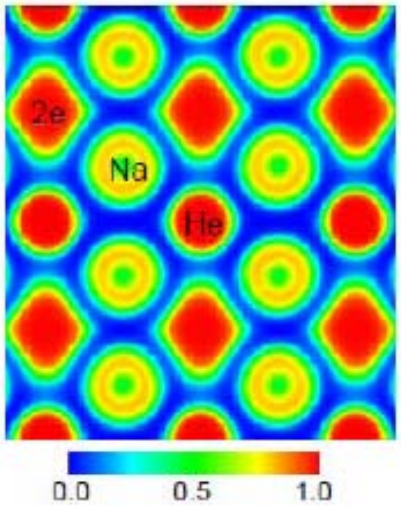
Novel Chemistry under Pressure

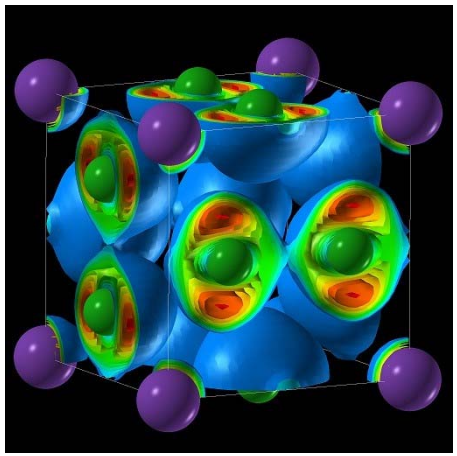
Alexander Goncharov

Geophysical Laboratory, Carnegie Institution of Washington

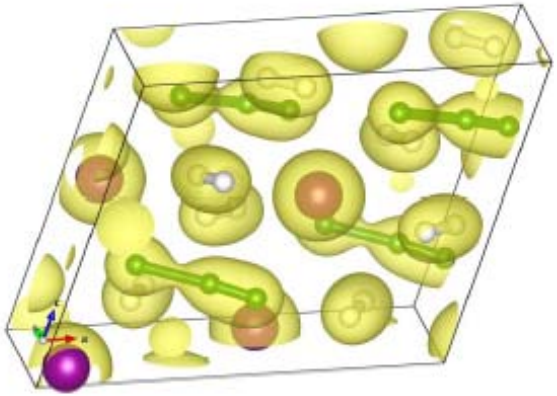
Na_2He



$NaCl_3$



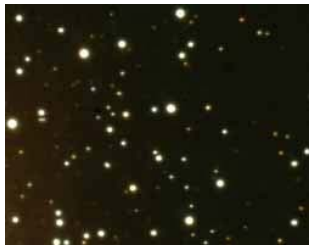
NaH_7



RANGE OF PRESSURE IN THE UNIVERSE

Pressure (Atmospheres)

10^{-32} Hydrogen gas in intergalactic space



10^{-24} Interplanetary space

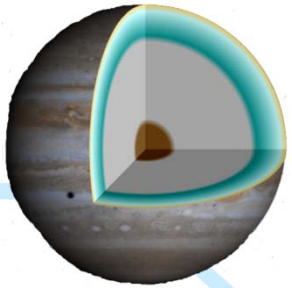
10^{-16} Atmosphere at 300 miles

10^{-8}

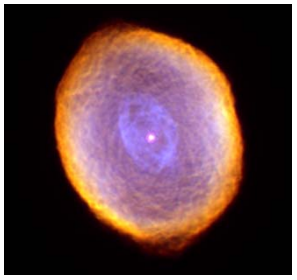
1

10^{8} Center of Jupiter

Center of Sun



10^{16} Center of white dwarf



10^{24} Center of neutron star

10^{32}

Pressure (Atmospheres)

10^{-8}

10^{-6} Best mechanical pump vacuum

10^{-4}

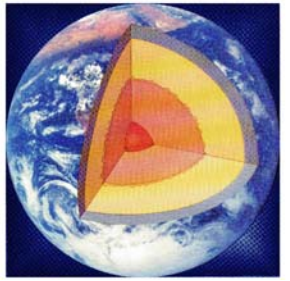
10^{-2} Water vapor at triple point

1 Atmospheric pressure (sea level)

10^{2} Deepest ocean

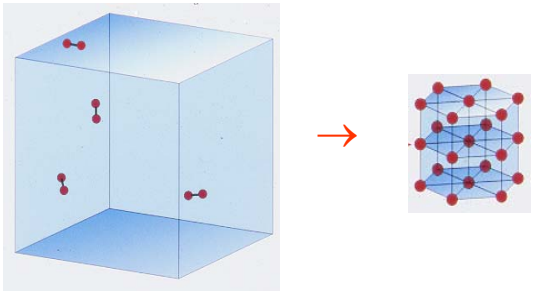
10^{4}

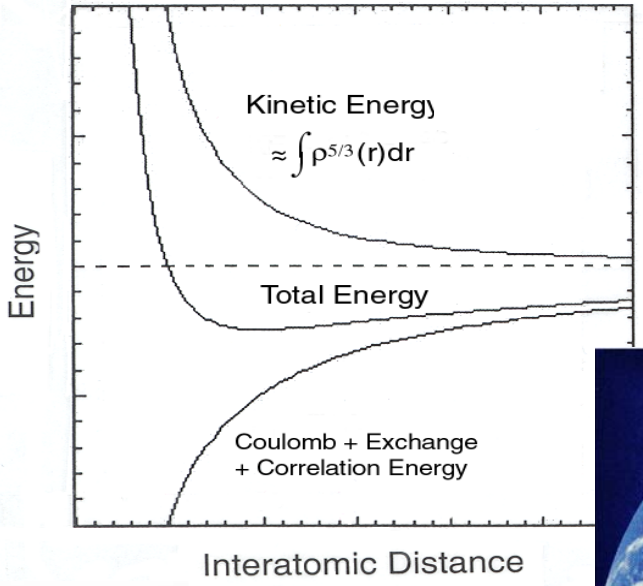
10^{6} Center of the Earth



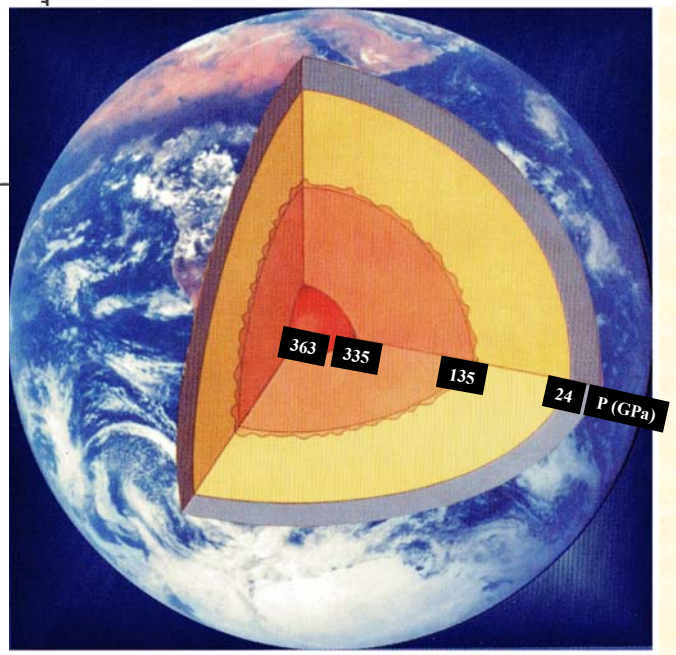
10^{8}

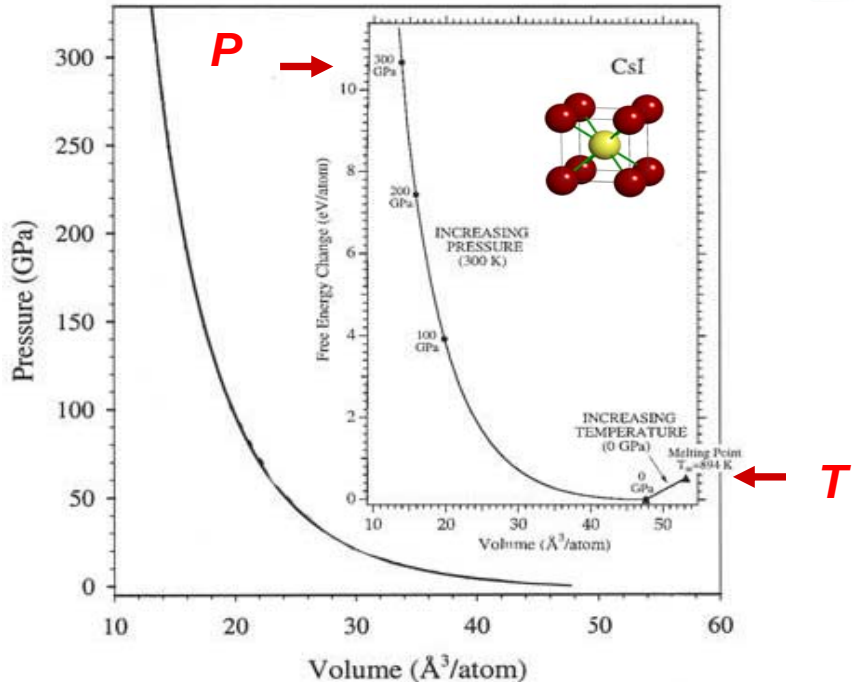
Effects of Pressure *and Temperature* on Materials





$$P = -\frac{\partial E}{\partial V}\bigg|_T$$

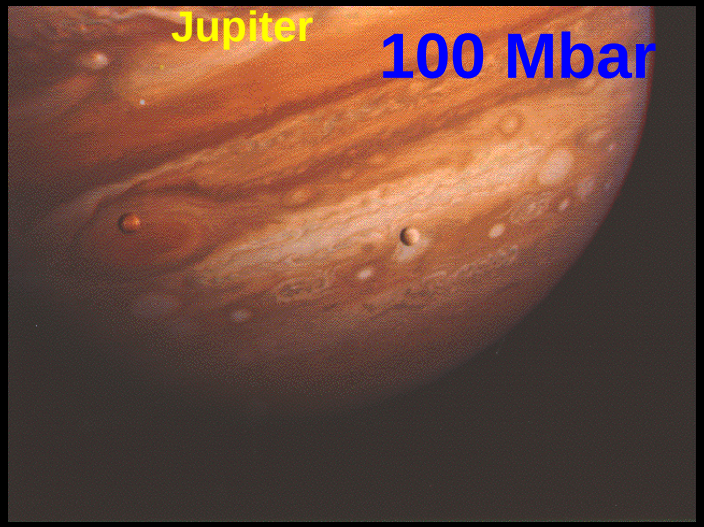




1 Mbar=100 GPa

$$\frac{e^2}{2a_0^4} = 14{,}720 \text{ GPa} \approx 147 \text{ Mbar}$$

High Pressures in Nature

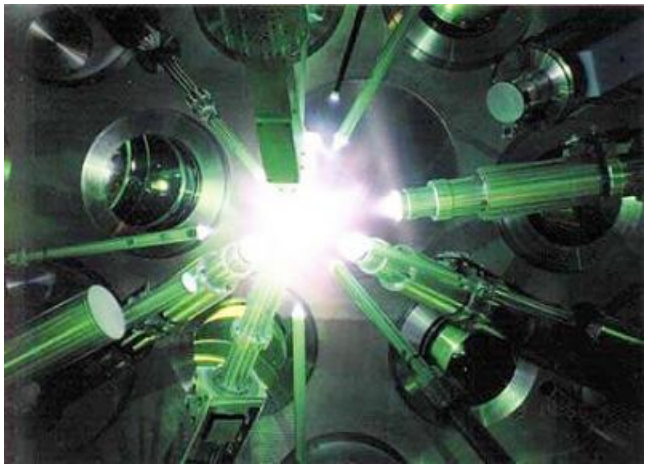


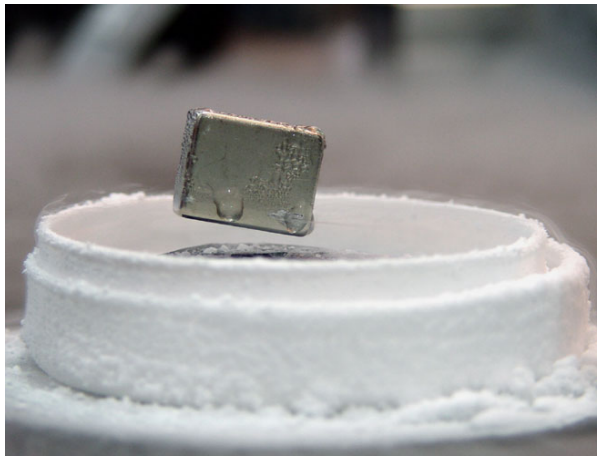
- deep interiors of giant planets and sub-stellar objects (e.g., brown dwarfs),
- final stages of planet formation (giant impacts)

