Novel Chemistry at Extreme Conditions

Maddury Somayazulu, S. G. Gramsch, Muhtar Ahart, Ivan Naumov, Russell J Hemley (*CDAC team*)

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CDAC collaborations and related Research Projects

Muhtar Ahart, Takaki Muramatsu, Tim Strobel, Stephen Gramsch, Ivan Naumov, Hanyu Liu, Ajay Mishra, Alex Goncharov , Sergey Lobanov, Zhenxian Liu, Jerry Potter, George Cody, Ho-Kwang Mao, Larry Finger and Russell Hemley at the **Geophysical Laboratory.**

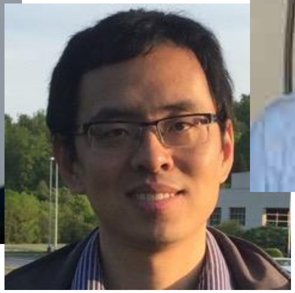
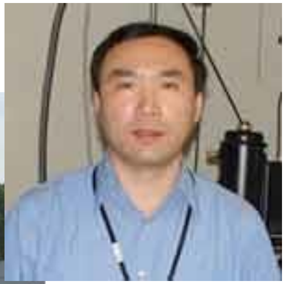
Raja Chellappa and Dana Dattelbaum from **LANL** – *Hydrazine and* $Xe\text{-}N_2$

Przemek Dera from **GL to GSECARS to Univ. Hawaii** – $Xe\text{-}H_2$ *and* $Xe\text{-}Cl_2$

Choong-Shik Yoo from **WSU** – *Hydride superconductors*

Jennifer Ciezak from **ARL** – *Boron Carbide and doped Boron Carbide*

Eva Zurek from **SUNY** – *Boron Carbide and Alkali Superhydrides*


Beamtime Support and Techniques Collaborators

- Maria Baldini (APS); Chen Li (SNS); Zhenxian Liu (NSLS)
- Viktor Struzhkin, Alex Goncharov and Reini Boehler at GL
- Przemek Dera and Vitali Prakapenka at GSECARS
- Yue Meng, Stas Sinogeikin and Changyong Park at HPCAT
- Peter Liermann at PETRA






Science News

from research organizations

Hydrogen-economy on the way? New hydrogen-storage method discovered

Date: November 25, 2009

Source: Carnegie Institution

Summary: Scientists have found for the first time that high pressure can be used to make a unique hydrogen-storage material. The discovery paves the way for a new approach to the hydrogen-storage problem. The researchers found that the normally nonreactive, noble gas xenon combines with molecular hydrogen under pressure to form a previously unknown solid with unusual bonding chemistry. The discovery debuts a new family of materials, which could boost hydrogen technologies.

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SCIENTIFIC METHOD / SCIENCE & EXPLORATION

Strange, unpredictable chemistry at high pressure

Extreme pressure has "a completely different atomic table," vital to understanding space

by John Timmer - Sep 29, 2013 6:15pm EDT

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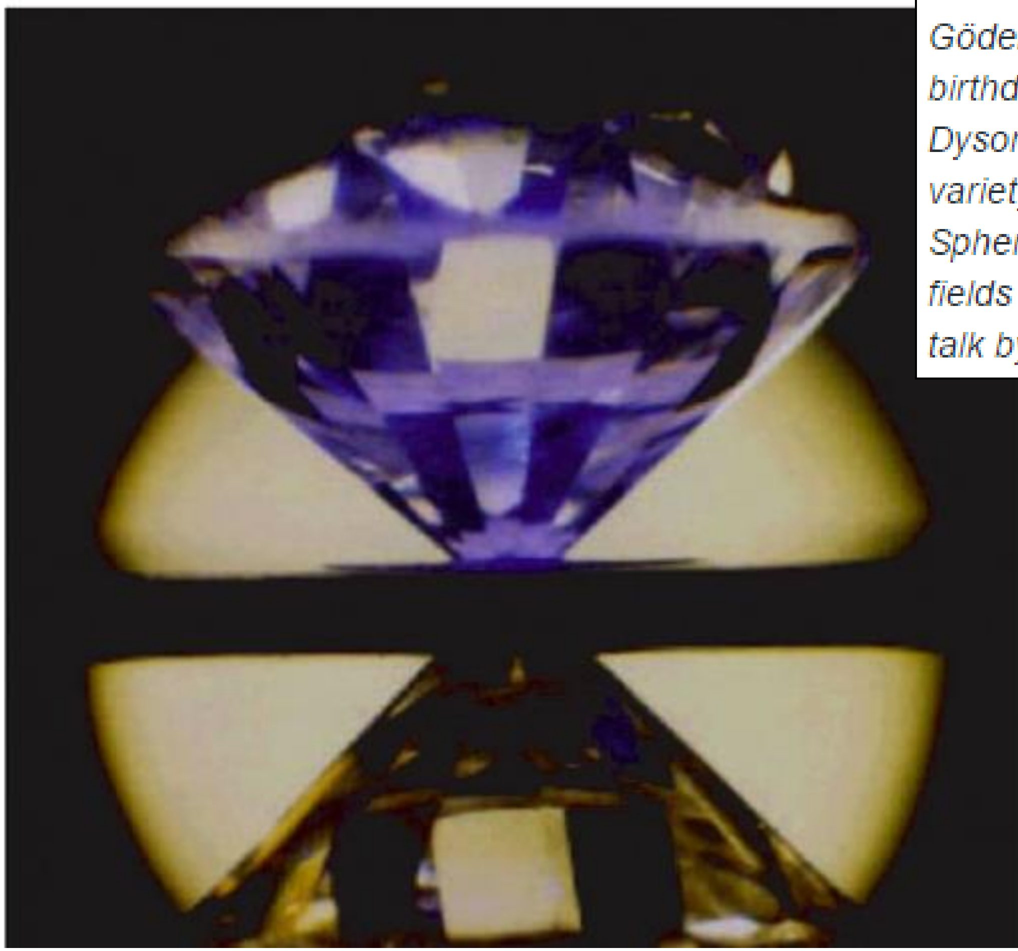


