How we discovered forbidden chemistry

Artem R. Oganov (ARO)

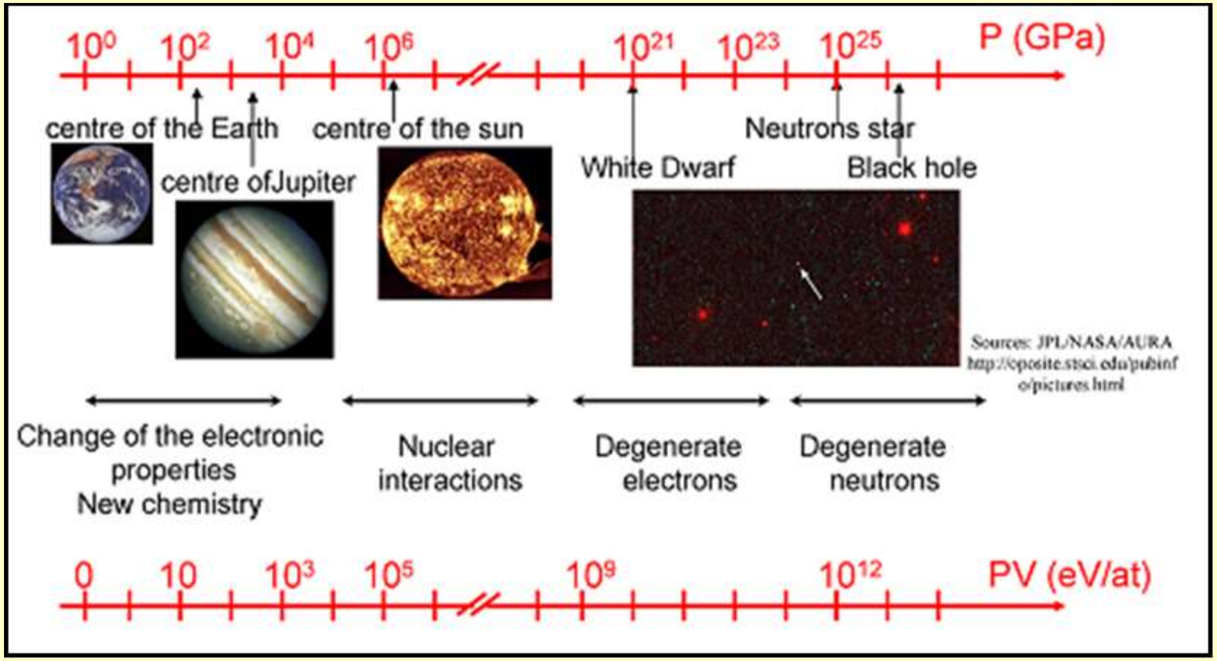
Department of Geosciences , Center for Materials by Design, and Institute for Advanced Computational Science, State University of New York, Stony Brook, USA

Moscow Institute of Physiics and Technology, Dolgoprudny, Russia

Northwestern Polytechnical University, Xi'an, China

Stony Brook University | The State University of New York

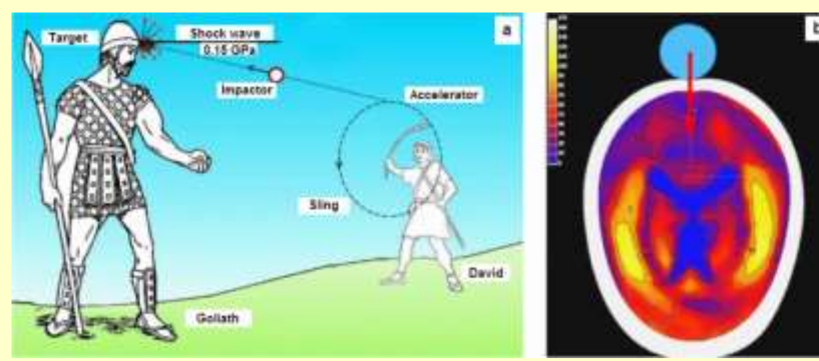
Matter under pressure: new phenomena and ubiquity in nature



P.W. Bridgman

1946 Nobel Prize for Physics

Units: **100 GPa = 1 Mbar =** **200x**  / 



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

Are Crystal Structures Predictable?

ANGELO GAVEZZOTTI*

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

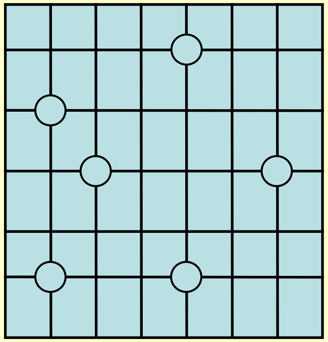
ONE of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition. Who, for example, would guess that graphite, not diamond, is the thermodynamically stable allotrope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

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

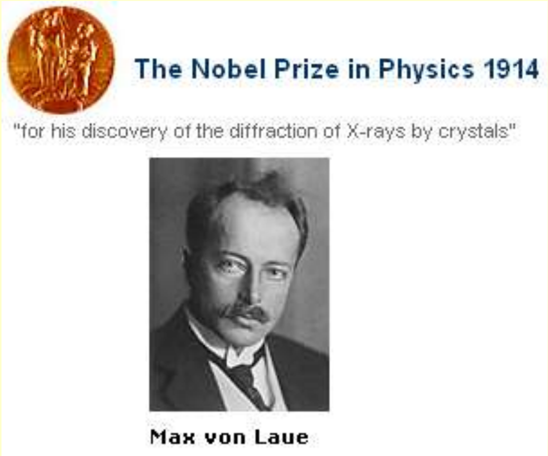
Crystal structure prediction – evolutionary or revolutionary crystallography?

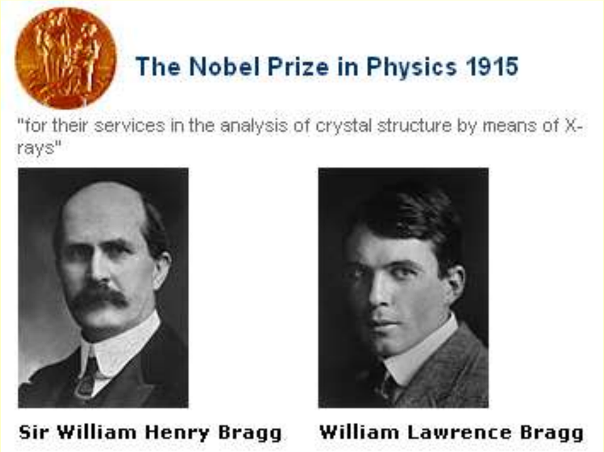
S. L. Chaplot and K. R. Rao

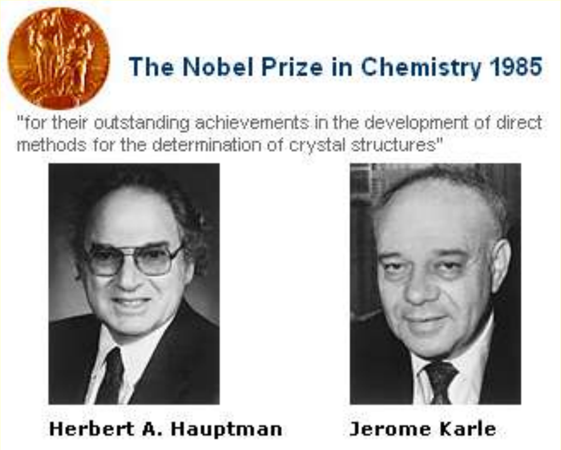
CURRENT SCIENCE, VOL. 91, NO. 11, 10 DECEMBER 2006

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

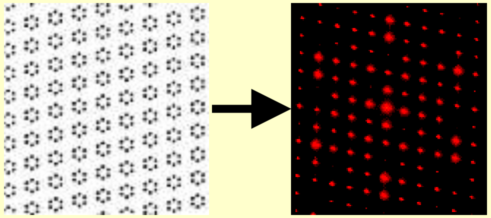
Structure is the basis for understanding materials and their properties





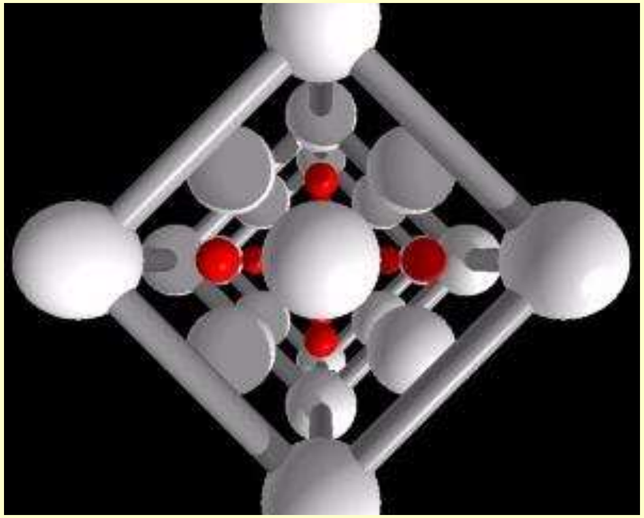


(from http://nobelprize.org)