Developments of new technologies require novel materials with superior properties

Our Goals:

- Novel materials require properties tailored to the application
- Environmentally benign and sustainable
- Synthesized at conditions compatible with mass production



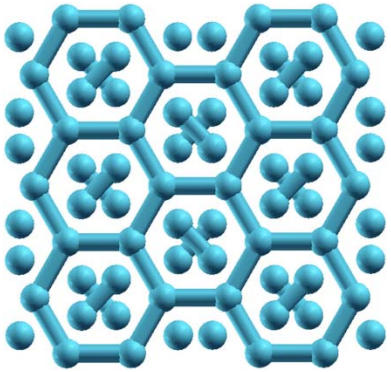


- high energy-density
- conducting & superconducting
- superhard

→ **Hydrides and chlorides of Na**
Na-He, C-N, N-H

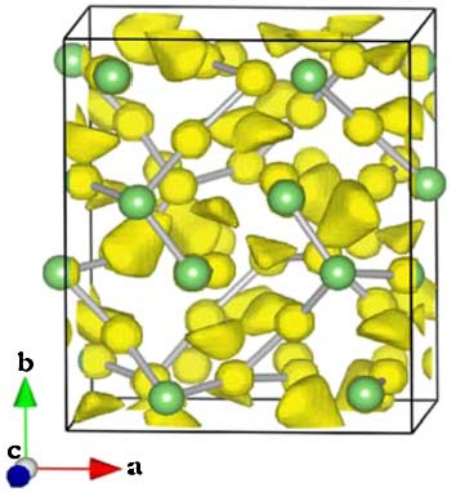
Search for new paradigm to synthesize novel materials : Fundamental physics and chemistry challenges

Quantum melting



Mixed molecular and graphene-like hydrogen
Pickard & Needs, 2007
Howie *et al*., PRL, 2012

Molecular breakdown



Electride semiconducting lithium,
Lv *et al*., PRL, 2011

Multicenter and electride chemical bonds

- Discovery of novel physical states and chemical structures
- Manipulate chemical bonds to recover the materials
- Experiments are needed to validate and reinitiate theory

Chemical laws at high pressures:

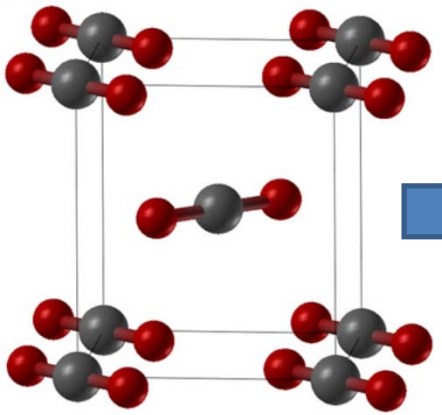
Prewitt and Downs' 1998 Crystal Chemistry Rules (Rules of thumb)

4. ***Increasing pressure increases coordination number***

8. ***High-pressure structures tend to be composed of closest-packed arrays of atoms***

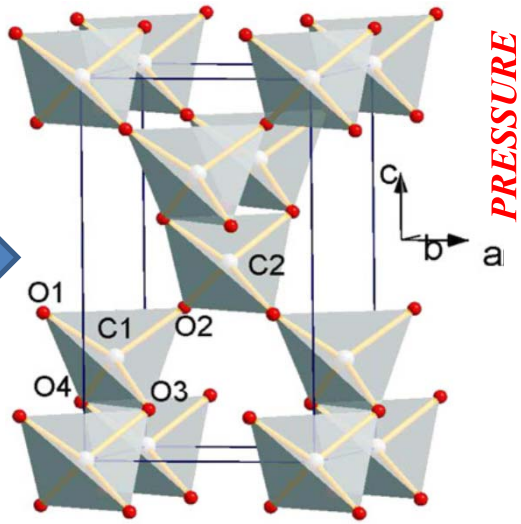
9. ***Elements behave at high pressures like the elements below them in the periodic table at lower pressures***

Molecular CO_2



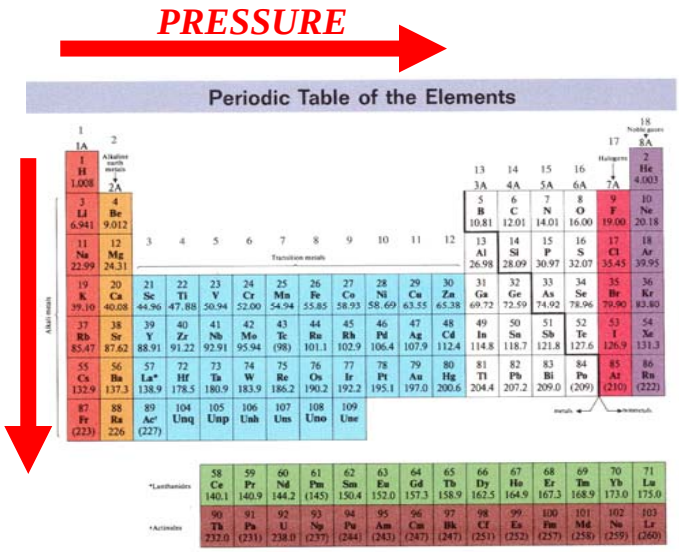
Oganov *et al.*, 2008

Polymeric CO_2



β-cristobalite phase of SiO_2 (high –T polymorph)

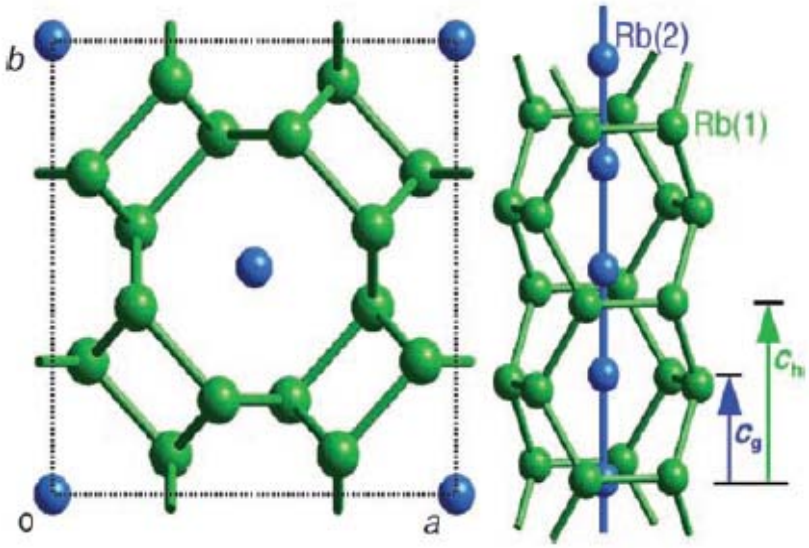
Datchi *et al.*, 2013



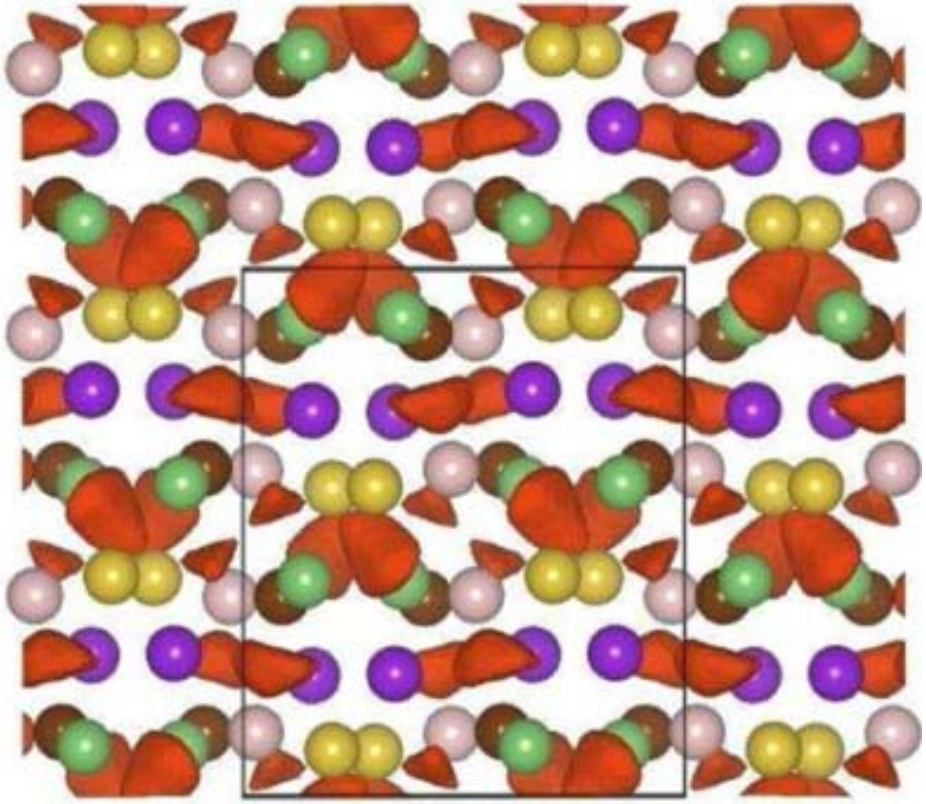
- **Filling of *s*, *p*, *d*, … orbitals**
- **Simple structures**

Chemical laws at high pressures:

Prewitt and Downs' 1998 Crystal Chemistry Laws (Rules of thumb)



Rb-IV 17 GPa
McMahon & Nelmes, 2004



***C2cb*-40 Li at 85 GPa**
Marques *et al.*, 2011

Astonishingly complex structures have been found in many elements et high pressures. Why?

Chemical laws at high pressures:

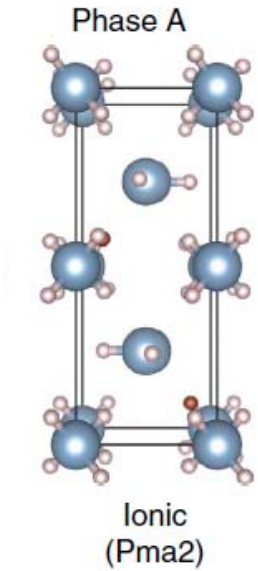
Grohala's (2007) rules

C) **Increased coordination through donor– acceptor bonding … to multicenter bonding … is a mechanism for compactification**

H) **Under extremely high pressure, electrons may move off atoms, and new "non-nucleocentric" bonding schemes need to be devised**

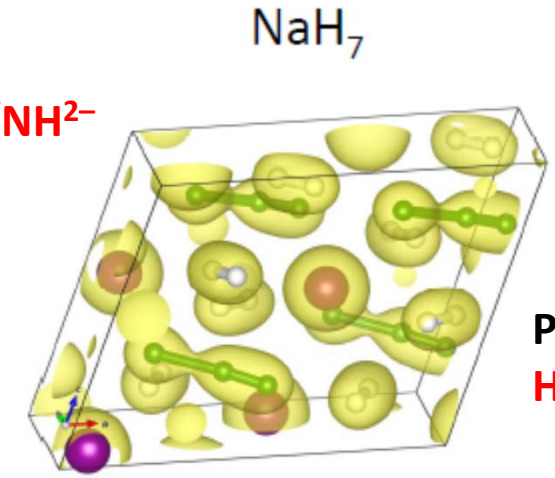
I)**…still denser packing may be achieved through electronic disproportionation and through nonclassical deformation of spherical electron densities**

J) **Pressure may cause the occupation of orbitals that a chemist would not normally think are involved.**