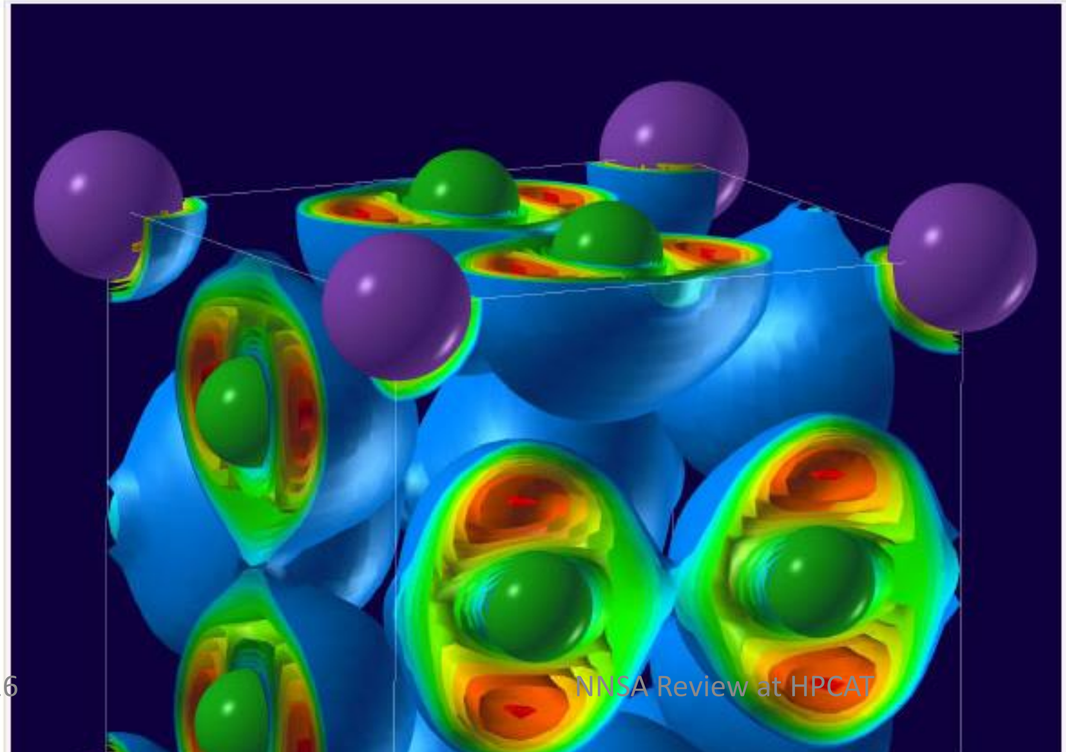
The Institute for Advanced Study, which has played host to such luminaries as Albert Einstein and Kurt Gödel, is holding a series of talks to celebrate the birthday of another one of its famous faculty: Freeman Dyson. Dyson made important contributions to a huge variety of fields and gave us the concept of the Dyson Sphere. The talks in his honor covered many of the fields that he influenced, and here, we'll describe the talk by chemist Russel Hemley.

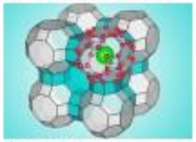
'Impossible' Sodium Chlorides Challenge Foundation of Chemistry

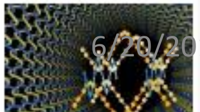
Dec 20, 2013 by Editors

« PREVIOUS | NEXT »

A team of researchers led by Prof Artem Oganov of Stony Brook University has shown that, under certain conditions, ordinary rock salt can take on some surprising forms that violate textbook rules of chemistry.