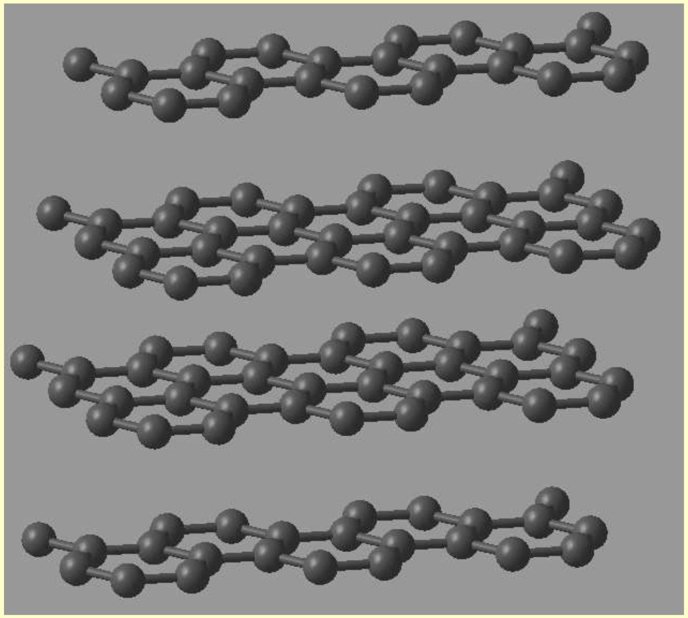


Structure **Diffraction**

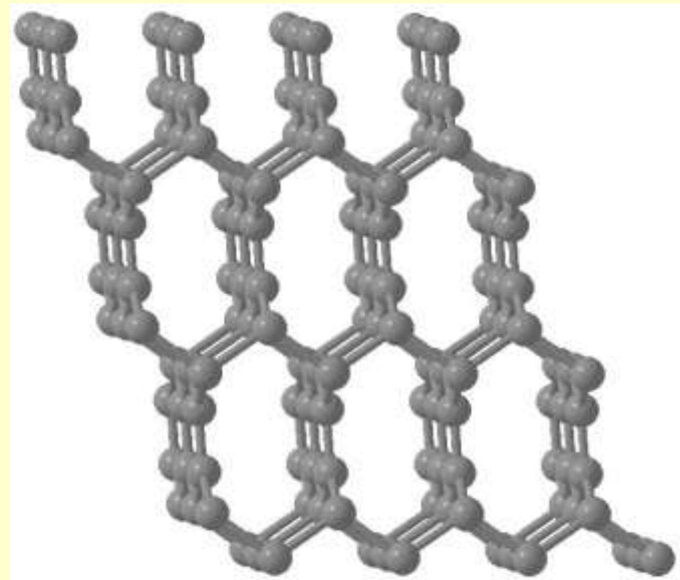
Zincblende ZnS.
One of the first structures solved by Braggs in 1913.



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



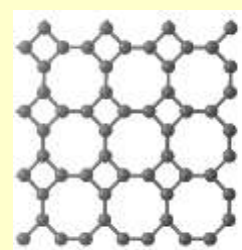
Graphite, correctly predicted to be the stable phase at 1 atm



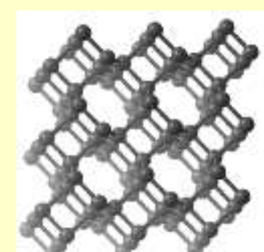
Metastable superhard sp^2-forms with 3D-topology. First proposed by R.Hoffmann (1983)

Low-energy structures reveal chemistry

sp-hybridisation (carbyne)



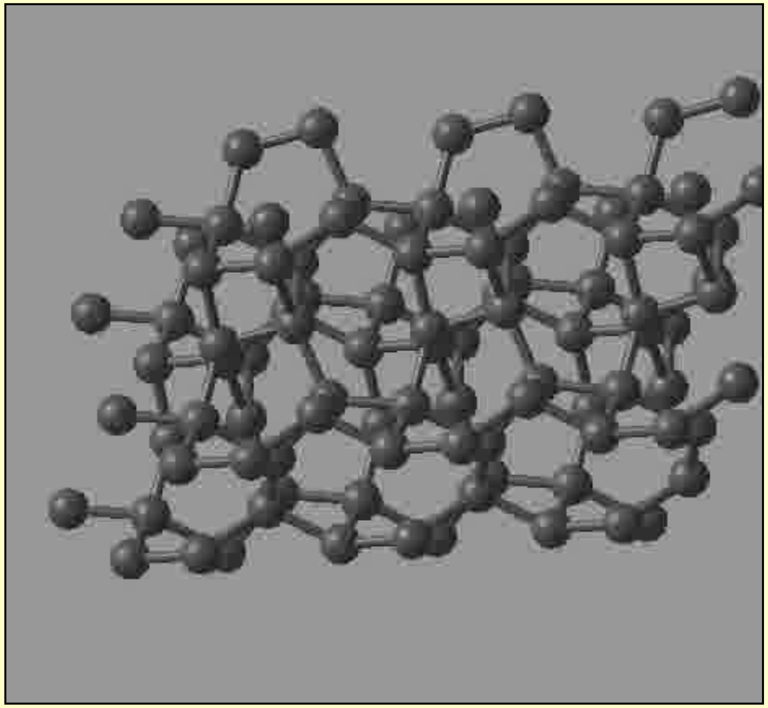
sp^2-hybridisation



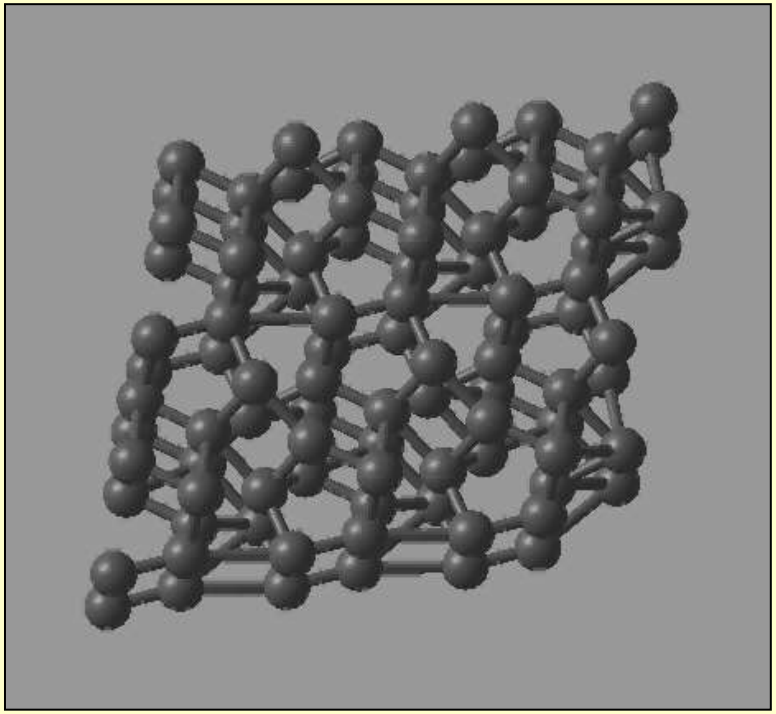
sp^3-hybridisation

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

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

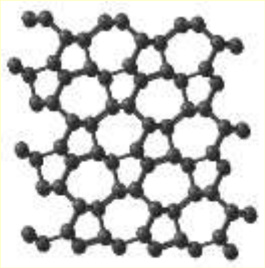


<u>100 GPa:</u> **diamond is stable**



<u>2000 GPa:</u> **bc8 phase, potentially important in astrophysics**

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



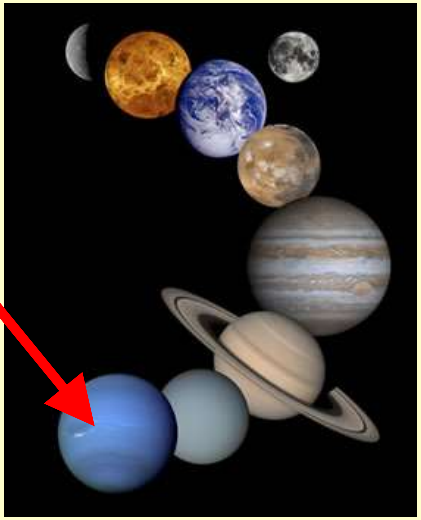
+found metastable form that matches „superhard graphite“ of W.Mao
(Li, ARO, et al., PRL 2009)

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

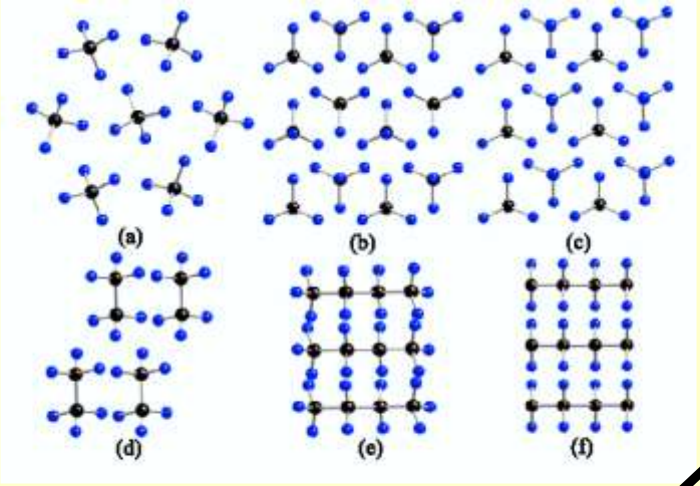
Story 1: Diamonds on Neptune?