Ionized ammonia NH^{4+}/NH^{2-}

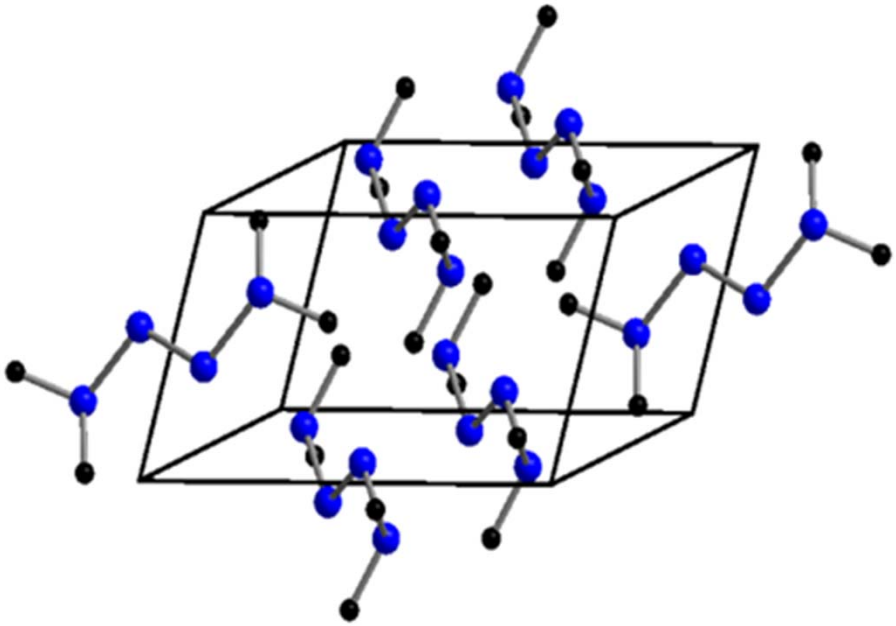
Palasyuk et al., 2014



Polyhydride with H_3^- groups

Modification of chemical bonding laws under pressure

- **Polymerized states become preferable**
- Higher hybridized states become preferable
- Interstitial (localized) electron bonding
- Materials with unusual stoichiometry



novel oligomeric and/or polymeric hydronitrogens

NH

Modification of chemical bonding laws under pressure

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- **Higher hybridized states become preferable**
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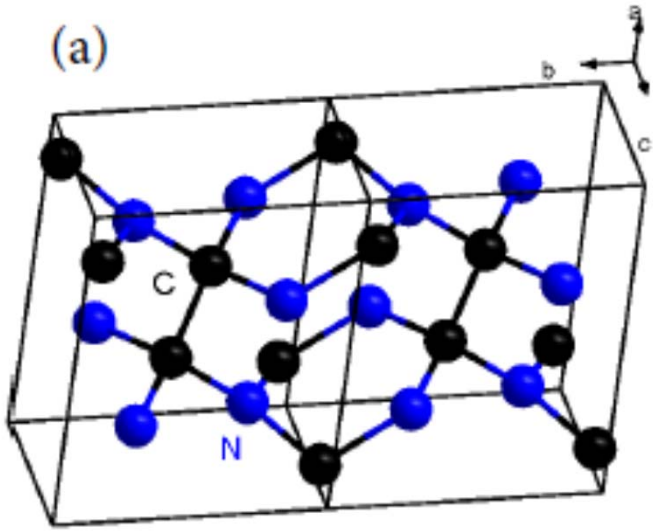
- Materials with unusual stoichiometry



sp^3 bonded C-N compound

CN

Modification of chemical bonding laws under pressure

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- Higher hybridized states become preferable
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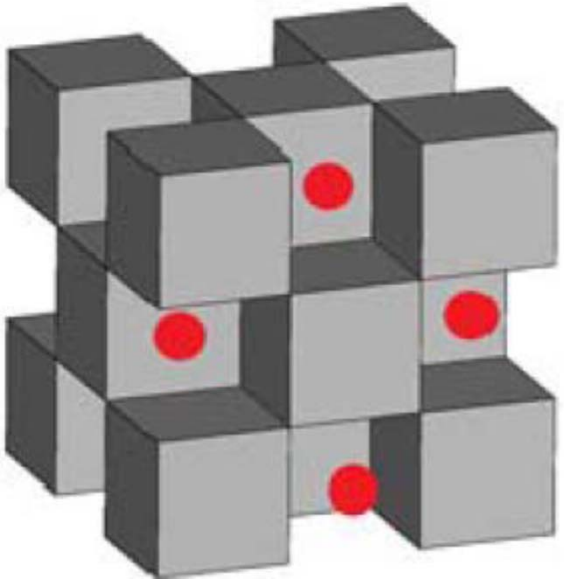


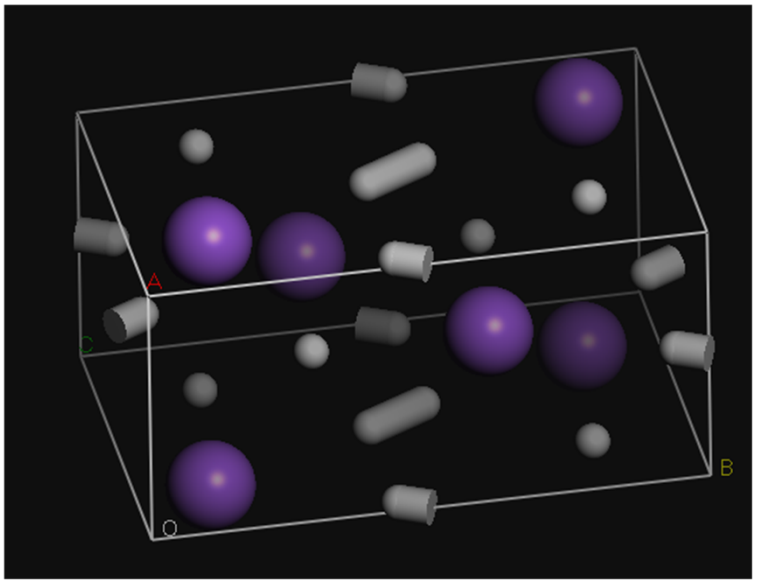
first electride compound of He:

Na_2He

Van der Waals compound $NeHe_2$
Loubeyre *et al.*, 1993

Modification of chemical bonding laws under pressure

- Polymerized states become preferable
- Higher hybridized states become preferable
- Interstitial (localized) electron bonding
- **Materials with unusual stoichiometry**

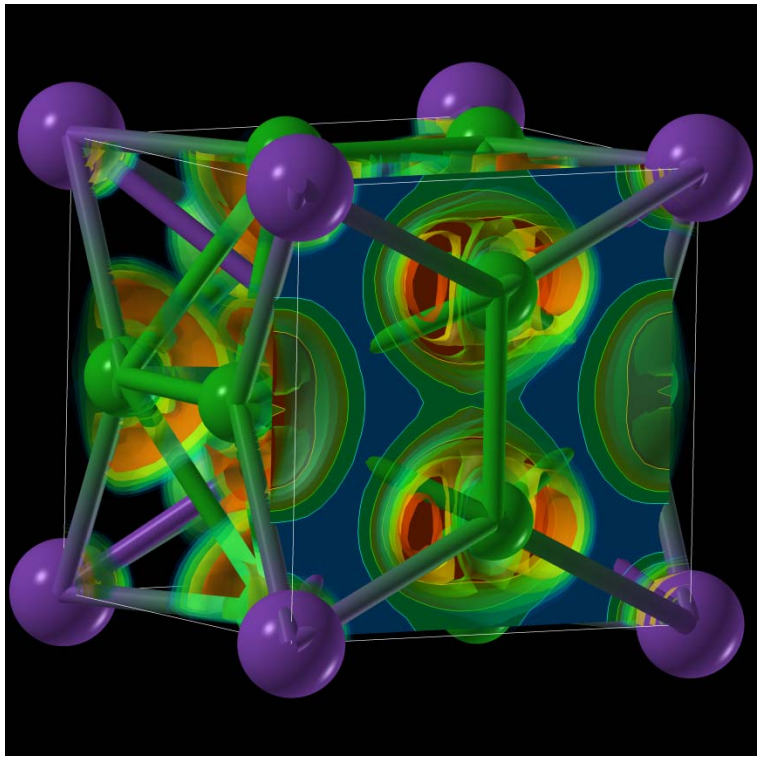


first synthesized polyhydides

NaH_7

Modification of chemical bonding laws under pressure

- Polymerized states become preferable
- Higher hybridized states become preferable
- Interstitial (localized) electron bonding
- **Materials with unusual stoichiometry**



nonstoichiometric chlorides of Na and K

KCl_3

Single-bonded nitrogen as perfect energetic material

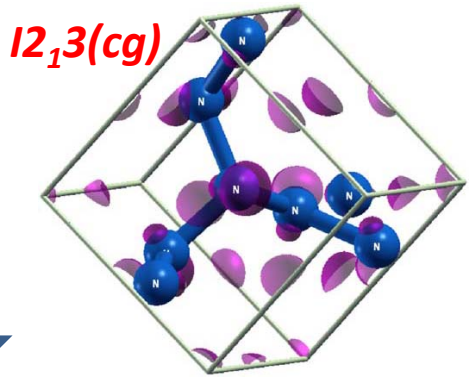
- Polymerized states become preferable
- Higher hybridized states become preferable
- Interstitial (localized) electron bonding
- Materials with unusual stoichiometry

80 kJ/mole vs 477 kJ/mole

Pressure

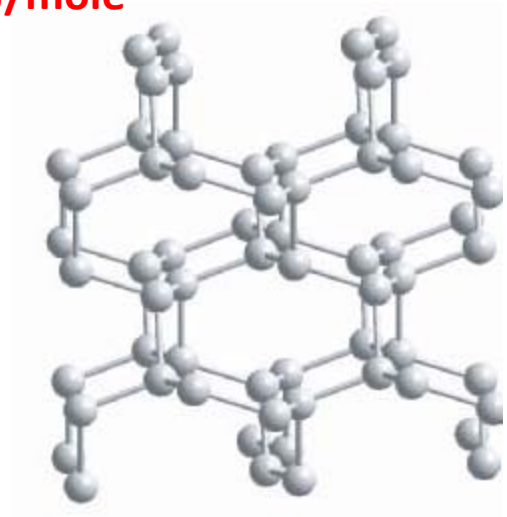
N

$P2_1/c$



$I2_13(cg)$

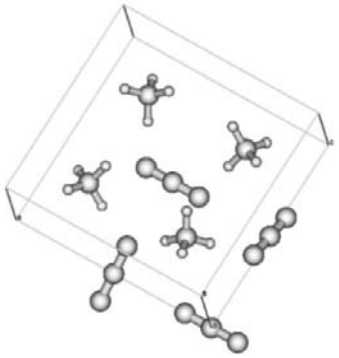
Pickard & Needs, 2011
Chen et al., 2008



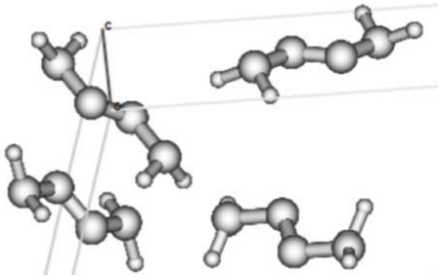
Monatomic single-bonded highly energetic nitrogen (Eremets et al., 2004)

Are there any alternative materials which can be easily synthesized and sustained ?

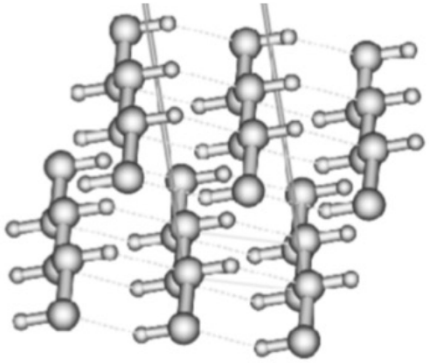
Hydronitrogens: new path to high energy-density materials



ammonium azide

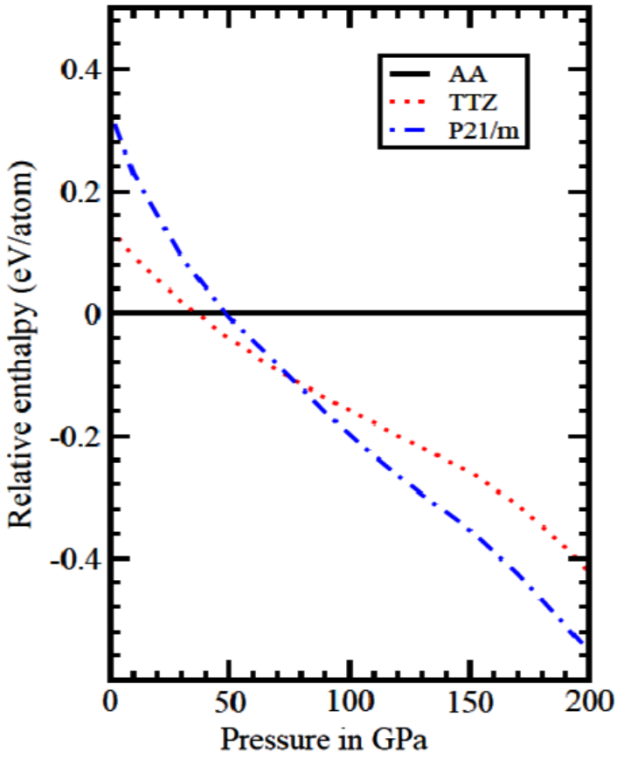


trans-tetrazene



Polymeric hydronitrogen (prediction)