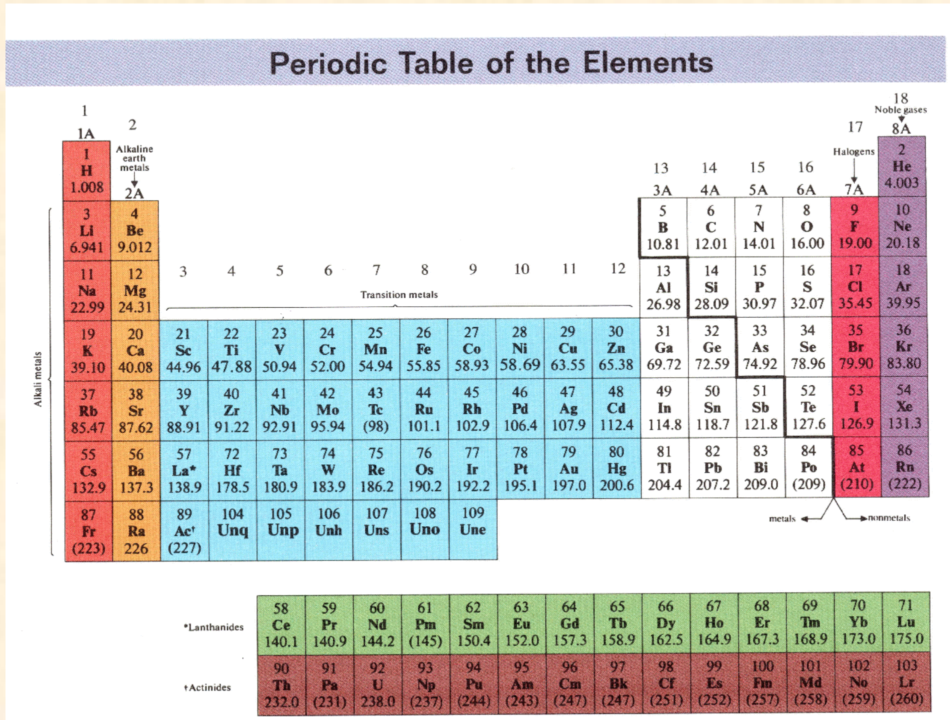






PRESSURE

PRESSURE

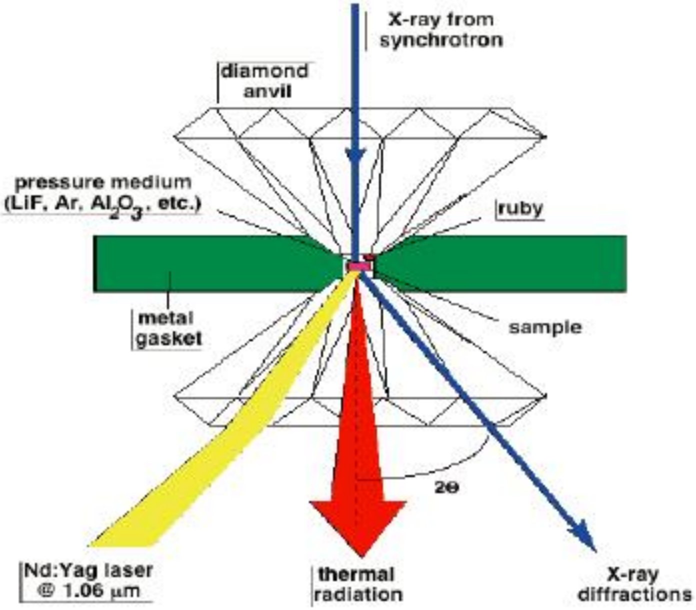


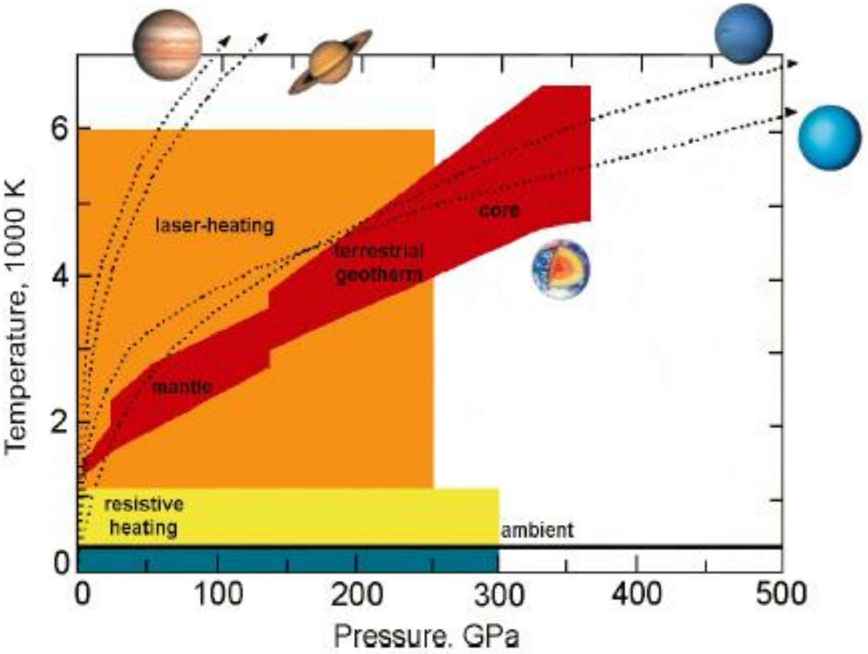
Under Pressure

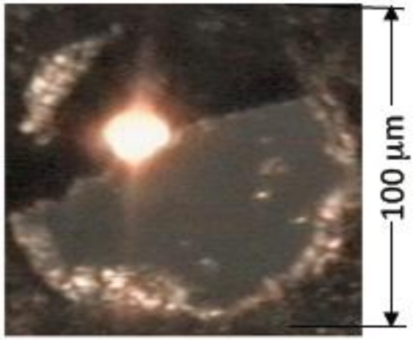
- **Orbital hybridization (*s* → *d*)**
- **Complex structures/electronic structure**
- ***Valence-core hybridization at more extreme pressures?***

valence electrons

Static high pressures: Laser-heated DAC





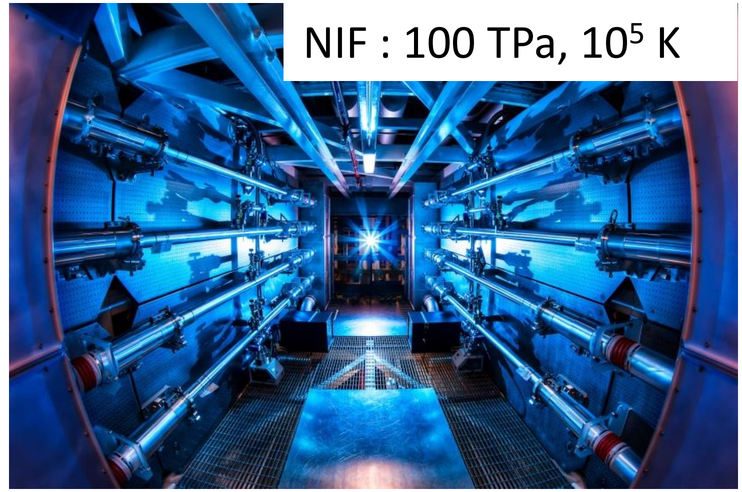


DAC research requires **micro-probing technologies** such as a laser and an intense μm-size x-ray beam at third-generation synchrotron sources

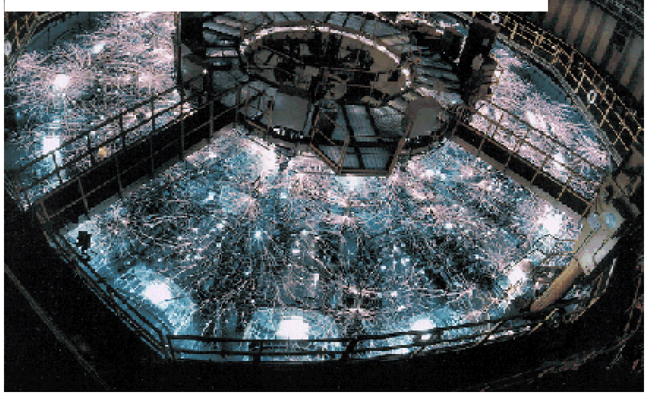
Dynamic High Pressure – Real Extreme Conditions