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

CH_4



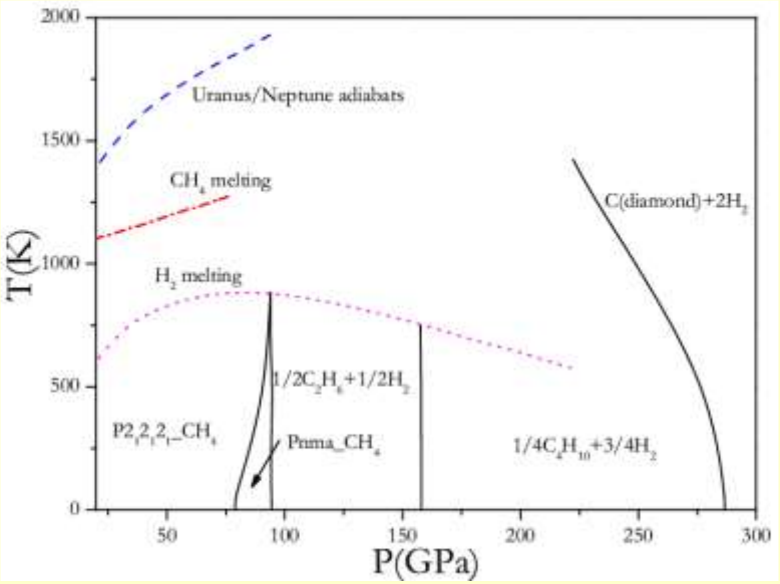
- Uranus and Neptune: $H_2O:CH_4:NH_3$ = 59:33:8.
- Neptune has internal heat source (Hubbard'99).
- Ross'81 (and Benedetti'99):
  CH_4=C(diamond) + $2H_2$. <u>Sinking of diamond – main source of heat in Neptune?</u>
- Theory (Ancilotto'97; Gao'2010) confirms this.



methane

hydrocarbons

diamond



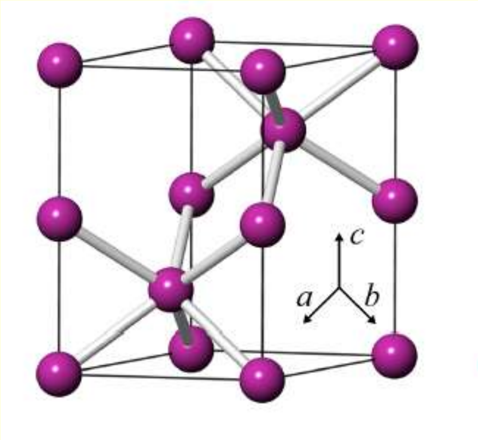
[Gao, ARO et al., *J. Chem. Phys.* 133, 144508 (2010)]

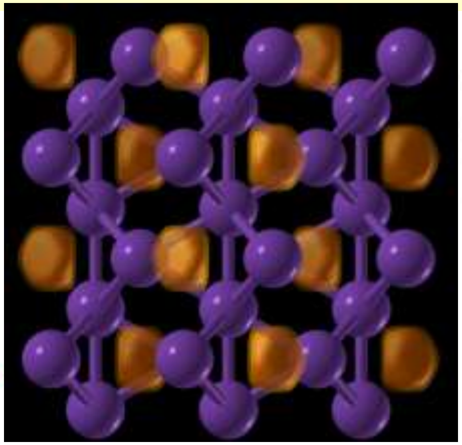
Story 2: Transparent sodium

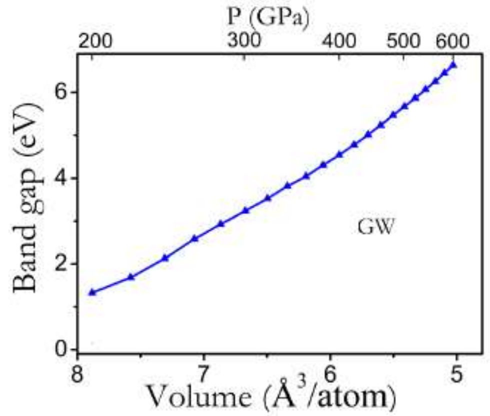
Alkali metal going non-metallic

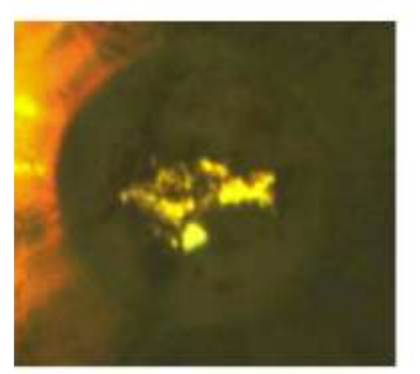
Na

- **Surprise: core electrons become essential and cause demetallization of Na and Li. Na becomes transparent at 200 GPa (Ma, Eremets, Oganov, Nature 2009).**





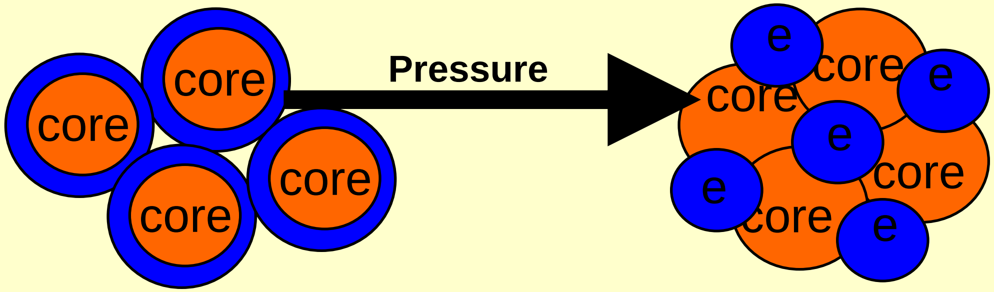




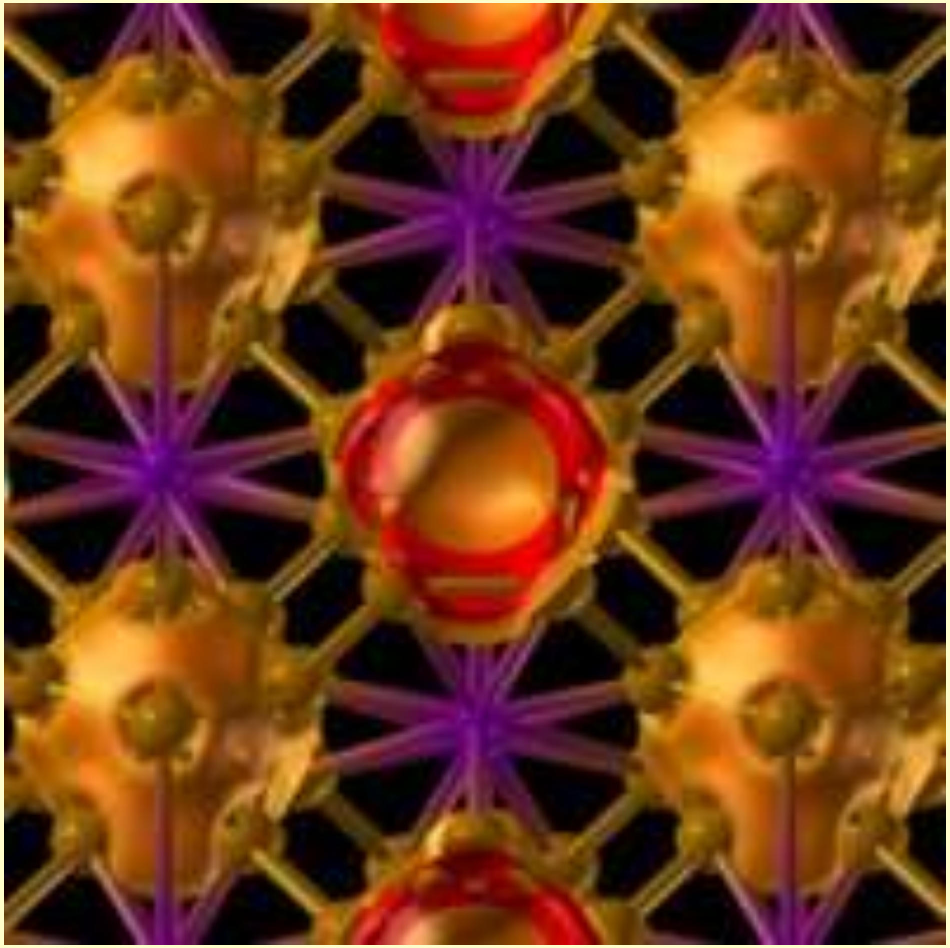
199 GPa

Localized interestitial electron pairs make Na insulating.

Explanation: Models of Ashcroft (1999, 2008)

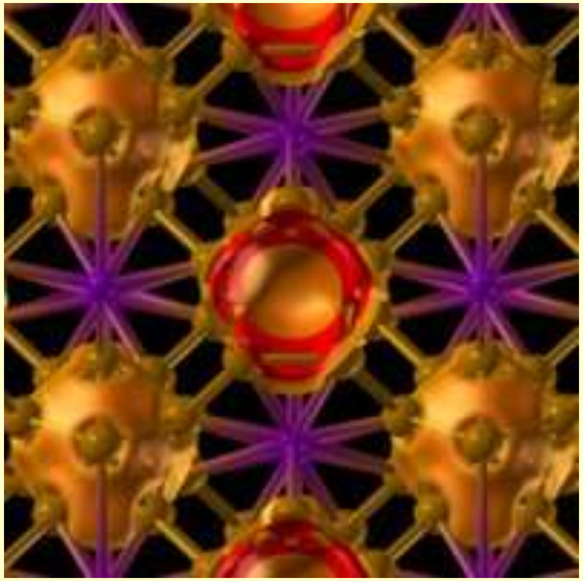


Story 3: Ionic element

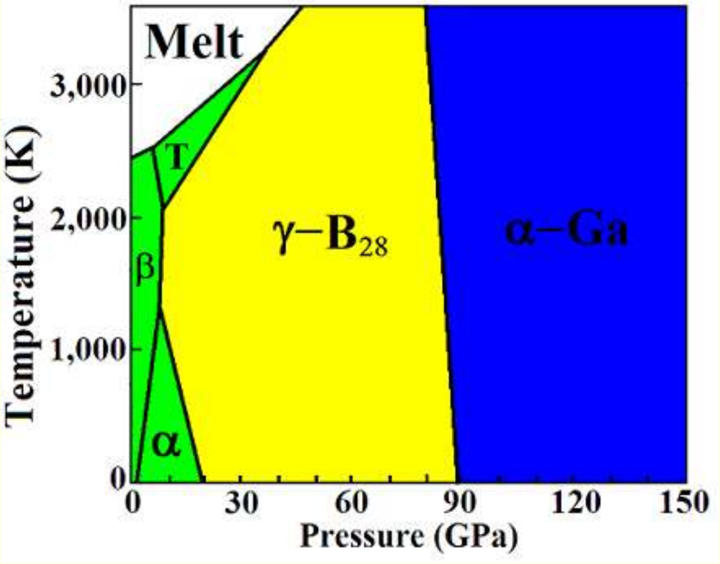


New phase of boron: superhard and partially ionic

- **Surprise: before metallization – formation of unusual partially ionic states (B, H).**
- **Crystallographycally distinct boron sites develop opposite charges!**