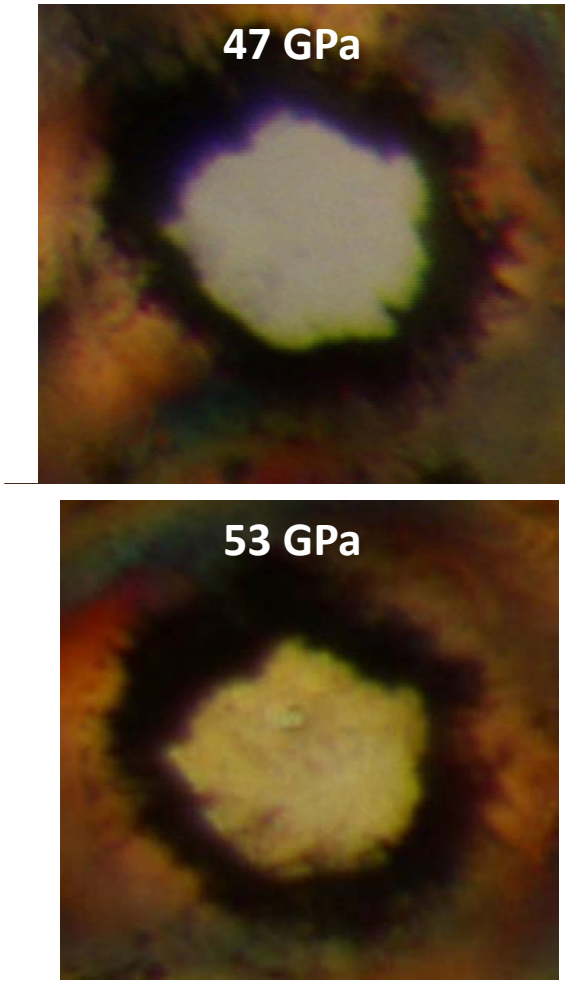
Hu and Zhang, 2011



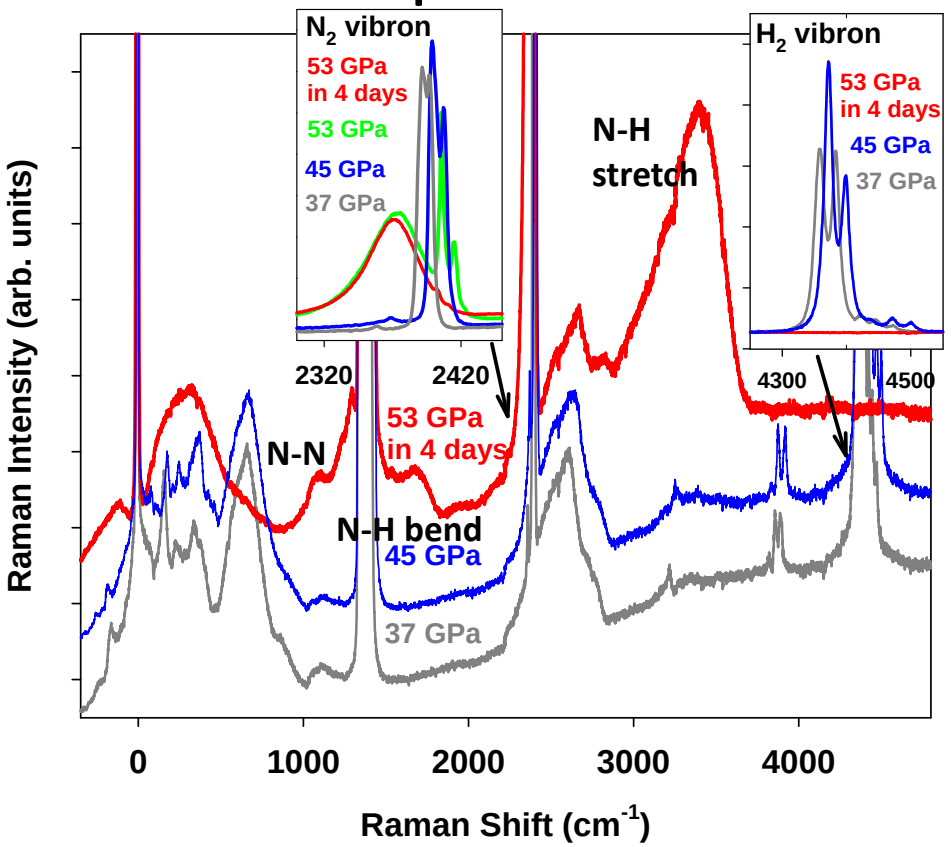
- **Hydronitrogens reveal diverse bonding schemes and stoichiometries**
- **Looking for larger stable molecules and polymers forming 3D materials**

Hydronitrogens: N_2 and H_2 molecular mixture experiences transition above 47 GPa

Change in sample appearance



Raman spectra at 300 K

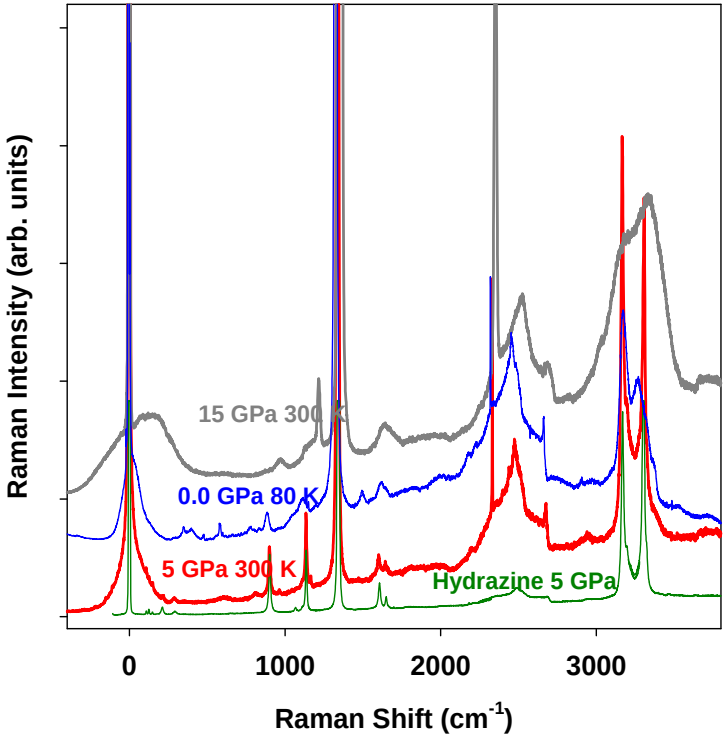


- **Chemical reaction occurs which results in formation of N-H and single N-N bonds**
- **N-H bands are also observed in IR absorption spectra**

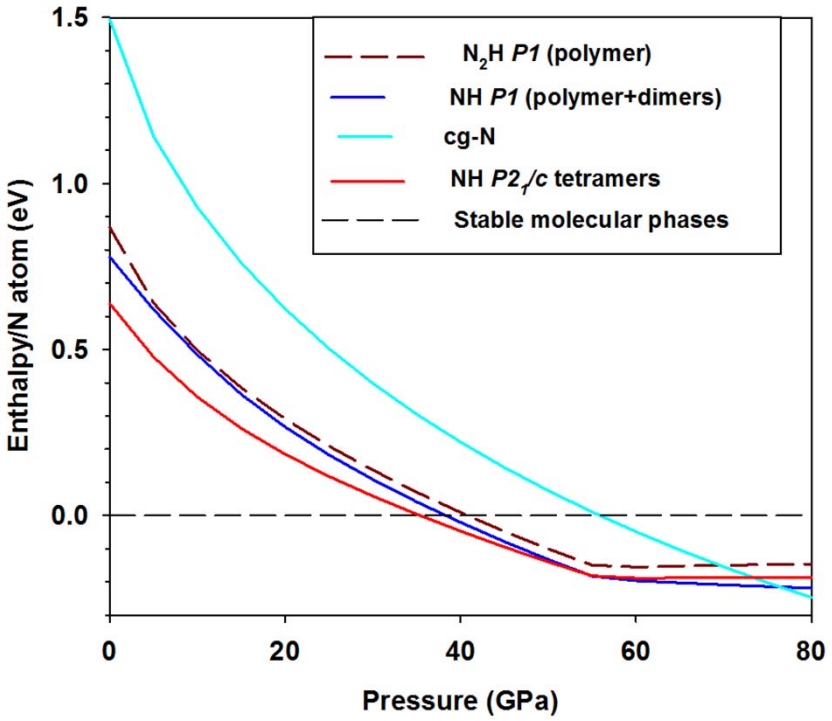
Two-photon induced reaction has been observed at 10 GPa

Hydronitrogens: metastability of new polymer/oligomer compound to ambient pressure

Raman spectra on unloading



Enthalpies on new polymers/oligomers



➢ **new phases possess an energy yield up to 61 % of that of cubic gauche nitrogen (depending on the length of the –N-N- chains).**

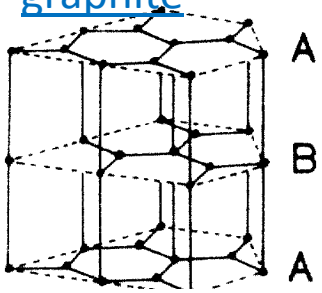
Goncharov et al., submitted

Searching for new superhard materials

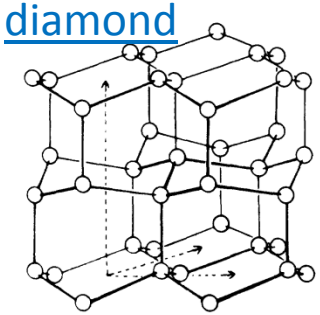
- Polymerized states become preferable
- **Higher hybridized states become preferable**
- Interstitial (localized) electron bonding
- Material with unusual stoichiometry

Pressure

graphite



diamond

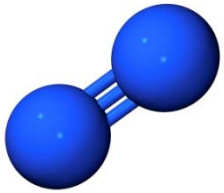


Fahy et al., 1987

Is there any material which challenge diamond?

Superhard materials

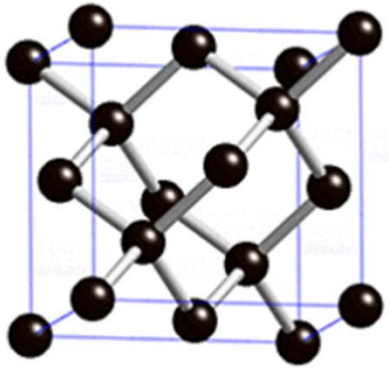
1. Strong covalent bond



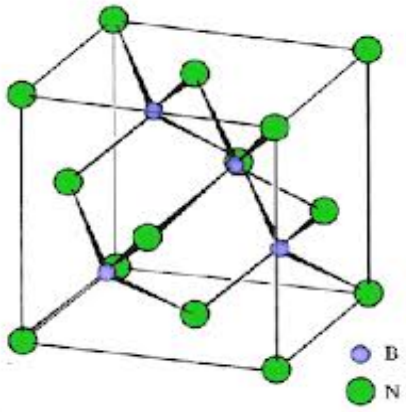
2. Extended network

C-N bond shorter than C-C bond

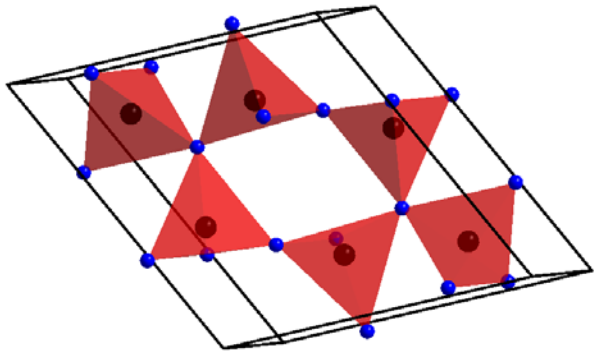
3. Isotropic structure



Diamond B = 442 GPa



cBN B = 369 GPa



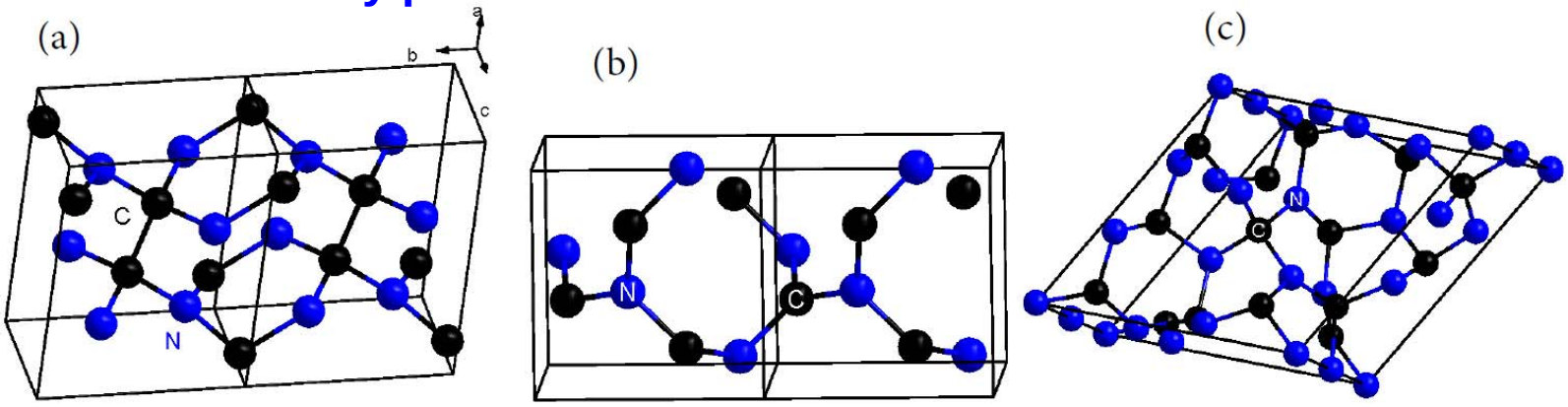
cubic C_3N_4 = 496 GPa

Teter & Hemley, 1996

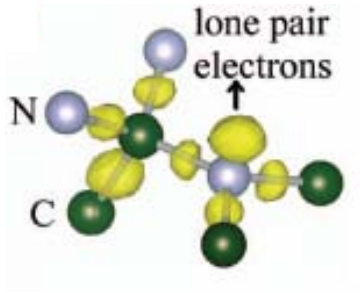
Are there any alternative materials which can be synthesized at high P and sustained ?