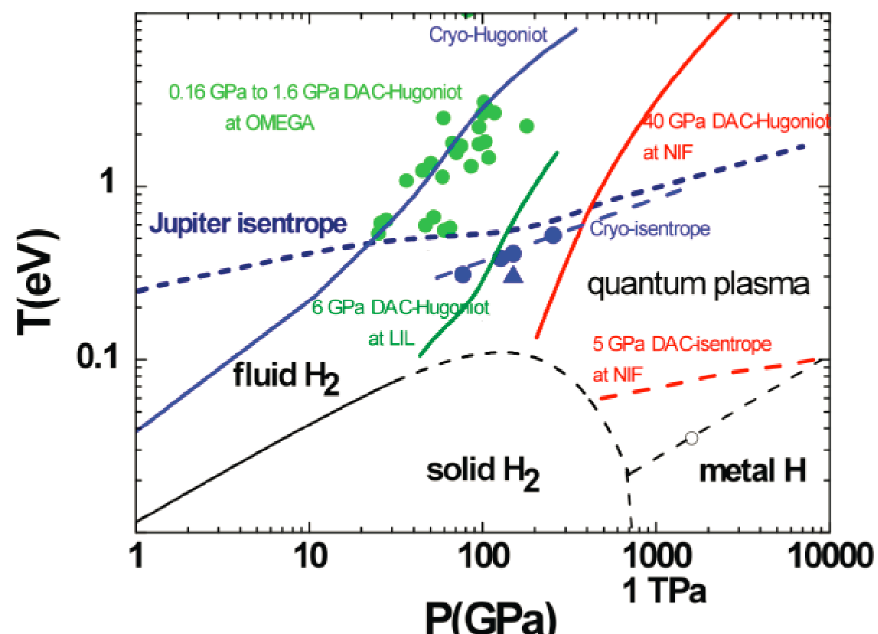
Gas gun : 300 GPa, 10^3 K

NIF : 100 TPa, 10^5 K



Z pinch : 100 GPa, 10^6 K





core electrons

Tools of research are major facilities

- HPCAT, GSECARS, PETRA, SNS (Current)
- SLAC, DCS-CAT, NIF (Future)

1. CDAC beamtime scheduled every run cycle.
2. Beamtime split between LH and BM-D to allow broader access amongst CDAC partners to the more sought after LH beamtime.
3. Beamtime available for spectroscopy (XANES, EXAFS, IXS) and BM-B based PE cell measurements is becoming crucial for some studies.

CDAC Science

- Discover new Materials (energetic materials, structural materials)
- Understand strategic, superhard Materials – PVT EOS, elastic-plastic deformation, dynamic loading, bonding changes
- Validation of modelling of strategic materials
- Enable the scientific research across all CDAC partners (gas loading, novel cell assemblies, national and international facilties

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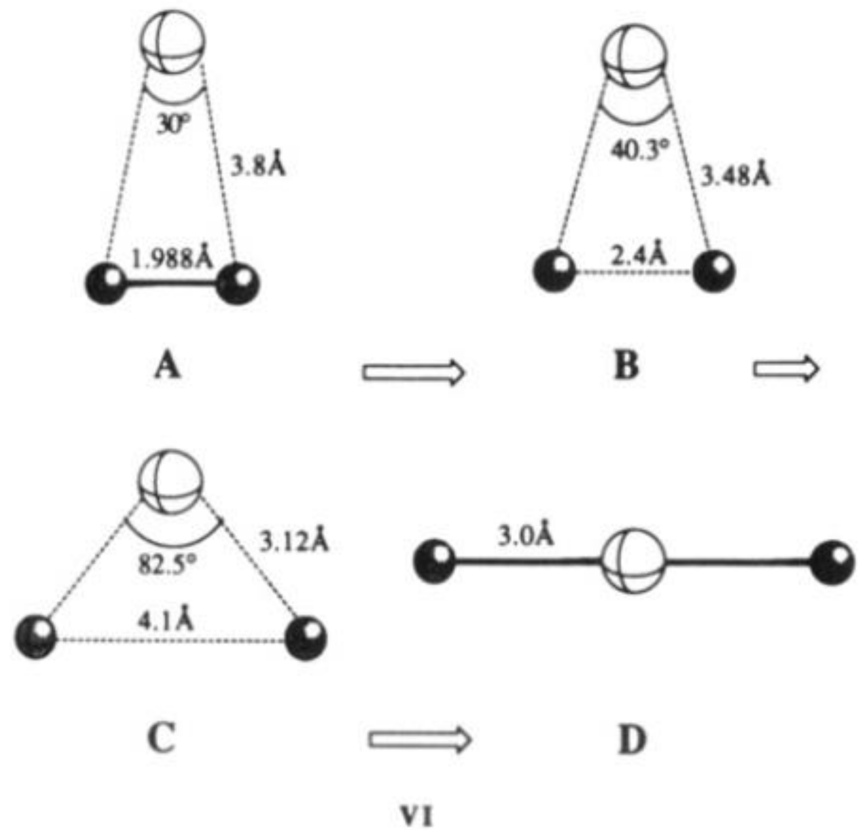
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

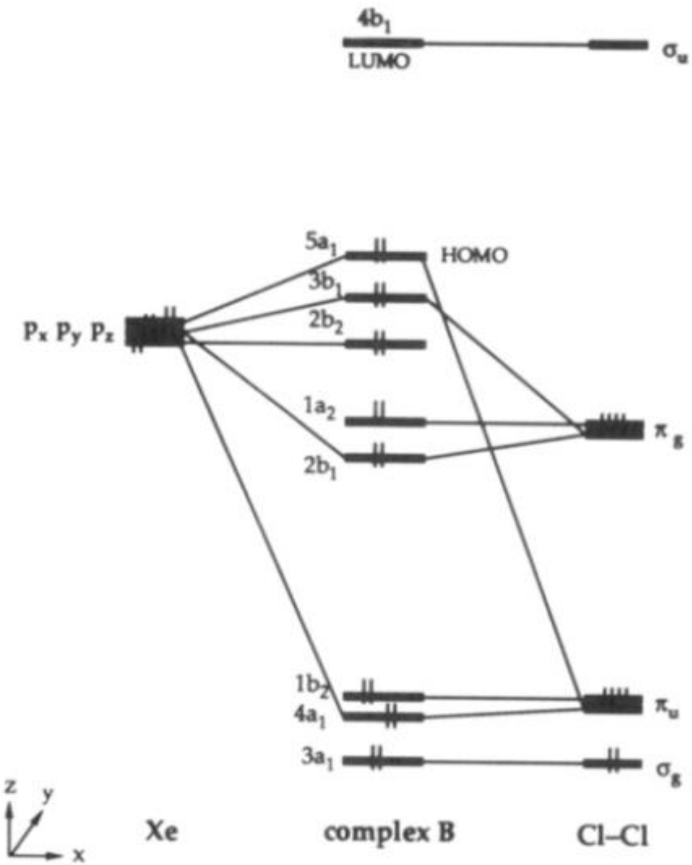
Novel Xenon Chemistry

The xenon-chlorine conundrum: van der Waals complex or linear molecule?