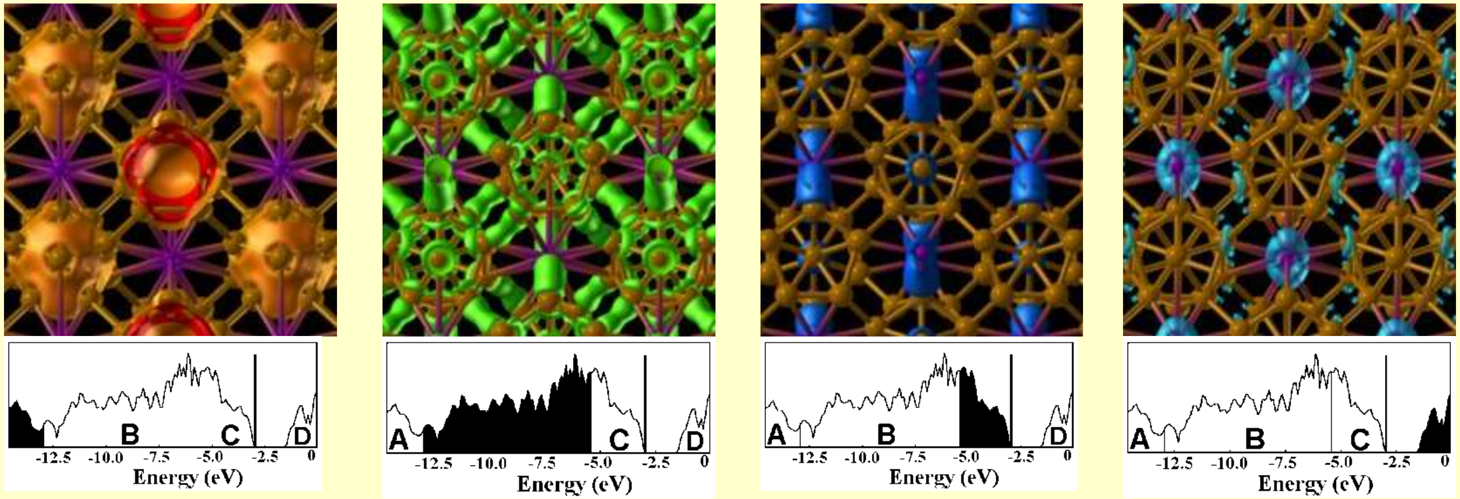


NaCl-like structure of γ-B_{28}
(Oganov et al., Nature 2009)



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

Non-trivial chemistry of boron – field for new discoveries



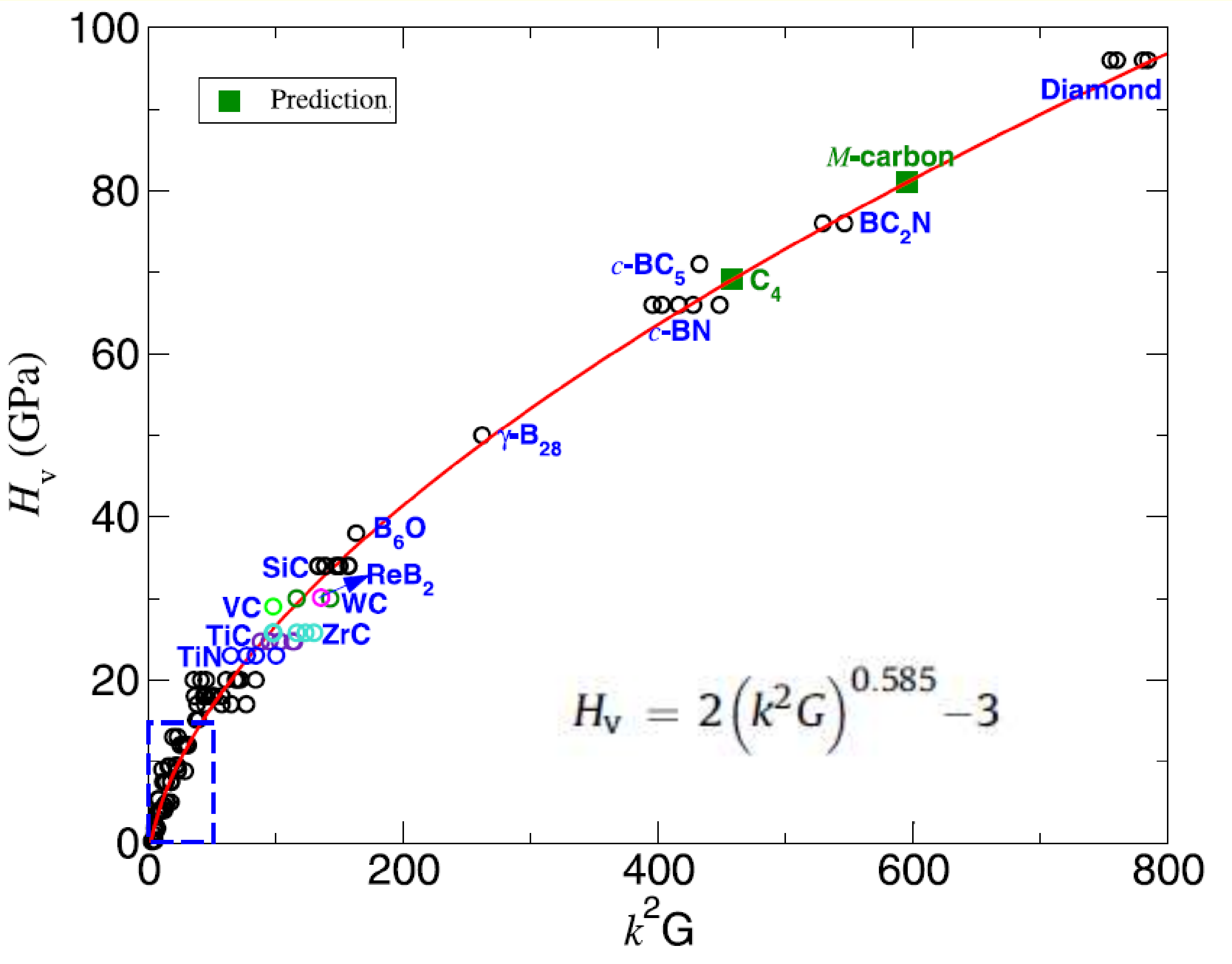
Charge separation between B_{12}-icosahedra and B_2-pairs is clear from DOS

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

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)

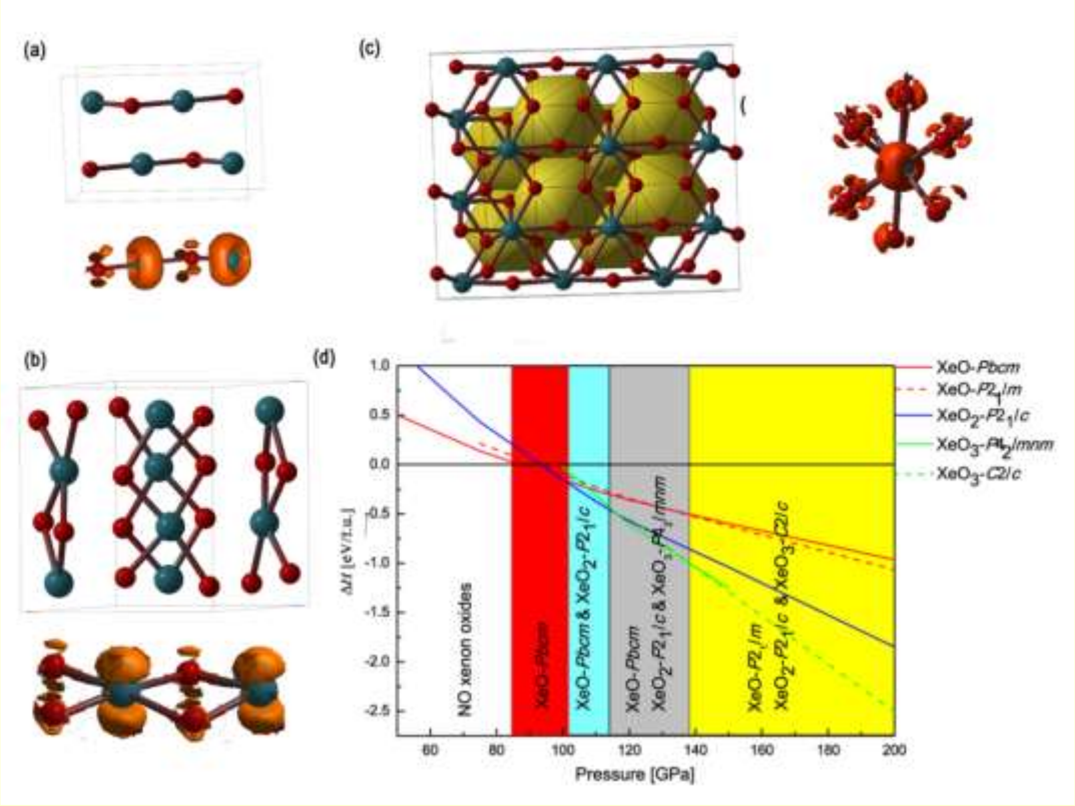
γ-B_{28} has hardness of 50 GPa (Solozhenko, ARO, 2008)

Story 4: Noble reactions

Xenon oxides become stable under pressure

Xe-O

- **At normal conditions, only Xe fluorides are stable. Xe oxides are metastable, some decompose explosively.**
- **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)

What is the chemically most inert element?

- Helium or neon.

- Helium is the 2nd most abundant element in the Universe (24 wt.%).

- Helium:

ionization potential = 24.39 eV (record!)