Synthesis of C-N super hard materials

Theoretically predicted most stable structures



(a) β-InS-type crystal structure of CN
(b) cg-CN
(c) α-Si_3N_4-type crystal structure of C_3N_4



Wang , 2012

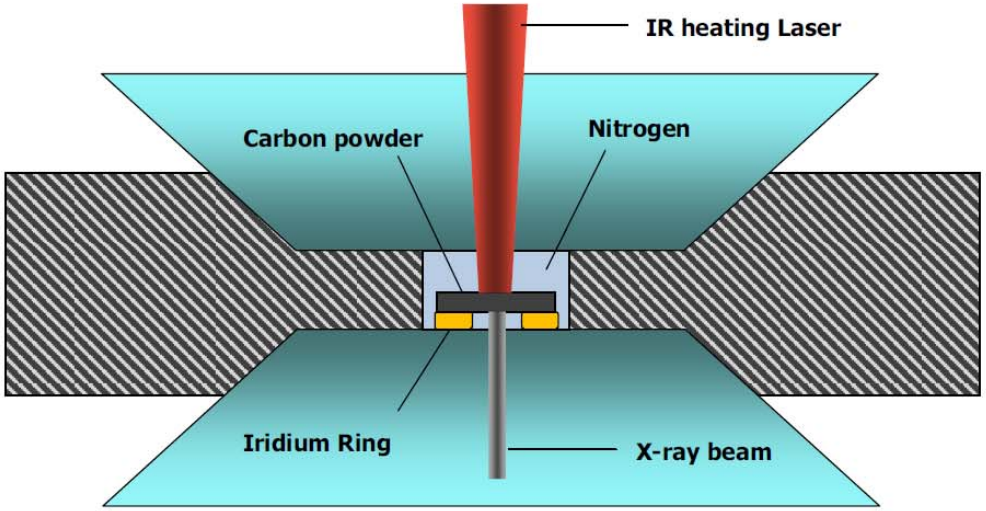
TABLE I. Calculated volume (V) and hardness (H) for diamond, c-BN, and *Pnnm* at zero pressure.

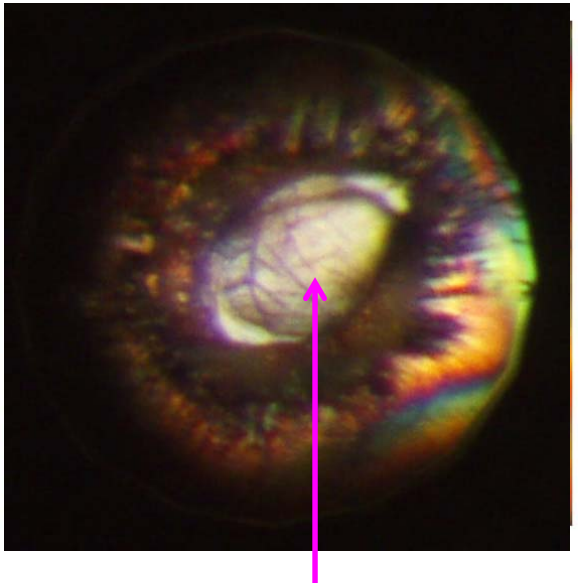
Materials	Methods	V (Å^3/atom)	H (GPa)
Diamond	This work	5.67	98.0
	Expt.	5.68[36]	60–120[37]
c-BN	This work	5.94	67.7
	Expt.	5.91[38]	47[39]
Pnnm	This work	6.12	62.3

What is the structure and composition of C-N compounds at high P?

Synthesis of C-N super hard materials

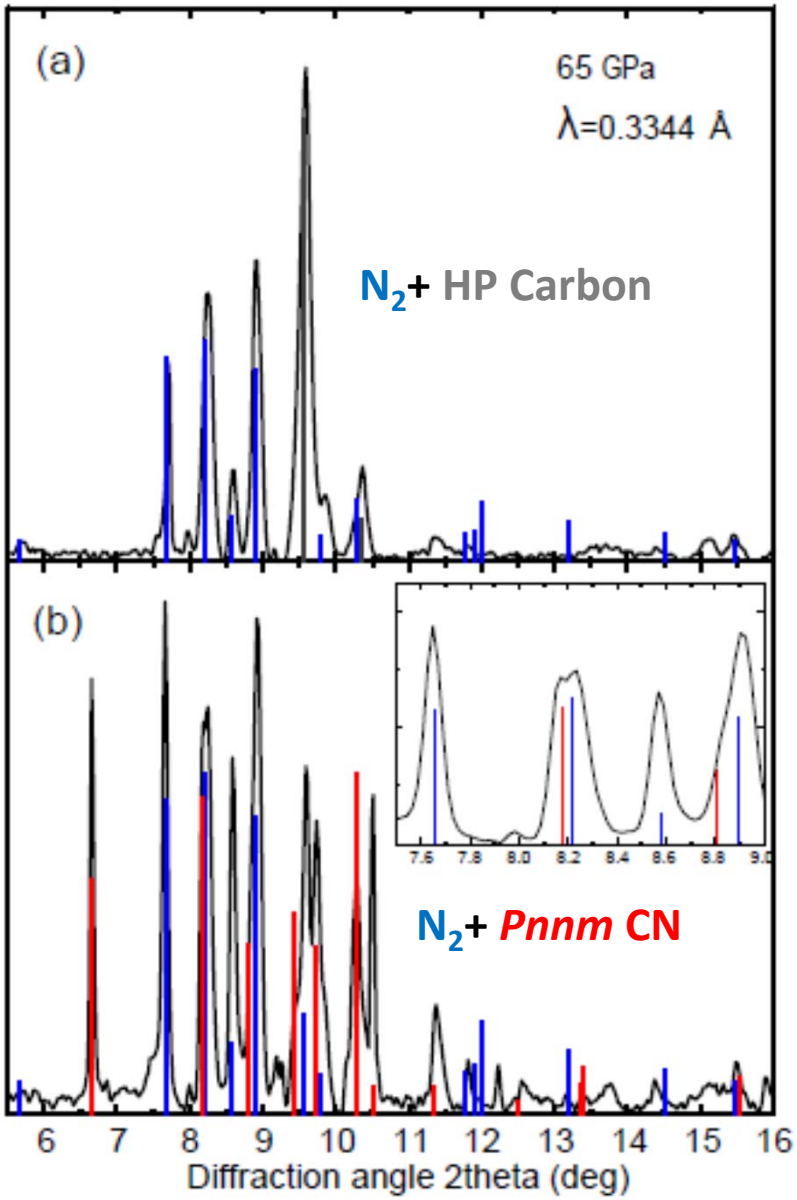
Experiment: laser heated DAC >40 GPa >2500 K



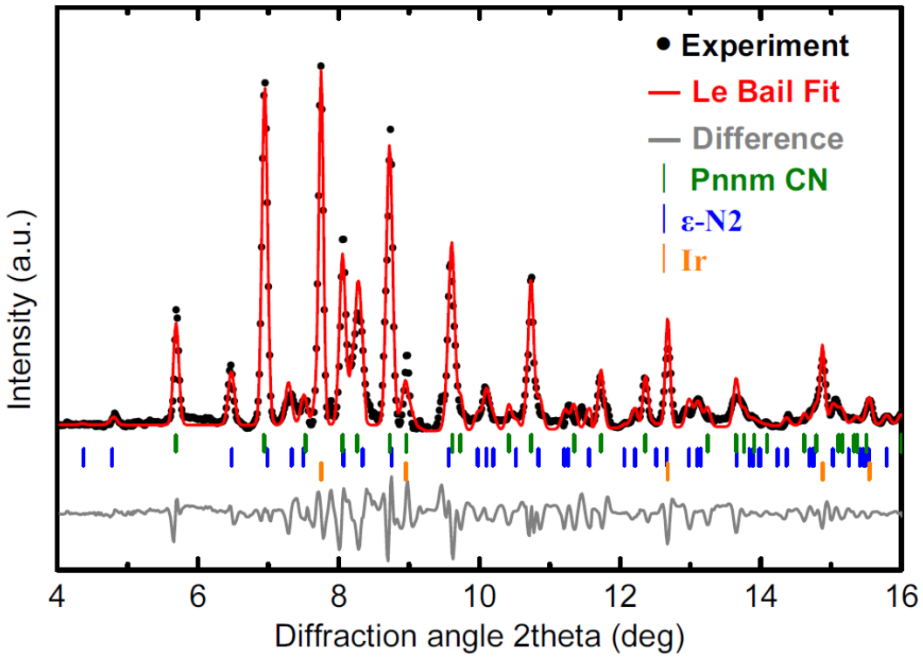


Transparent product

Synthesis of C-N super hard materials



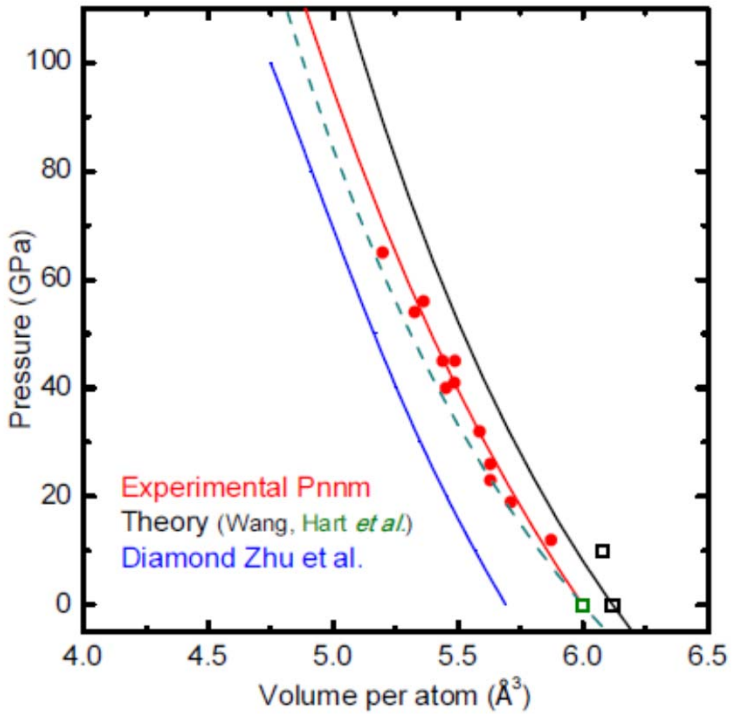
XRD synchrotron patterns before and after heating:
We synthesized a new material:
β-InS (*Pnnm*) CN