Davide M. Proserpio, Roald Hoffmann, and Kenneth C. Janda

J. Am. Chem. Soc., **1991**, 113 (19), 7184-7189• DOI: 10.1021/ja00019a014 • Publication Date (Web): 01 May 2002




$4b_1$
LUMO
σ_u
$5a_1$
HOMO
$3b_1$
$2b_2$
P_x P_y P_z
$1a_2$
π_g
$2b_1$
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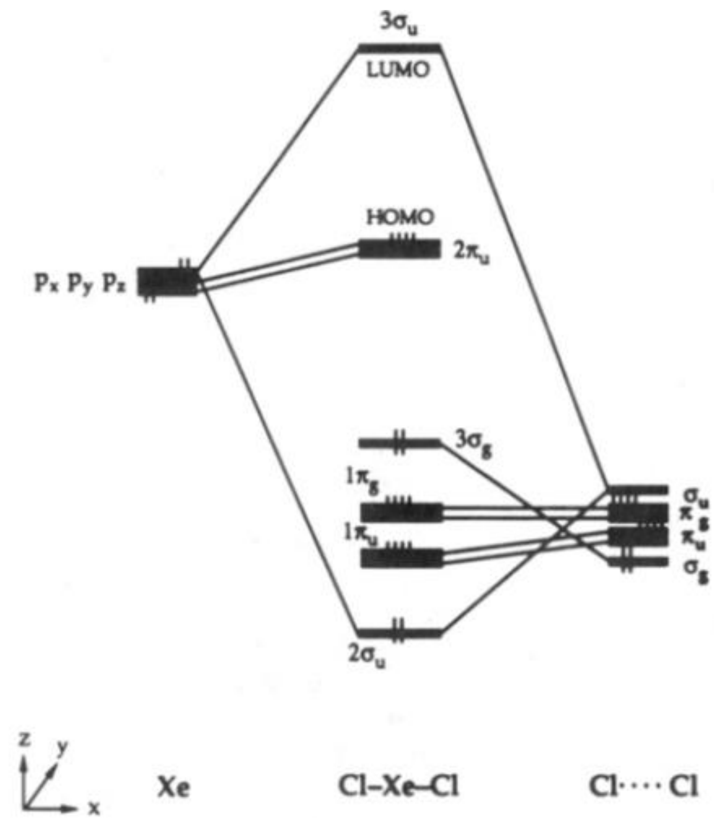
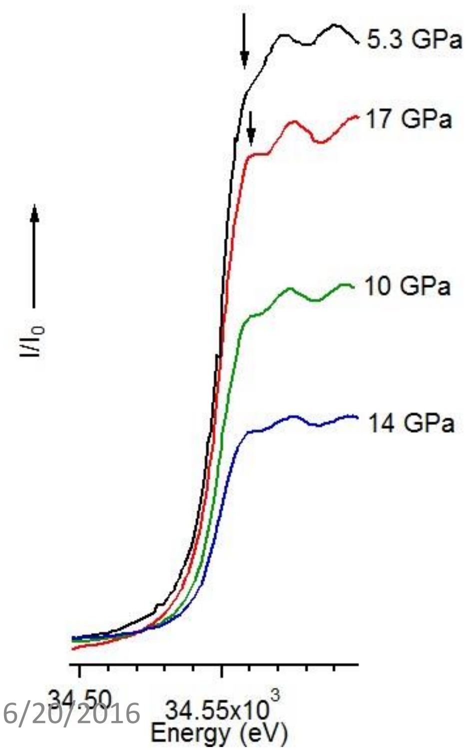
σ_g
z
y
x
Xe
complex B
Cl–Cl

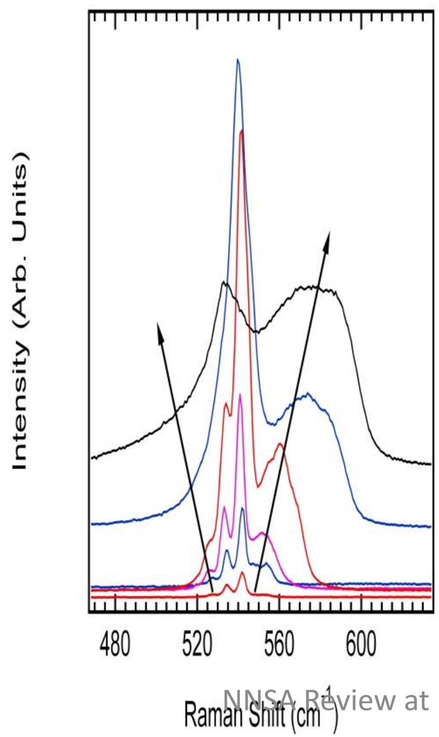

$3\sigma_u$
LUMO
HOMO
$2\pi_u$
P_x P_y P_z
$3\sigma_g$
$1\pi_g$
$1\pi_u$
σ_u
π_g
π_u
σ_g
$2\sigma_u$
z
y
x
Xe
Cl–Xe–Cl
Cl···Cl