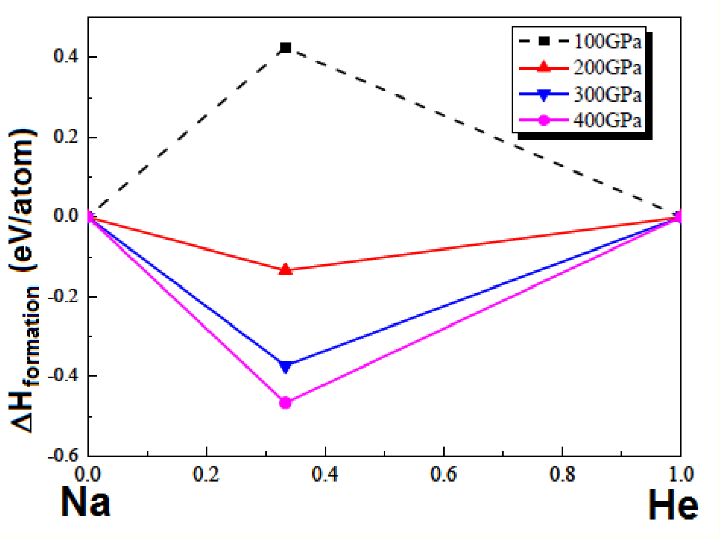
electron affinity = 0.08 eV

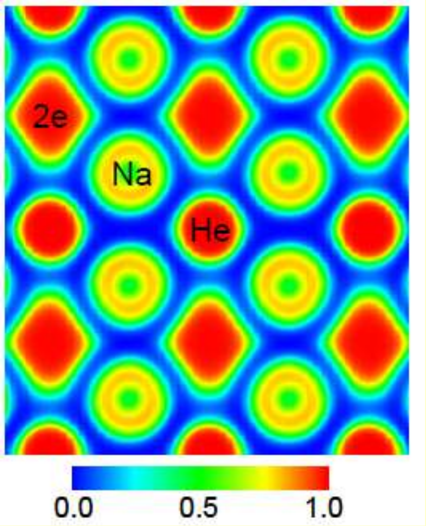
- No stable compounds are known at normal conditions.

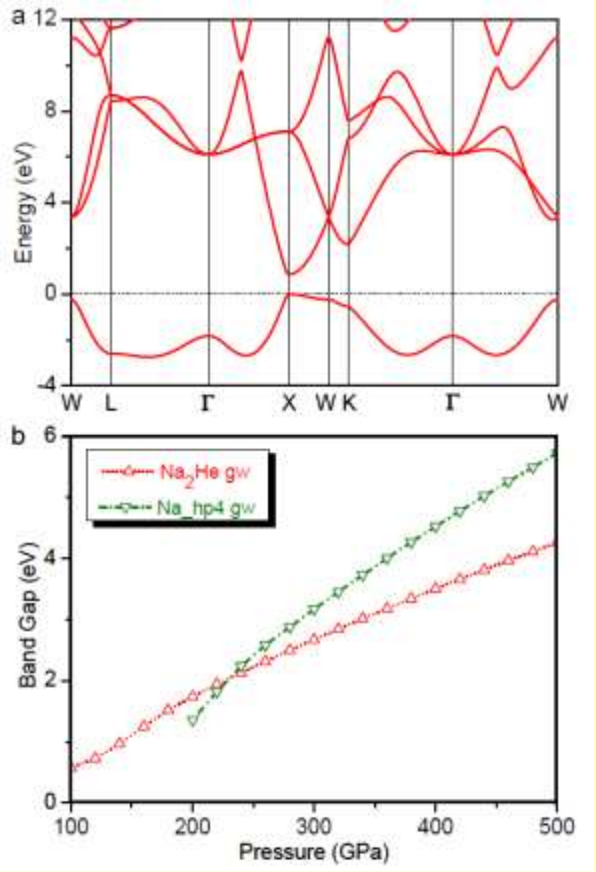
- Van der Waals compound $NeHe_2$ exists at high pressure (Loubeyre et al., 1993).

Na-He

Helium's unexpected chemistry: stable compound Na_2He (Dong, ARO, et al., 2013)