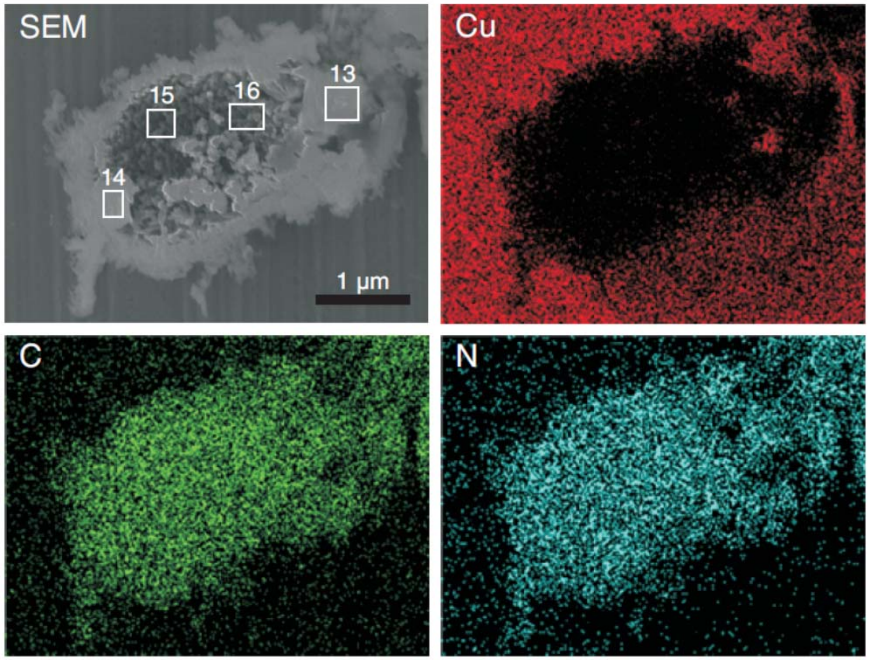
Stavrou et al., submitted

Metastability of C-N superhard materials

Equation of State



SEM images



Spectrum #	C, at%	N, at%	2σ
13	54.57	45.43	0.54
14	55.02	44.98	0.52
15	55.43	44.57	0.48
16	55.67	44.33	0.48

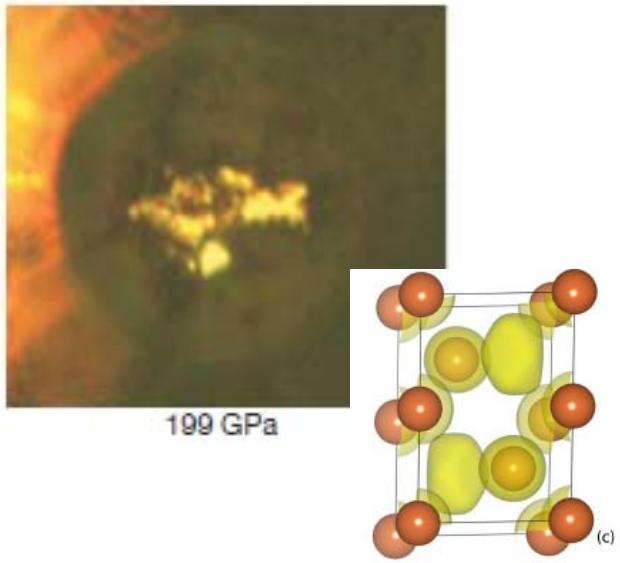
XRD and Raman of *Pnnm* phase disappear below 6 GPa; however the compound remains in almost predicted stoichiometry

Stavrou et al., submitted

Bonding through electrons in interstitial sites

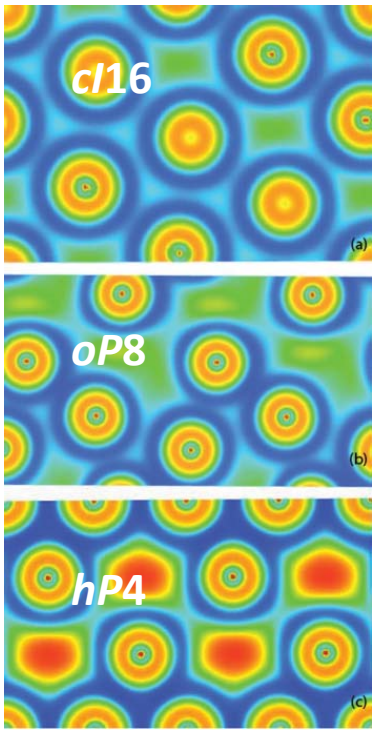
- Polymerized states become preferable
- Higher hybridized states become preferable
- **Interstitial (localized) electron bonding**
- Material with unusual stoichiometry

Pressure



Semiconducting ionically bonded sodium
(Ma et al., 2008)

Na

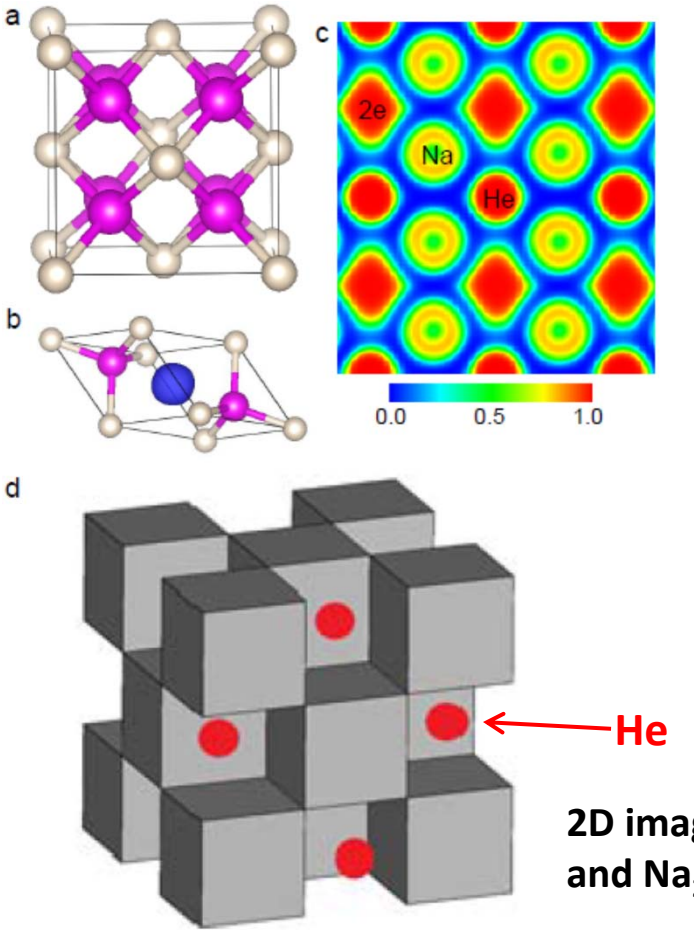


Marques et al., 2011

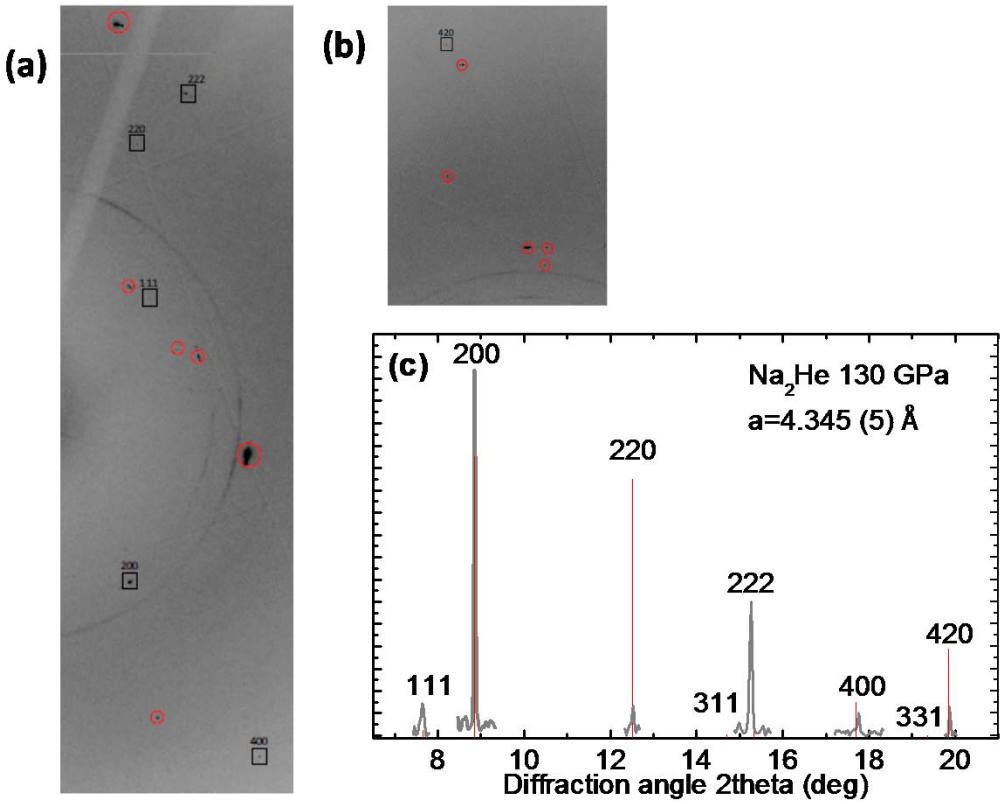
Do compounds form structures with electrides ?

Stable Compound of Helium and Sodium at High Pressure

Theoretical prediction of Na_2He 300 GPa



X-ray diffraction at 130 GPa



2D images, which show single crystal reflections of Na (oP8 and tI19) and Na_2He, marked by red circles and black squares, respectively

The electrides are electron-paired (higher density) unlike spin polarized at low P

Xiao Dong et al., 2014, Submitted

Creating multicenter bonding through change in stoichiometry

- Polymerized states become preferable
- Higher hybridized states become preferable
- Interstitial (localized) electron bonding
- **Material with unusual stoichiometry**

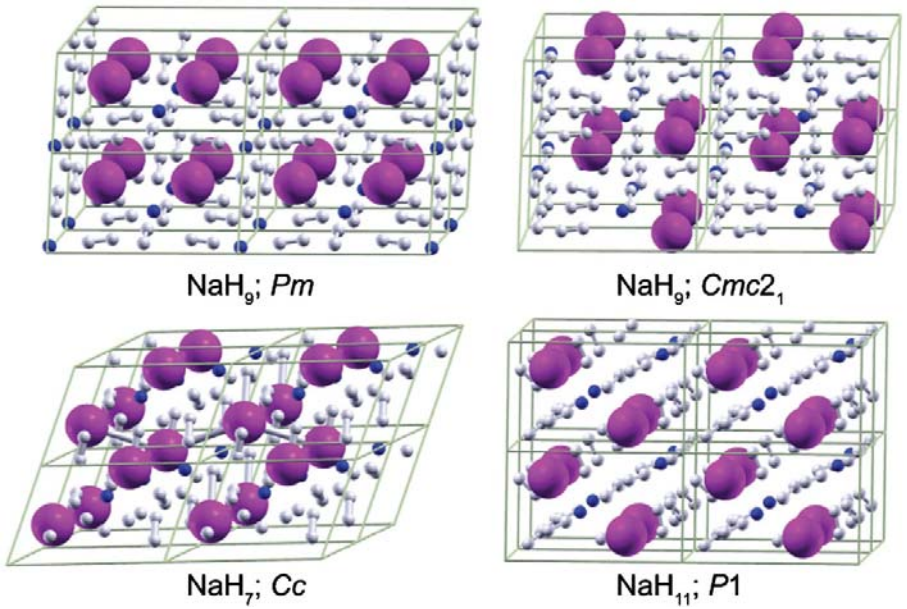
Pressure

Octet rule:

Are there any modification of valence rules under pressure?
Are hypervalent configurations promoted at high pressures?