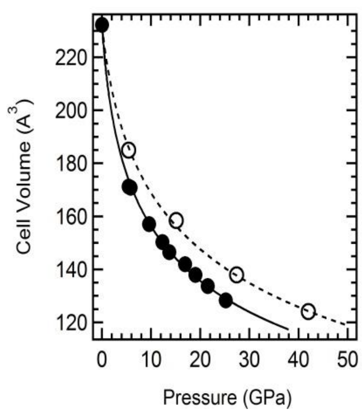
Xenon – Chlorine system in a diamond cell

- Mixtures of Xe and Cl_2 compressed in a diamond cell to pressures of the order of 100 GPa display formation of vdW compound at low pressures (2 GPa) that dissociate above 60 GPa (Xe and Cl_2 have similar vdW radii and therefore not surprisingly, we form an fcc (Xe)(Cl_2) compound)

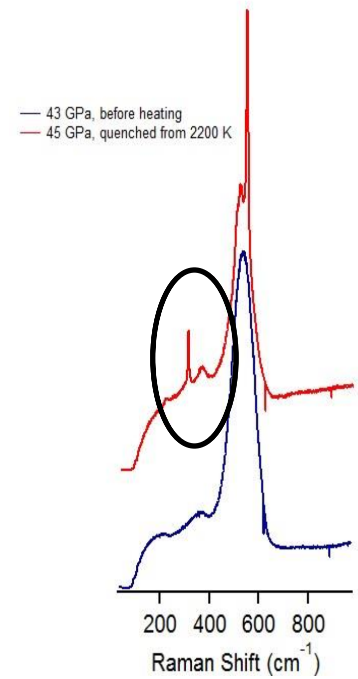
- Enormous increase in intensity of Cl-Cl stretch above 10 GPa (in the Raman) is accompanied by a change in the Xe XANES spectra indicative of change from s to p type character of xenon (Xe k edge is at 34.56 keV)







filled symbols $XeCl_2$ compound;
open symbols pure Cl_2



Orthorhombic $XeCl_2$

Novel Hydride Chemistry

VOLUME 92, NUMBER 18 PHYSICAL REVIEW LETTERS week ending 7 MAY 2004

Hydrogen Dominant Metallic Alloys: High Temperature Superconductors?

N.W. Ashcroft

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853-2501, USA
Donostia International Physics Center, San Sebastian, Spain

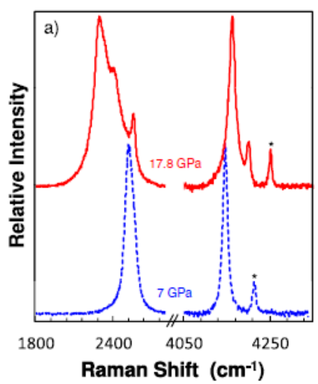
(Received 29 December 2003; published 6 May 2004)

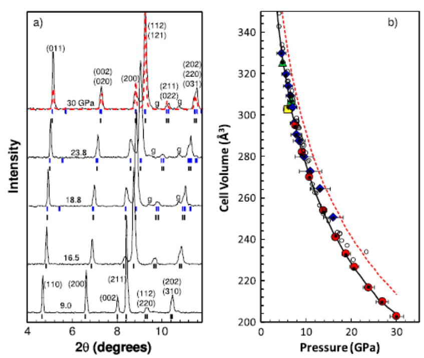
The arguments suggesting that metallic hydrogen, either as a monatomic or paired metal, should be a candidate for high temperature superconductivity are shown to apply with comparable weight to alloys of metallic hydrogen where hydrogen is a dominant constituent, for example, in the dense group IVa hydrides. The attainment of metallic states should be well within current capabilities of diamond anvil cells, but at pressures considerably lower than may be necessary for hydrogen.

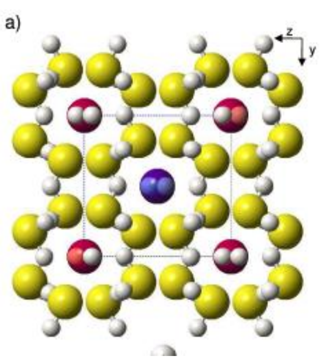
PRL **107**, 255503 (2011) PHYSICAL REVIEW LETTERS week ending 16 DECEMBER 2011

Novel Cooperative Interactions and Structural Ordering in H_2S-H_2

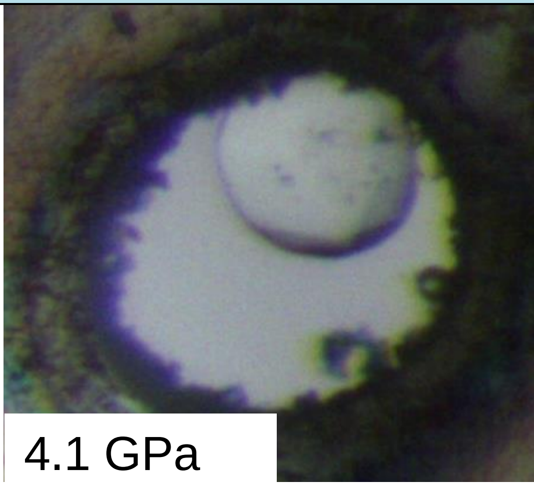
Timothy A. Strobel,[1,*] P. Ganesh,[2,†] Maddury Somayazulu,[1] P. R. C. Kent,[2] and Russell J. Hemley[1]



