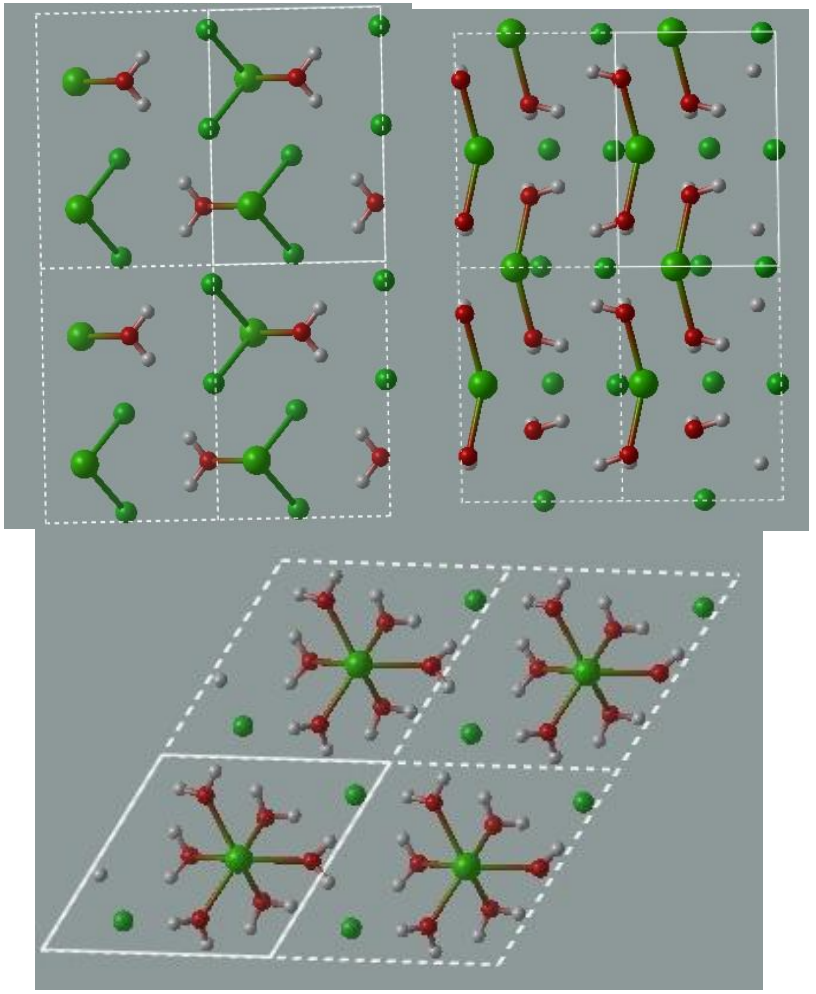


Talk by C. H. Hu on Wednesday

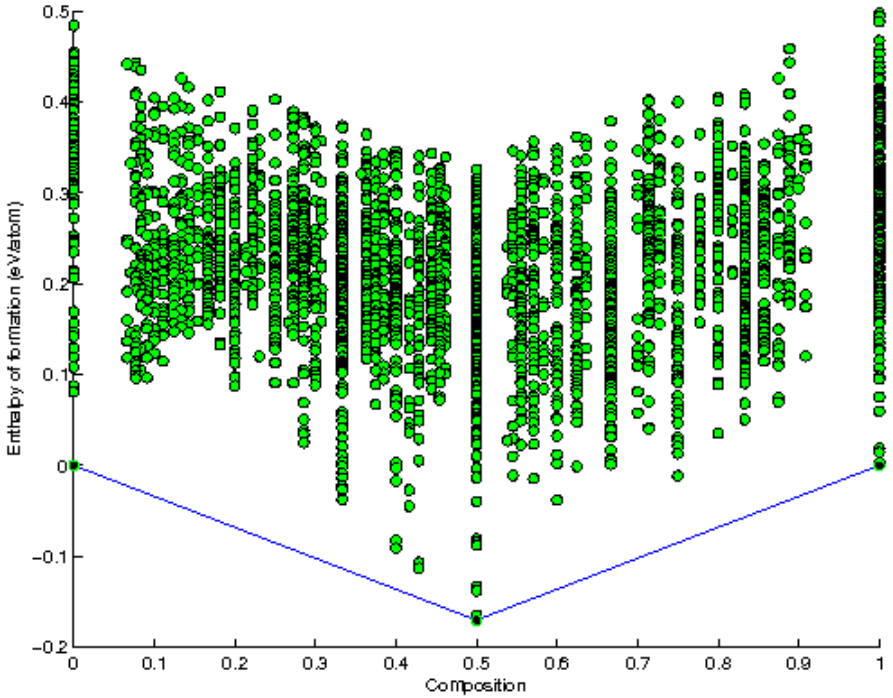
Hydrates



CaCl2-H2O



Quick start



MgO-SiO_2

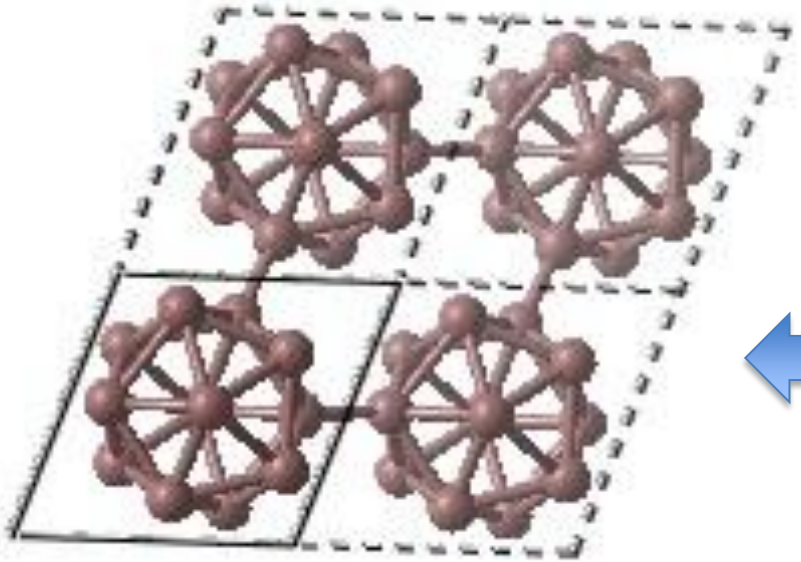
MgO
SiO_2

```
301: calculationType

% numSpecices
1 0 1
0 1 2
% EndNumSpecices

% atomType
Mg Si O
% EndAtomType

8    : minAt
16   : maxAt

% Latticevalues

% Endvalues
```

MgO
SiO_2

Single block prediction

To predict the phase of boron with Variable number of atoms per cell



α- boron: 12 atoms/cell

```
301: calculationType

% numSpecices
1
% EndNumSpecices

% atomType
B
% EndAtomType

8     : minAt
16    : maxAt

% Latticevalues
7.5
% Endvalues
```

USPEX: Computational Materials Design

Crystal Structure Prediction

System

- **Dimension**
  - 0: Nano-particle;
  - 1: polymers;
  - 2: surfaces/crystals;
  - 3: Bulk
- **Stoichiometry**
  - 0: fixed; 1: variable
- **Building block**
  - 0: atom; 1: molecule

Target

- Density
- Hardness
- Dielectric constants
- Band gap
- Magnetic moment
- ….

Crystal Structure:

300: Sunday talk by ARO
301: Sunday talk by Zhu
310: This talk
311: This talk

Low -Dimensions

000
110
200/201
-200

Wednesday!

Materials Discovery:

Next talk by ARO

Question:

What's the origin of stoichiometric variation?

- New valence states in Chemistry? (Xe-O)
- New interactions in Physics? (Mg_3O_2)
- Close packing Mechanically? (Alloys)
- ……..?

TO

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