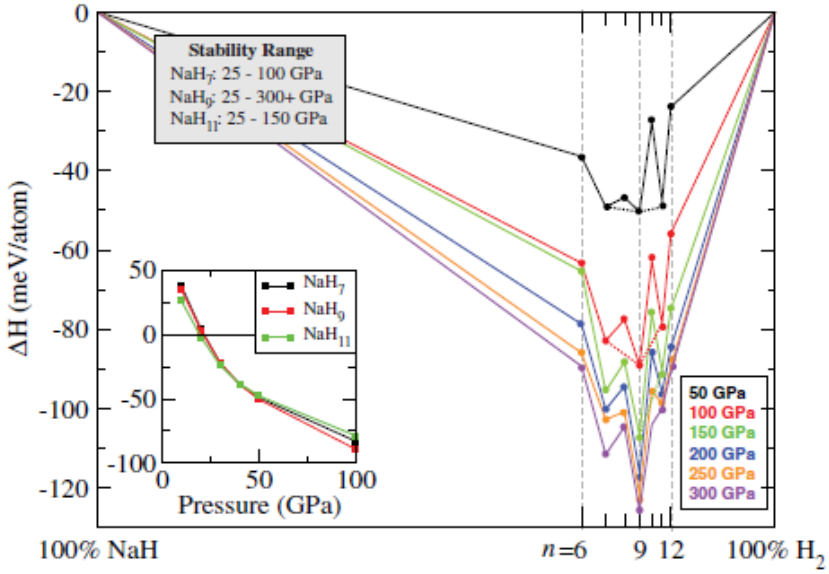
Synthesis of polyhydrides of alkali-metals at high pressures

Theoretical predictions:
Structures



Zurek et al., PNAS, 2009
Baettig & Zurek, 2011

Thermodynamic stability:
>25 GPa



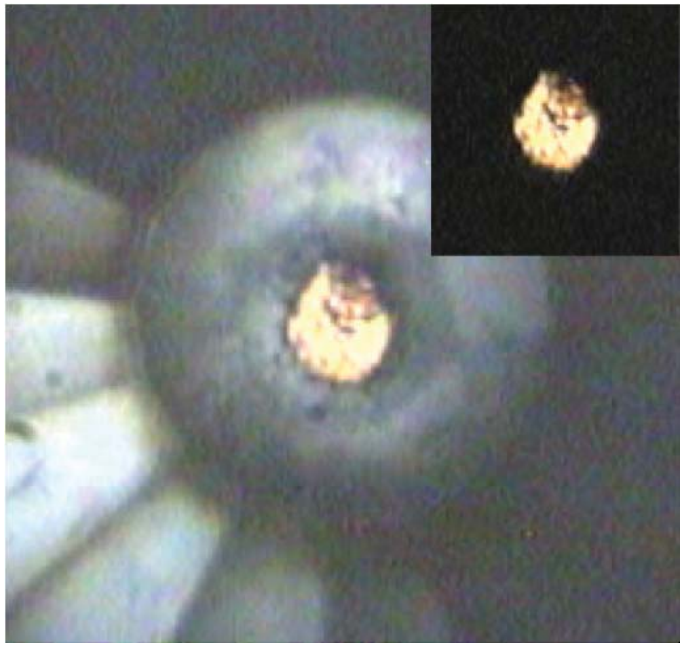
Metals at much lower pressures than pure hydrogen
(Ashcroft:, 2004 chemically pre-compressed)

Can polyhydrides be synthesized? Are they stable? Metallic?

Synthesis of polyhydrides of alkali-metals at high pressures

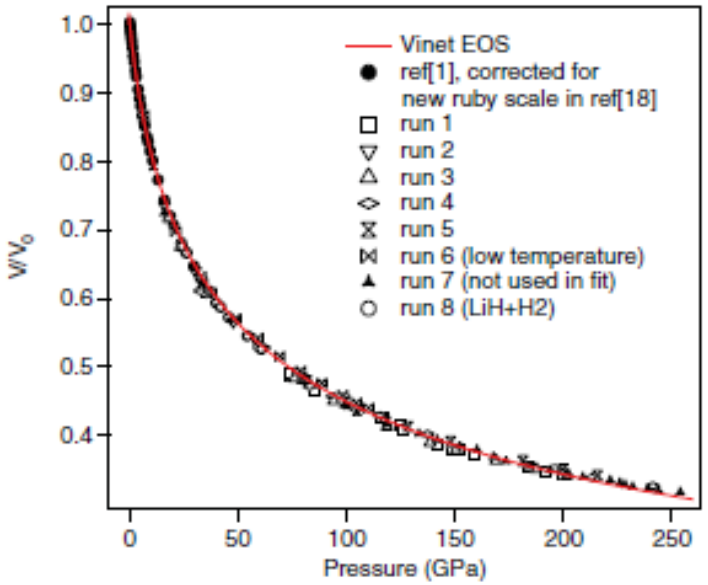
Only ionic materials with 1:1 stoichiometry are known so far

LiH: forms from Li and H_2 at as low as 50 MPa



Howie et al., 2012

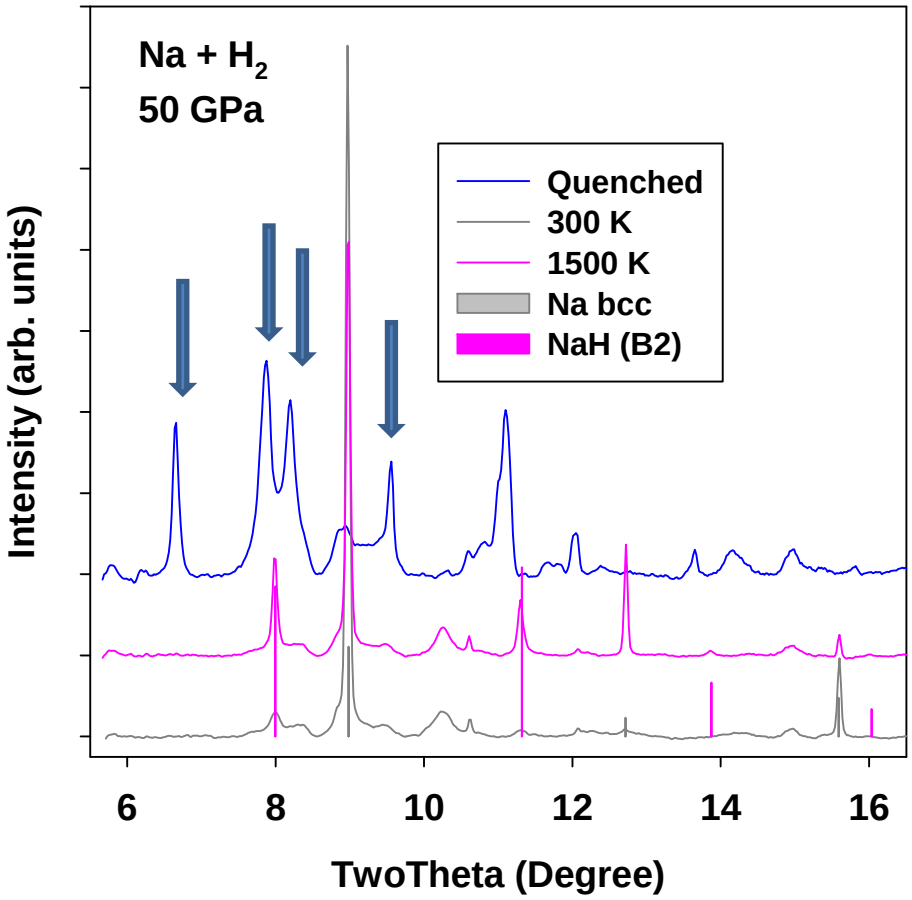
LiH: stable up to 250 GPa



Lazicki et al., 2012

Synthesis of polyhydrides of alkali-metals at high pressures

X-ray diffraction

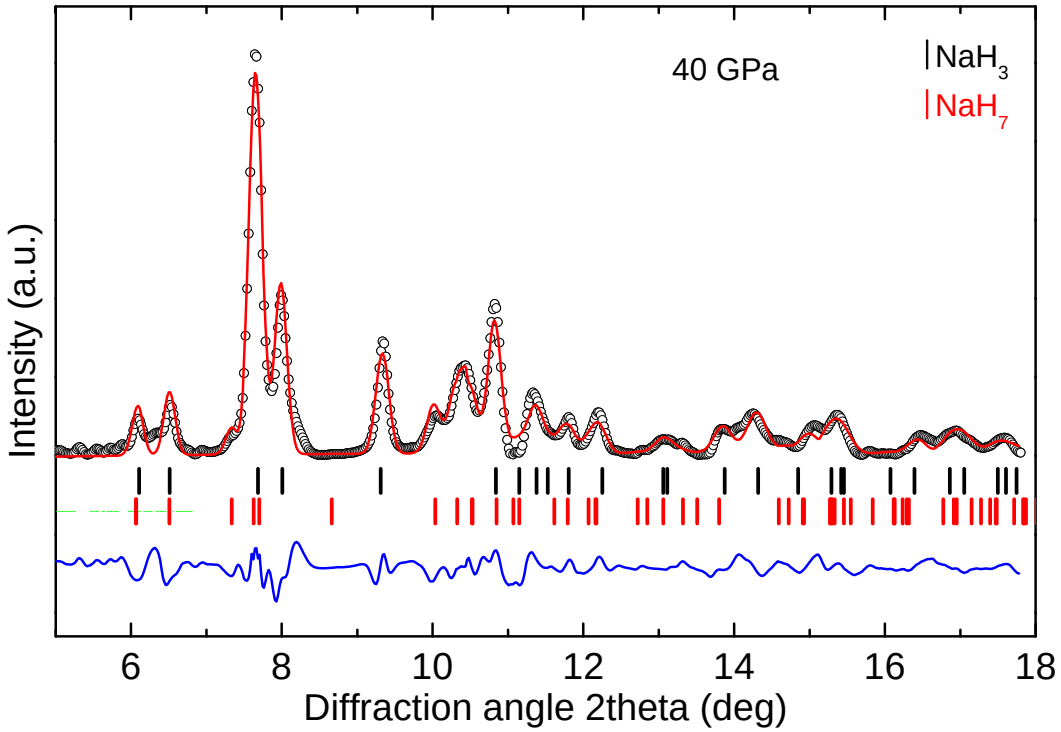


➢**A *new phase* forms from NaH after a prolonged heating at 1200-1500 K**

Struzhkin et al., 2014 submitted

Synthesis of polyhydrides of alkali-metals at high pressures

X-ray diffraction



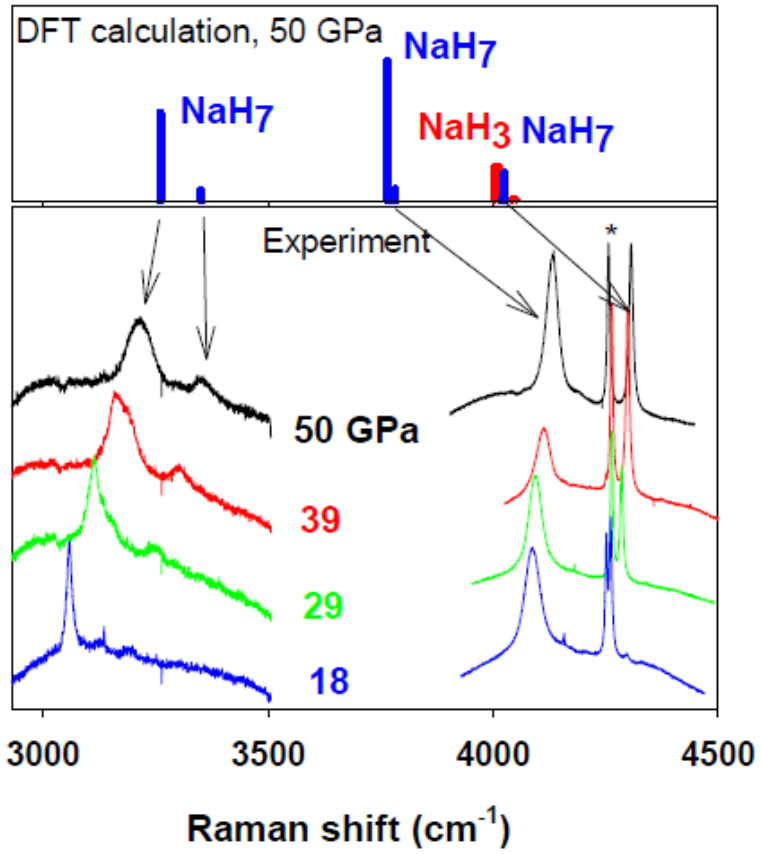
➢**We identified the products as NaH_3 + NaH_7**

Le Bail refinement for NaHn at 40 GPa. NaH_3 and NaH_7 peaks are marked with black and red vertical lines respectively