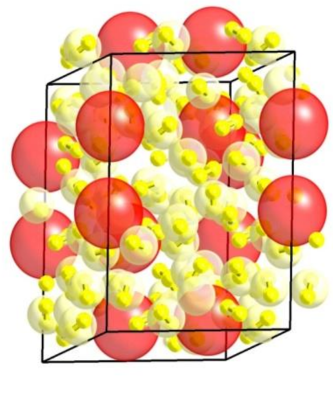




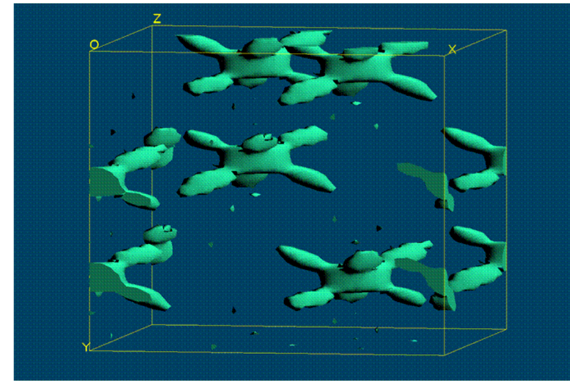
Formation of $Xe(H_2)_8$



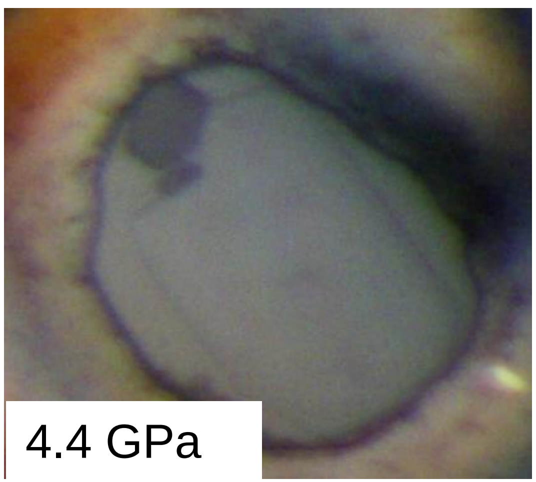
4.1 GPa



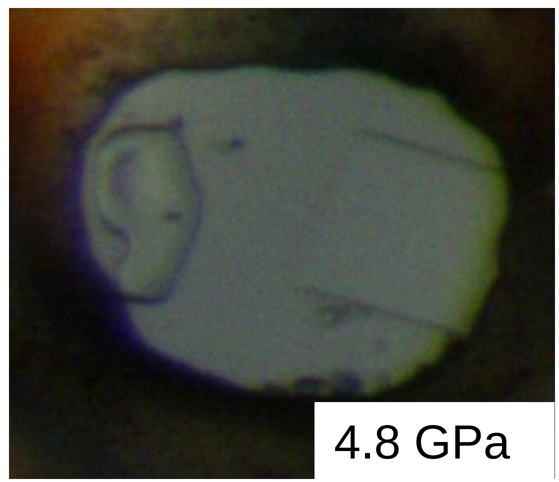
Xenon *'dimers'*



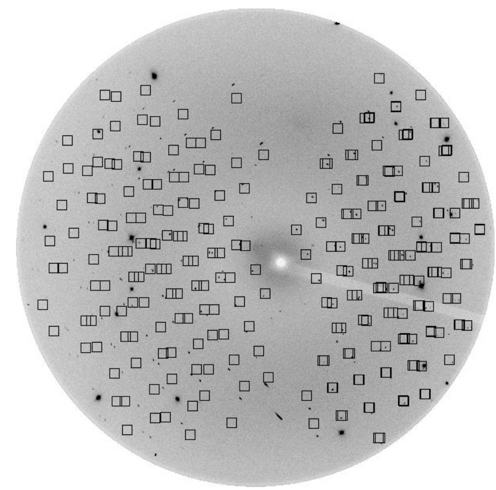
electron density of the *vdW compound*



4.4 GPa

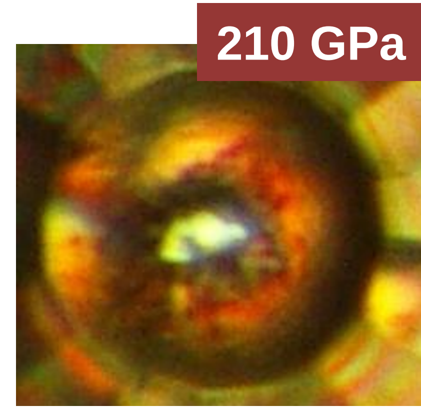


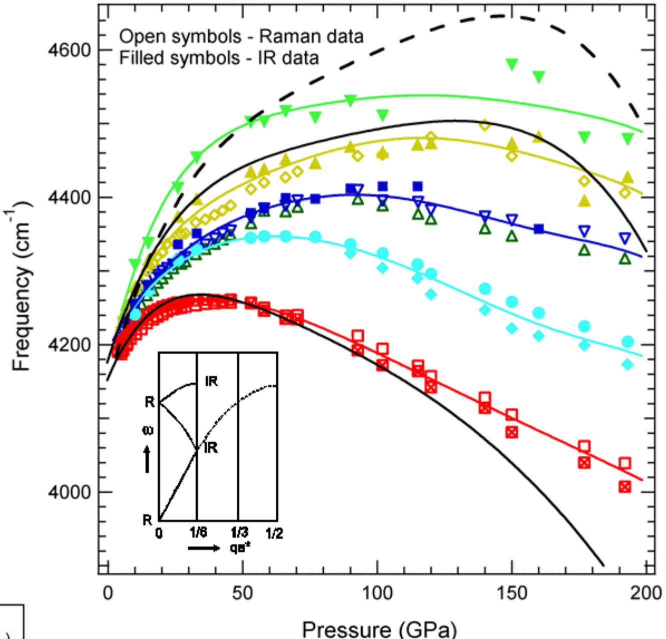
4.8 GPa

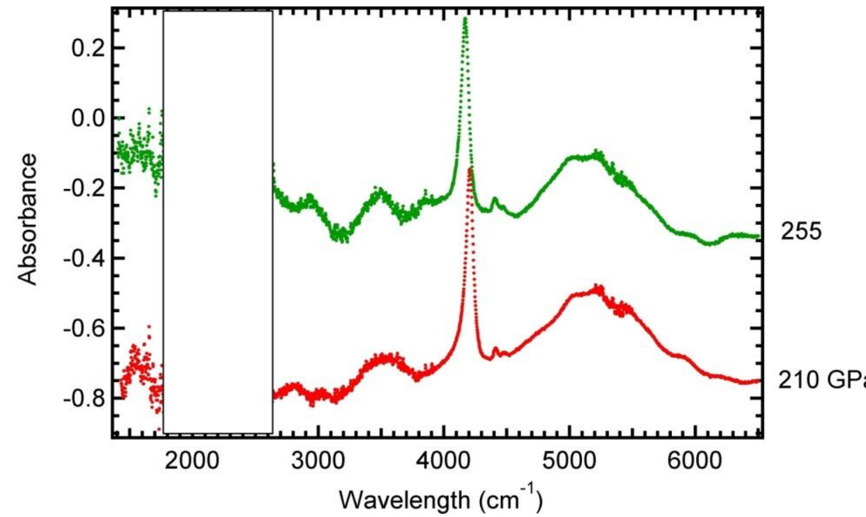


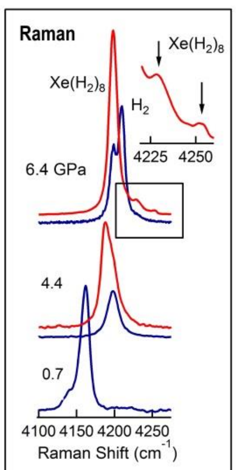
Single Crystal XRD