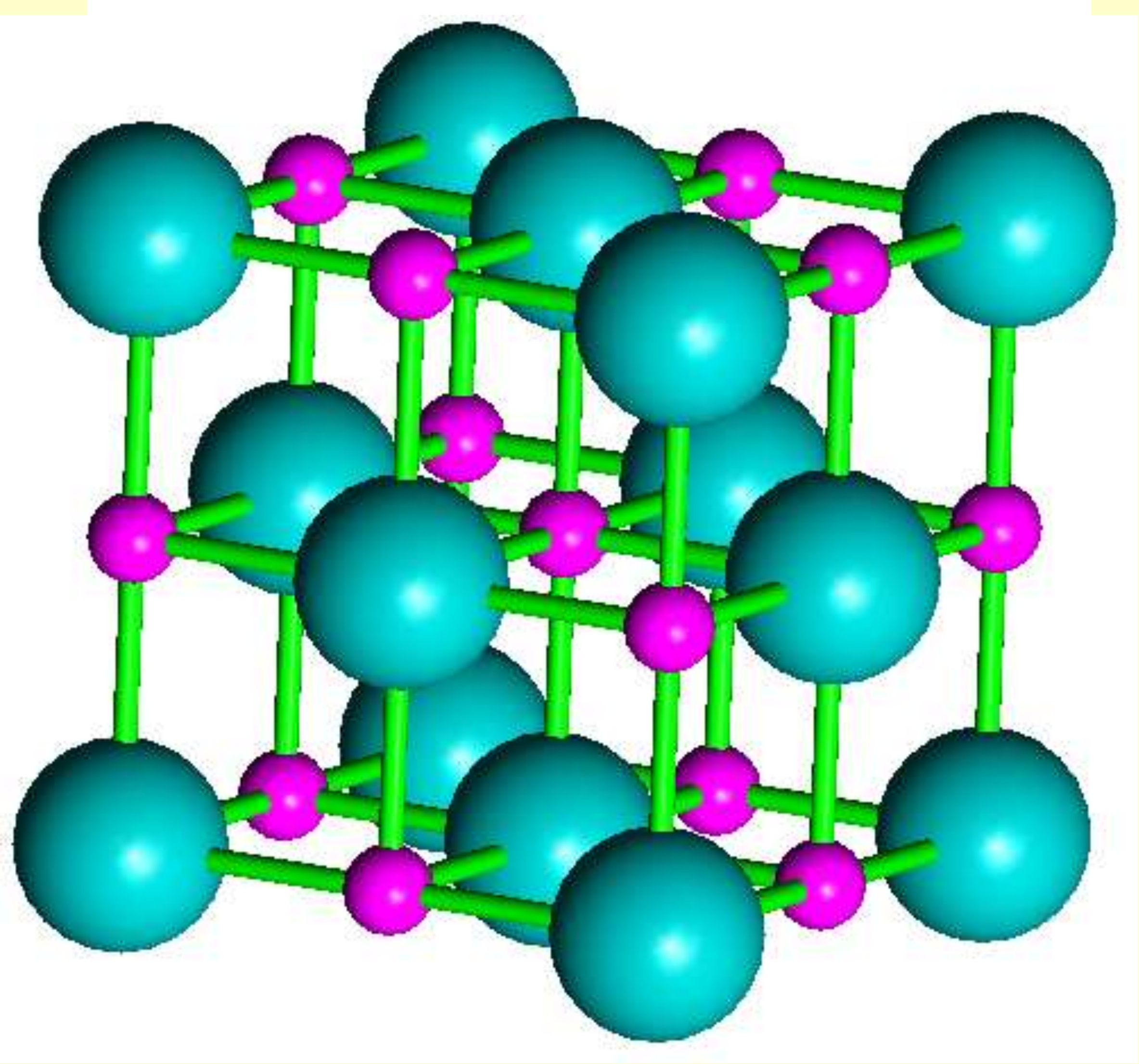




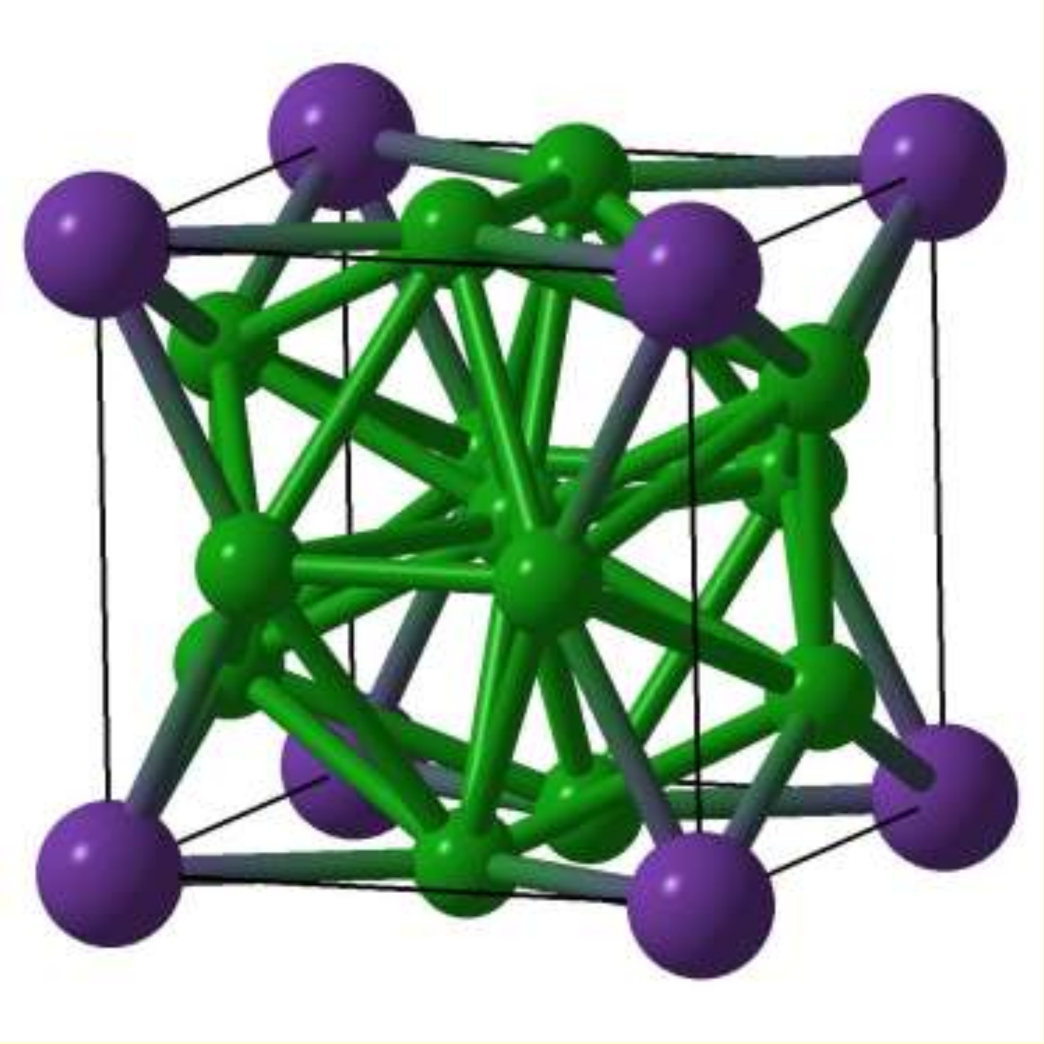


1. Na2He is stable at >160 GPa, at least up to 1000 GPa.
2. It is an insulating electride with direct gap.
3. Its band gap anomalously increases with pressure.

Story 5: Crazy salt

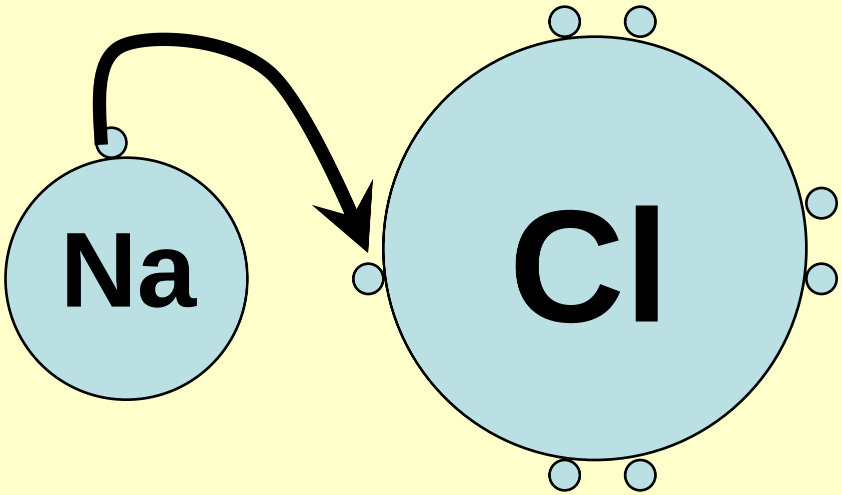


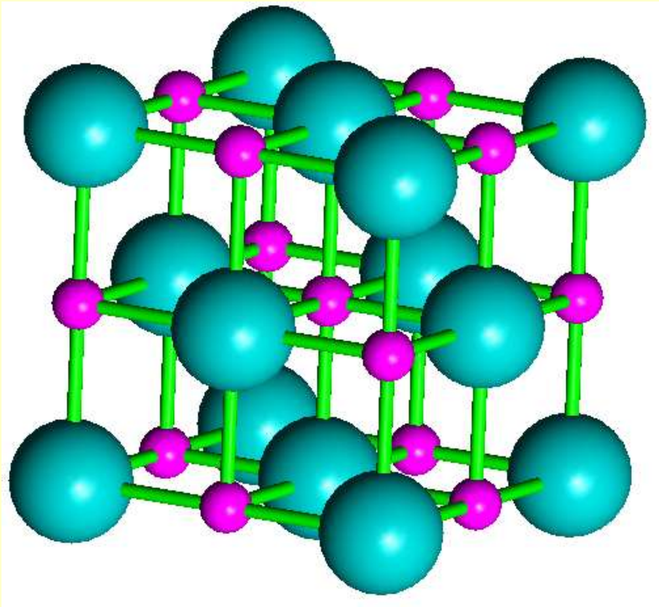
Story 5: Crazy salt



What classical chemistry tells us

- Large electronegativity difference (2.7) $\Rightarrow$ ionic bonding.
- Na and Cl have valence 1 $\Rightarrow$ Na^+ and Cl^-.
- The only possible compound is NaCl.



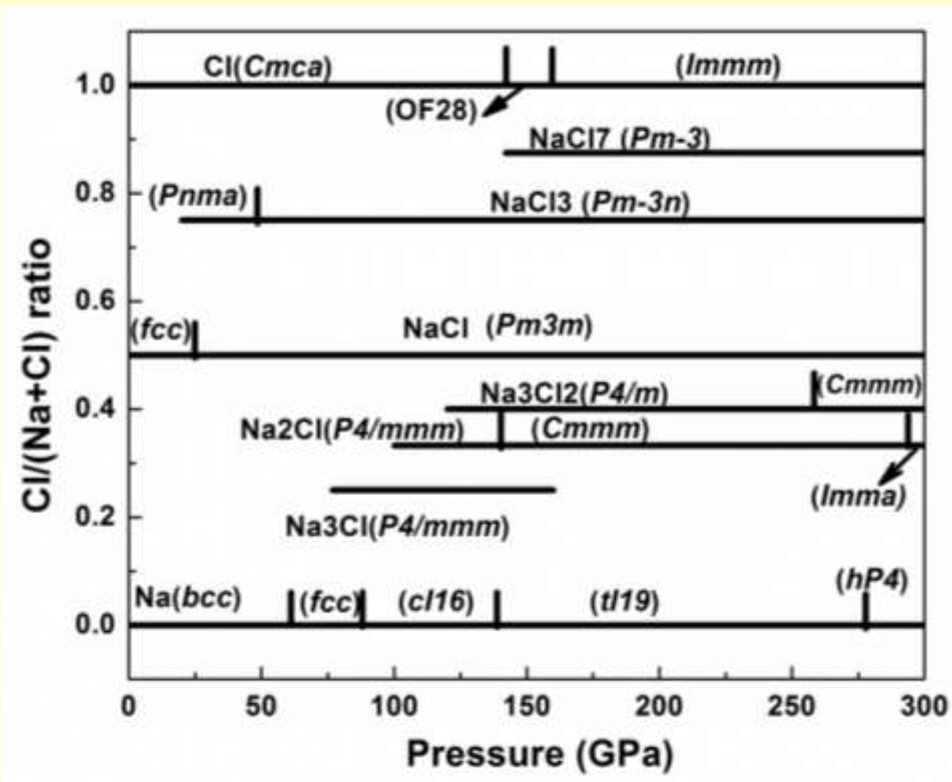


Crystal structure of NaCl (rocksalt)

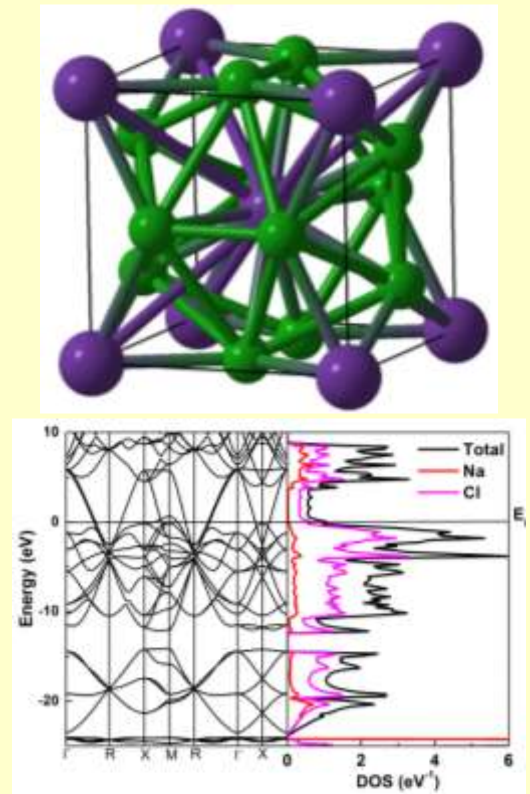
Unusual chemistry of the most usual compound

Na-Cl

- **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. *Science*, in press). Confirmed by experiment!**



Phase stability in the Na-Cl system



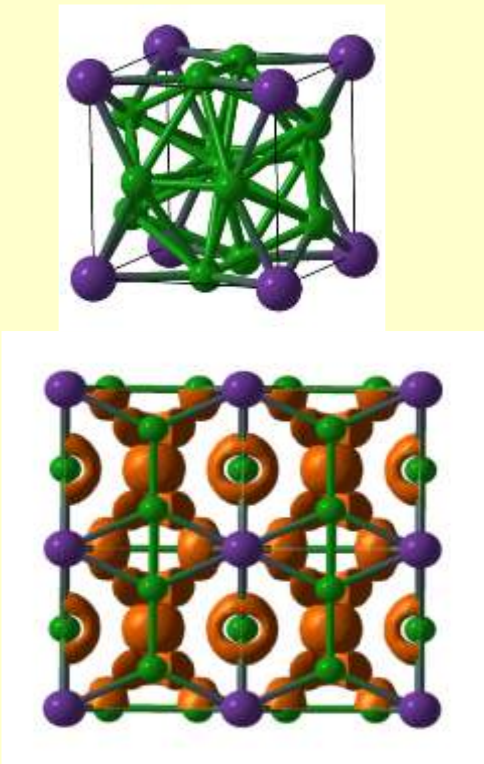
Atomic and electronic structure of cubic NaCl3