Struzhkin et al., 2014 submitted

Synthesis of polyhydrides of alkali-metals at high pressures

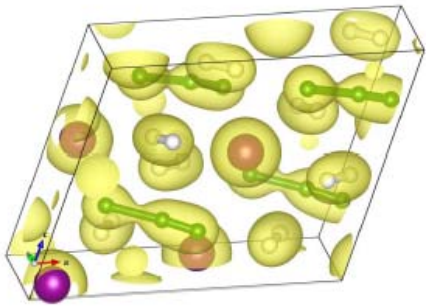
Raman spectra of quenched materials



Struzhkin et al., 2014 submitted

Dihydrides (Kubas) complexes

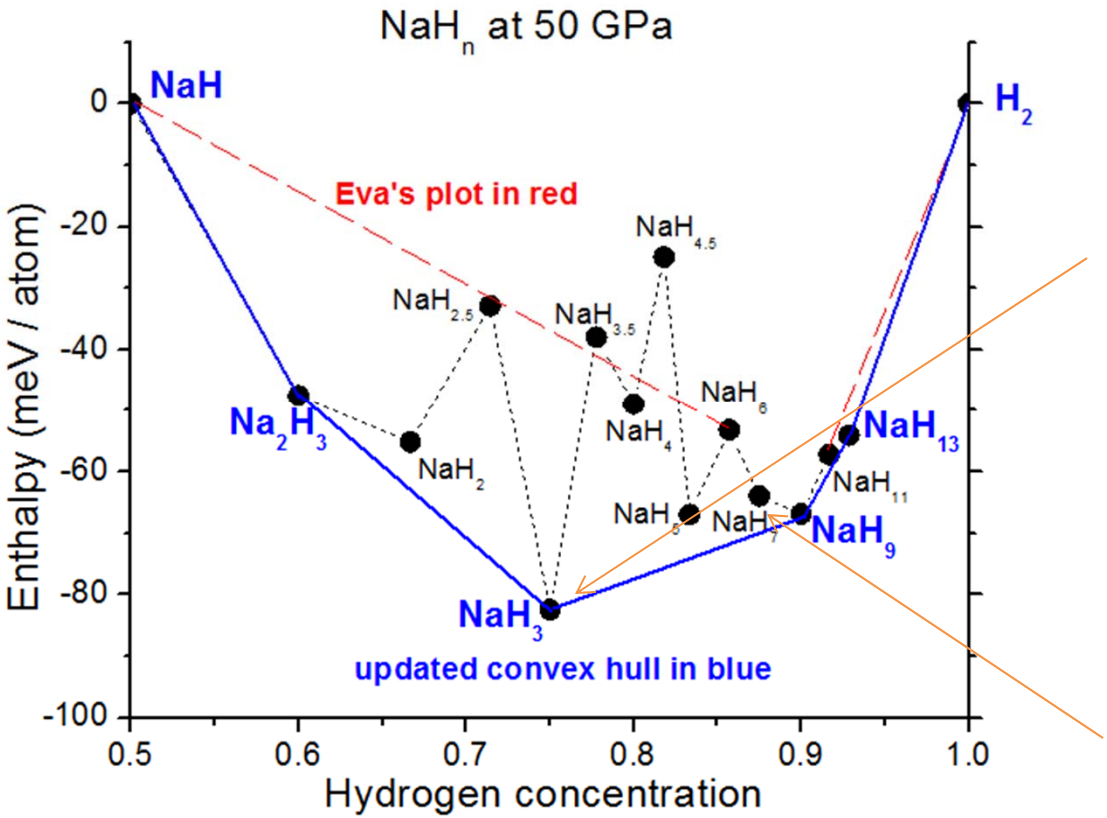
NaH_7

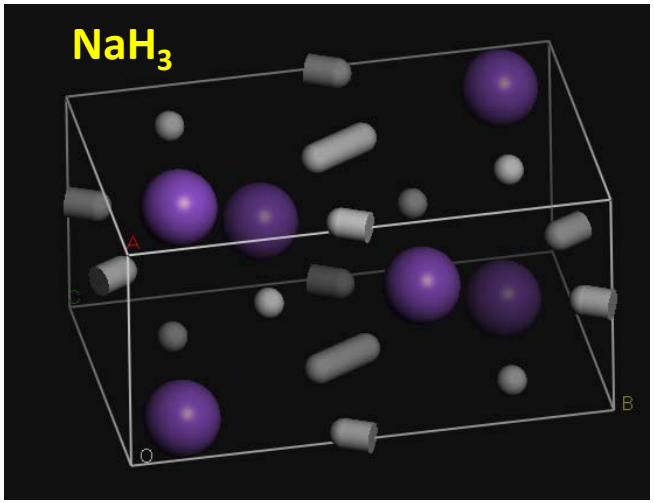


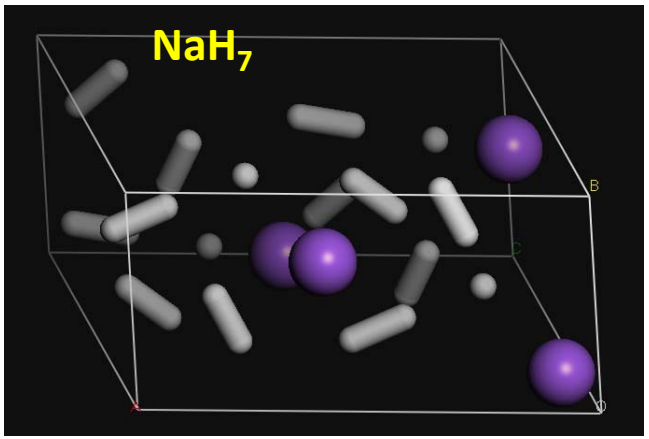
Raman spectra of a *new phase* show a vibron mode at much lower frequency than that in pure H_2 and a narrow phonon band indicating intramolecular bond destabilization and new compound formation

A 3200 cm^{-1} band corresponds to elongated molecules of H_2

Synthesis of polyhydrides of alkali-metals at high pressures



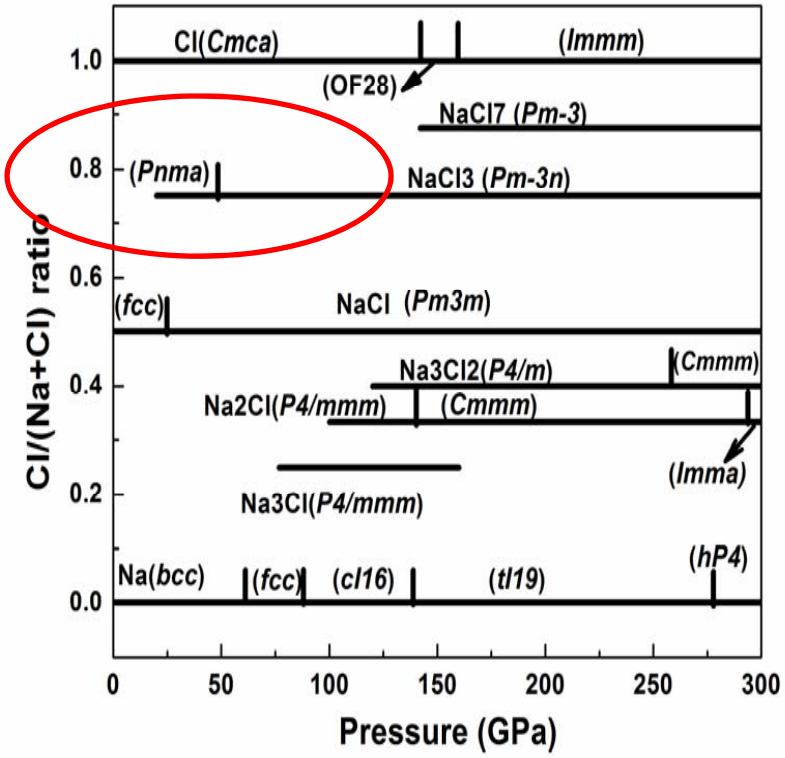




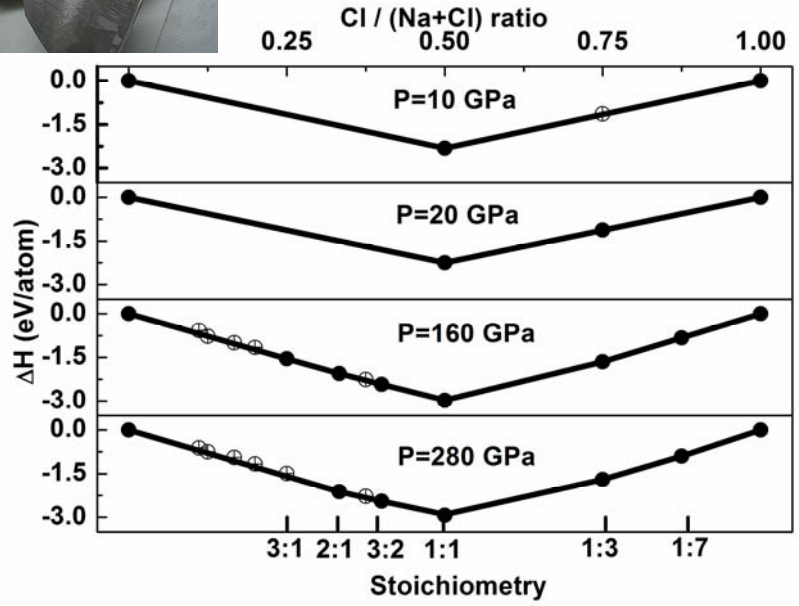
Struzhkin et al., 2014 submitted

Stability of new sodium chlorides

Pressure-composition phase diagram



Convex hull diagram for Na-Cl system at selected pressures



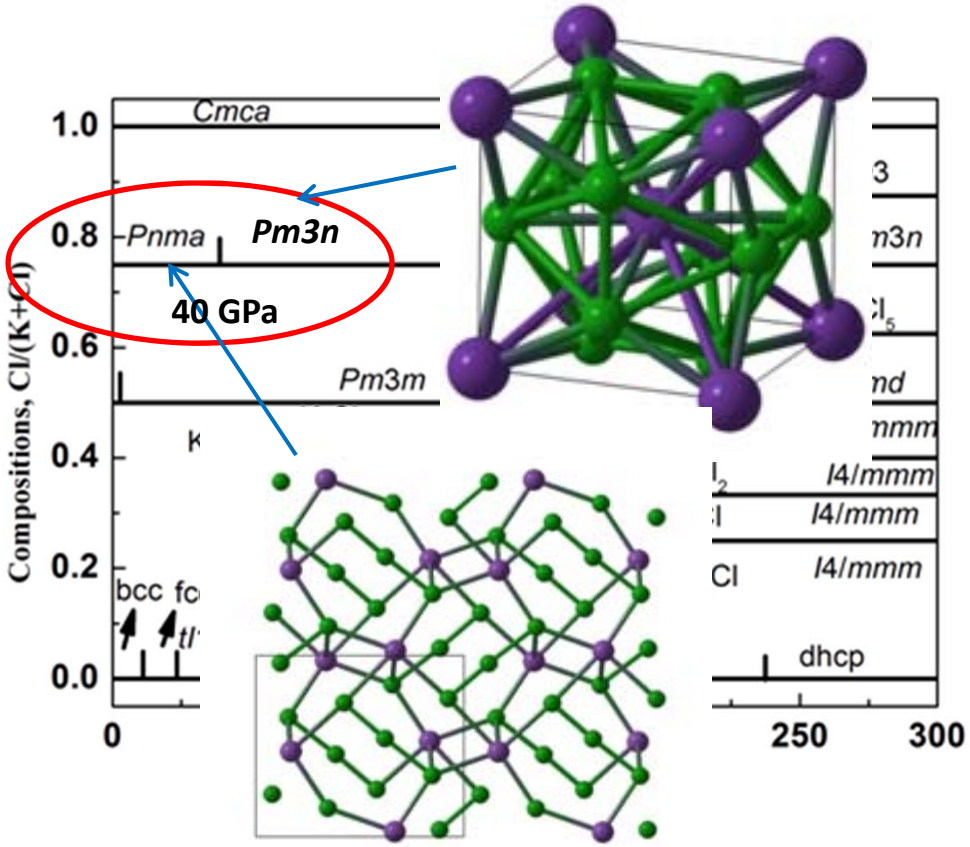
Solid circles represent stable compounds;
open circles - metastable compounds

Na-Cl compounds with various compositions become stable under pressure

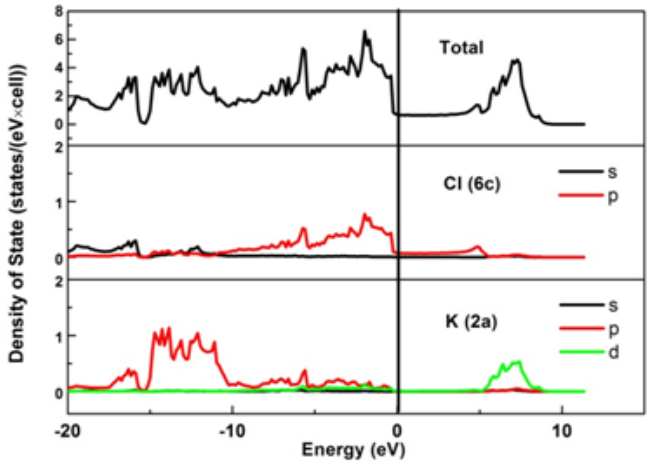
Zhang et al., Science (2013)

Stability of new potassium chlorides: theoretical predictions

Pressure-composition phase diagram



Electronic density of states of *Pm3n* KCl_3



Bad metal with a pseudogap

Theory predicts semiconducting *Pnma* KCl_3 to be stable at ambient pressure

Zhang et al., submitted.

Conclusions & Outlook

- High-pressure research open new fields for discoveries of novel materials with unique properties

- We synthesized new materials in the laser heated DAC which show unusual bonding schemes and stoichiometries
  - Energetic N_xH
  - Superhard CN
  - 2D conductor KCl_3
  - topologic insulator (?) Na_2He
  - high T superconductor (?) NaH_x

- Synergy of theory and experiments greatly helps in discovery of new materials

- Newly developed computational algorithms, such as evolutional search, do a good job in predicting new most stable phases and their stability limits.

However, experiments often find unexpected

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