Crazy sodium chlorides

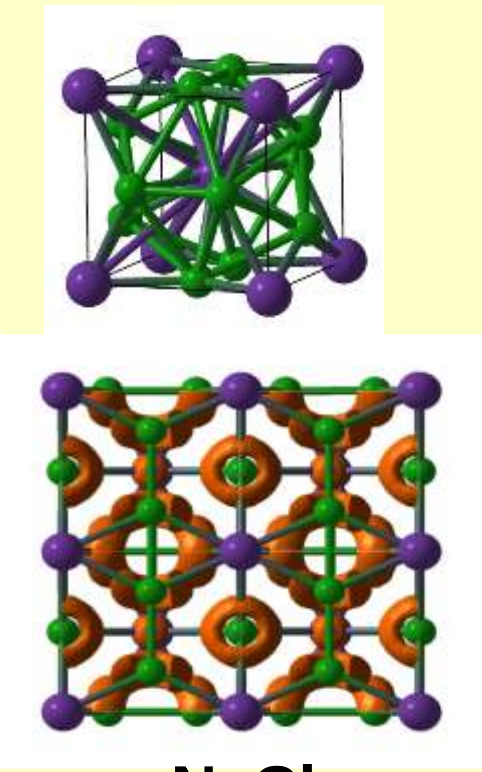
Na-Cl

Peculiar Na-Cl compounds:

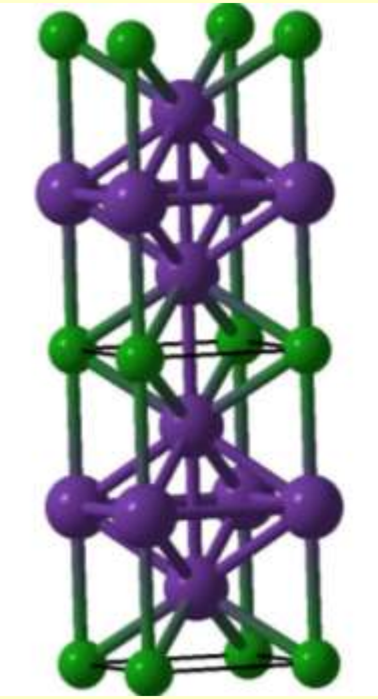
- **NaCl7: some Cl atoms have POSITIVE Bader charge (+0.07).**
- **Na3Cl: 2D-metal**



$NaCl_7$



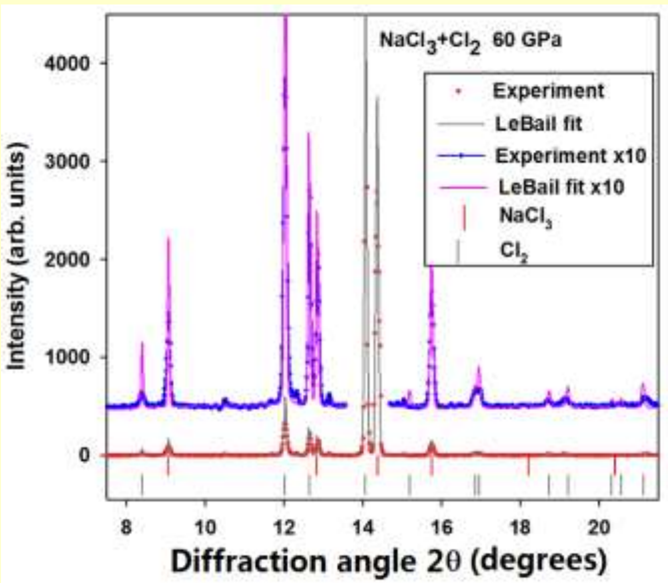
$NaCl_3$

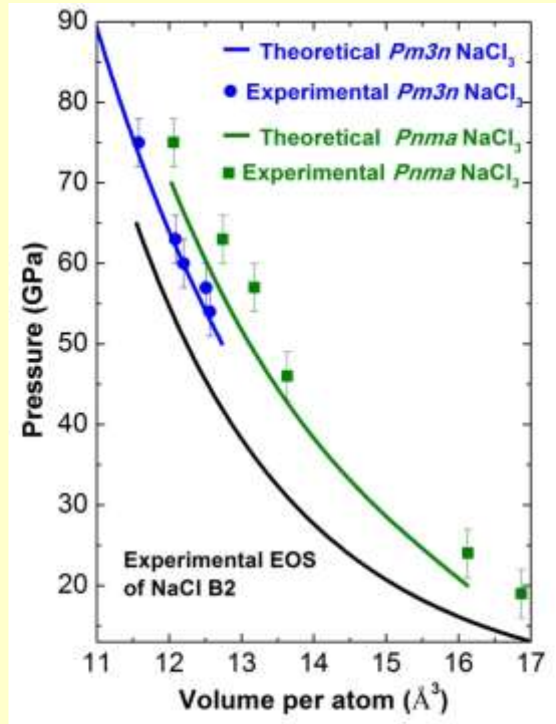


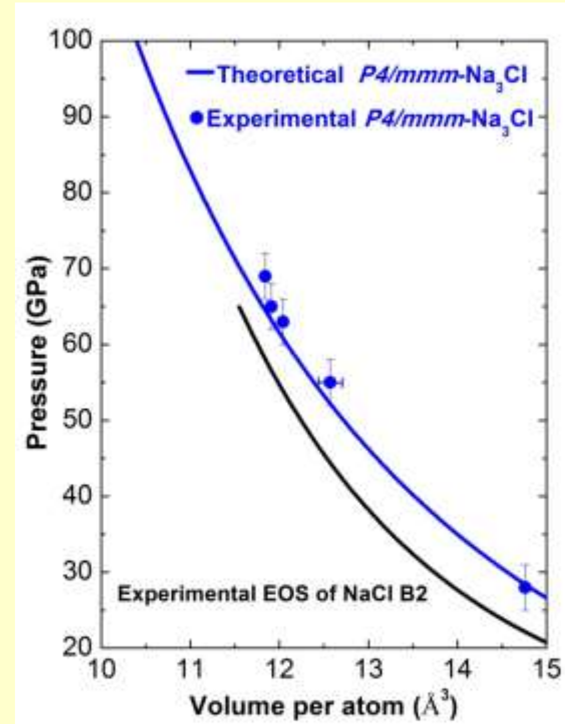
Na_3Cl

[Zhang, ARO, et al., Science, in press (2013)]

Experimental confirmation of $NaCl_3$ and Na_3Cl







Pm3n $NaCl_3$

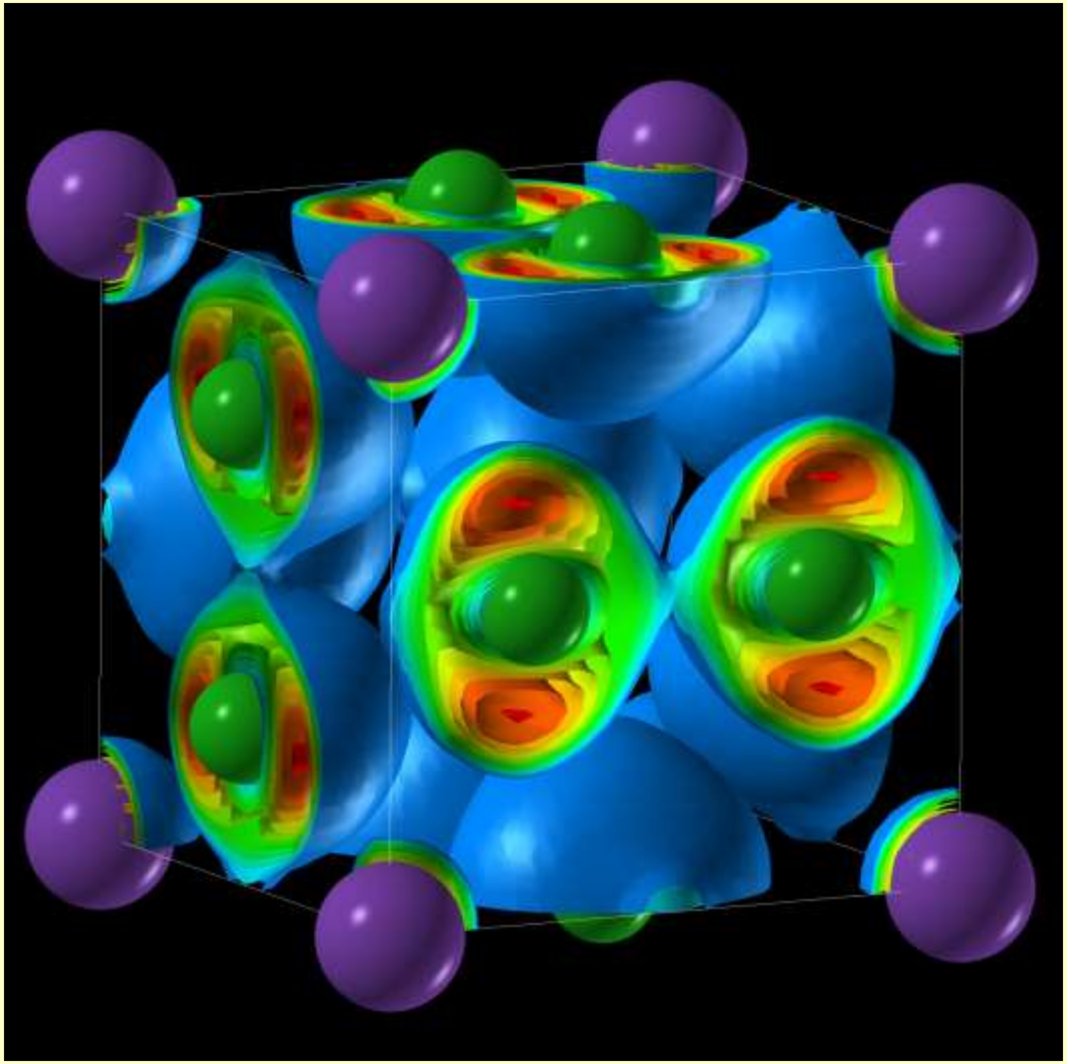
a= 4.6110(3) Å - experiment
a=4.602 Å - theory

Equations of state of $NaCl_3$ (left) and Na_3Cl (right): theory *vs* experiment

[Zhang, ARO, et al., Science, in press (2013)]

Artistic view: kissing onions in NaCl3

Na-Cl

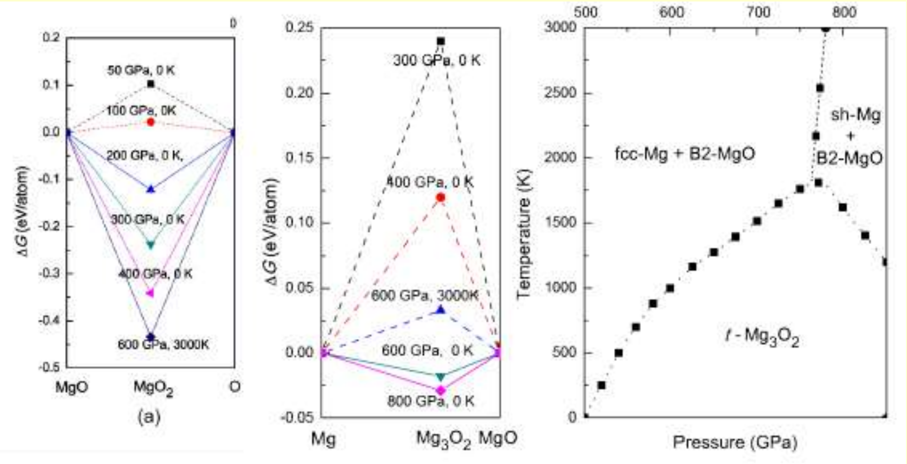


[Zhang, ARO, et al., Science, in press (2013)]

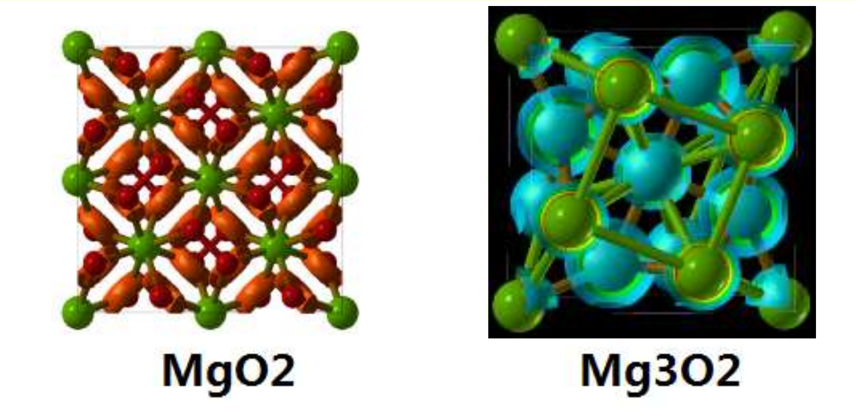
Similar crazy compounds occur in other systems

Mg-O

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

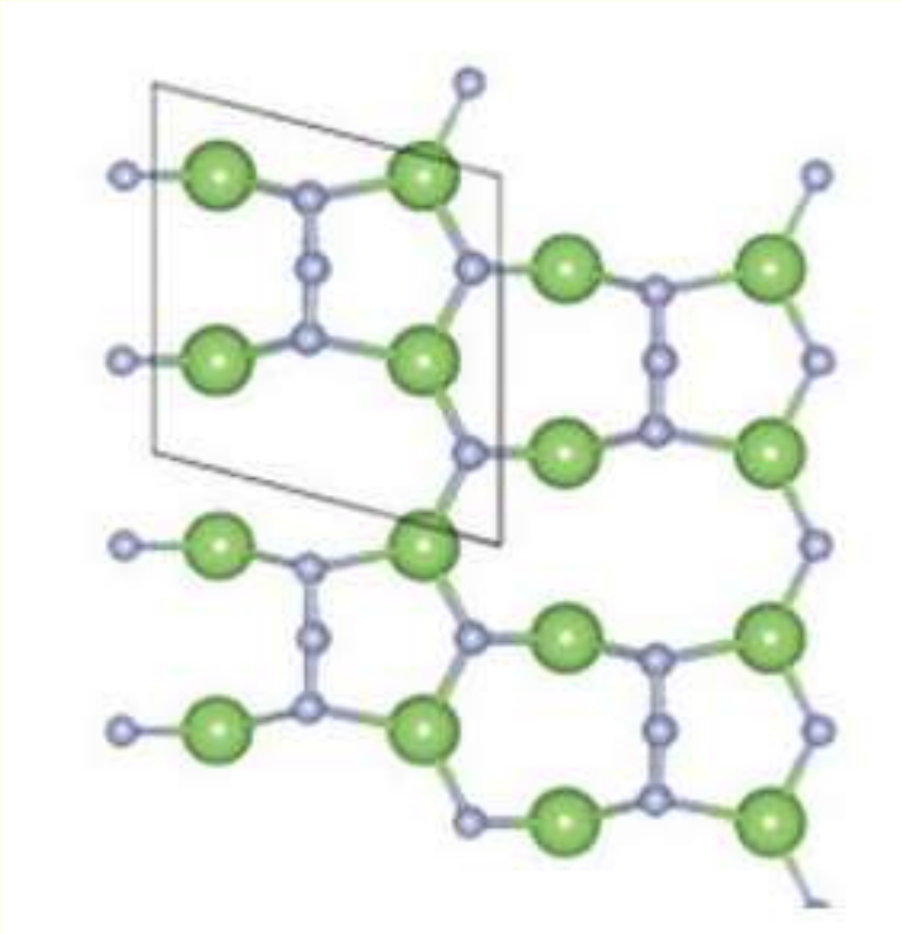


Phase stability in the Mg-O system

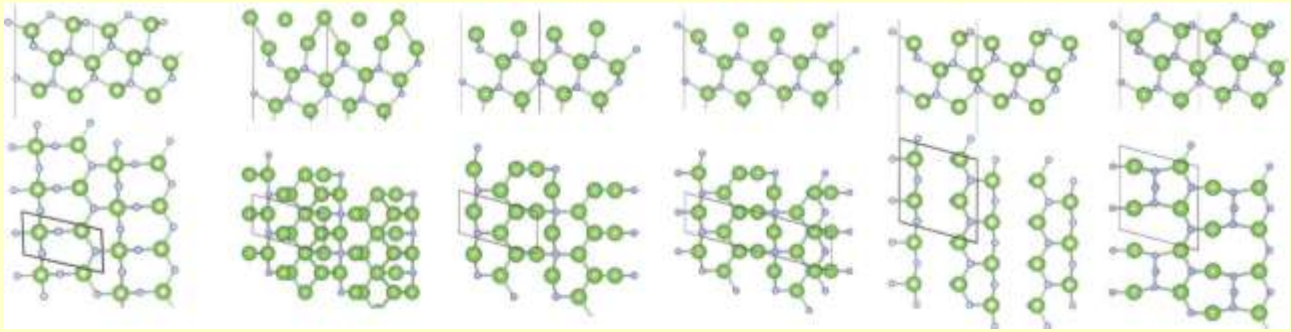


Crystal structure and electron localization function of MgO_2 and Mg_3O_2

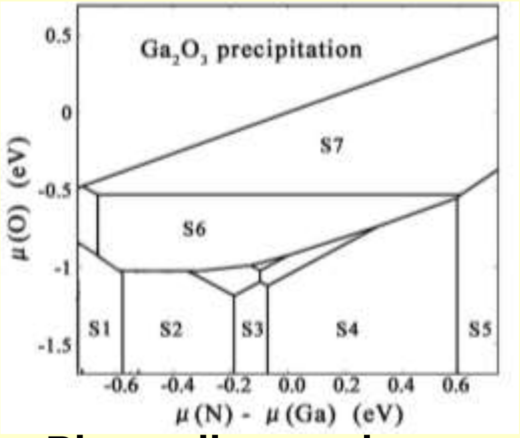
Story 6: Crazy chemistry is everywhere



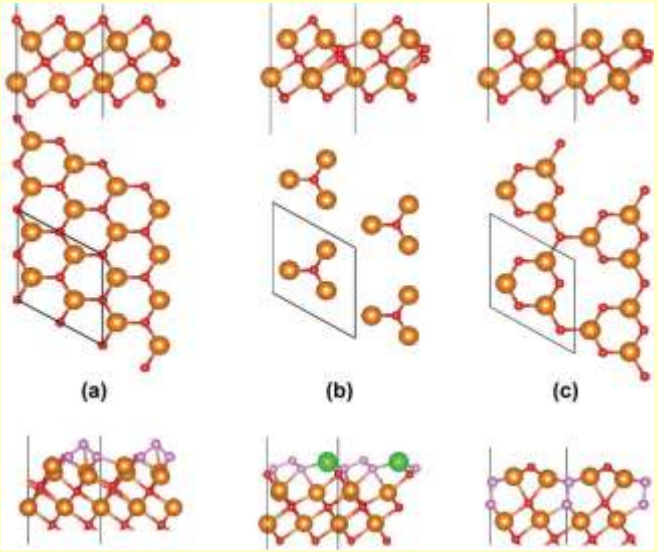
2D: Surfaces of crystals, new physics and chemistry… and medicine?



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



Phase diagram in presence of oxygen



Note peroxide (O_2^{2-}) groups at the surface

Structure of (111) surface of MgO.
One can see peroxide-groups, O_3-groups

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J. P. Pérez

C. Hu

- USPEX Users and Developers Community (>1500 people)

USPEX code is freely available at: http://han.ess.sunysb.edu/~USPEX

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Xiaodong Zhang
HongJiang Feng
Fei Qi
Junhui Peng
Congwei Xie
Jin Zhang
Shuyin Yu
Binxi Li
Yang Hu
Shuang Wang
Yang Yu

- USPEX Users and Developers Community (>1500 people)

USPEX code is freely available at: http://han.ess.sunysb.edu/~USPEX