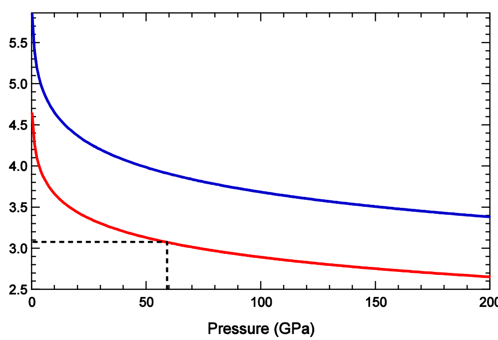
Unexpected High Pressure Stability of $Xe(H_2)_7$

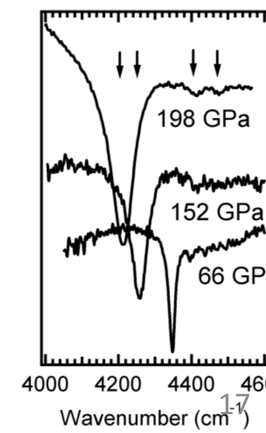






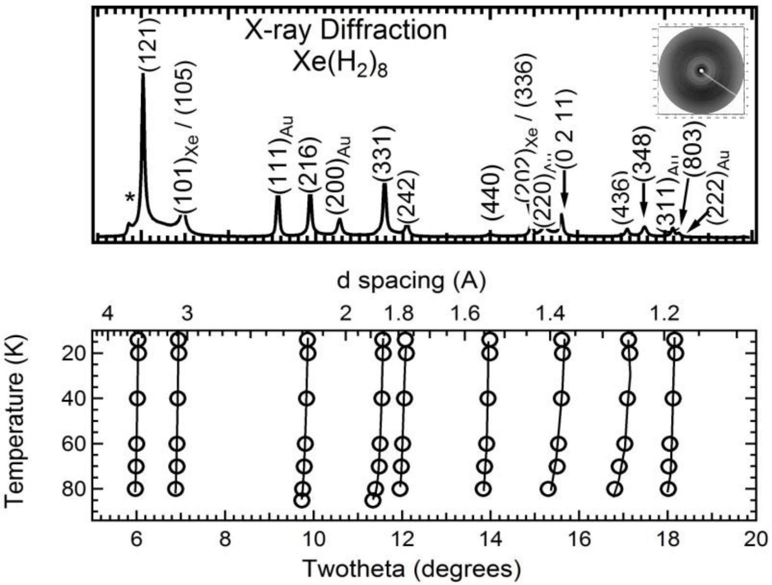




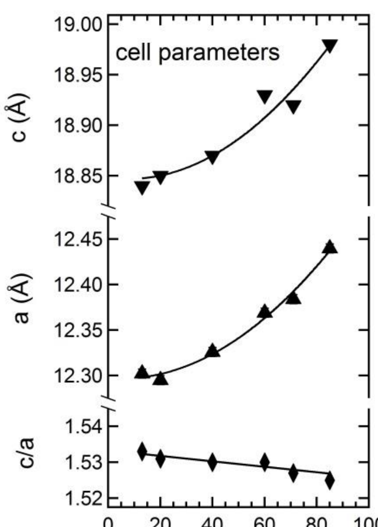


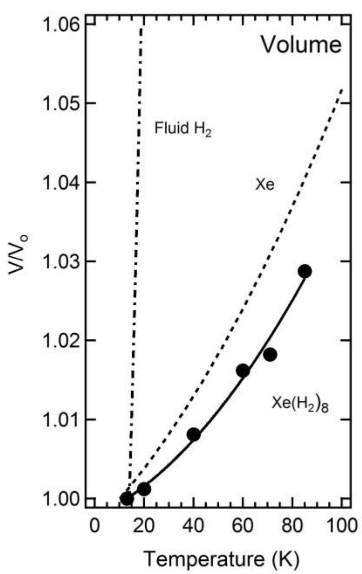
The 'dimers' would reach calculated Xe-Xe distance in hcp xenon at about 110 GPa, but obviously, there is no metallization of the Xe sublattice.

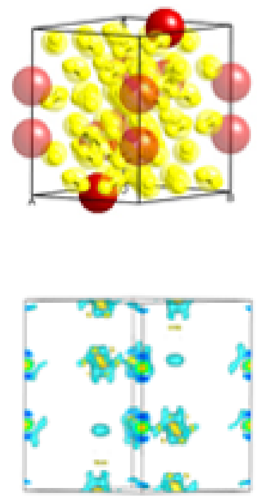
Unexpected Low Pressure Stability of $Xe(H_2)_8$

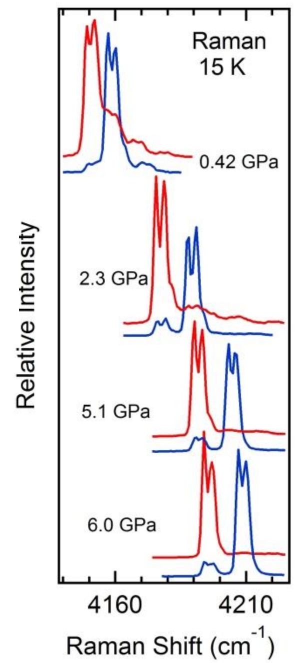


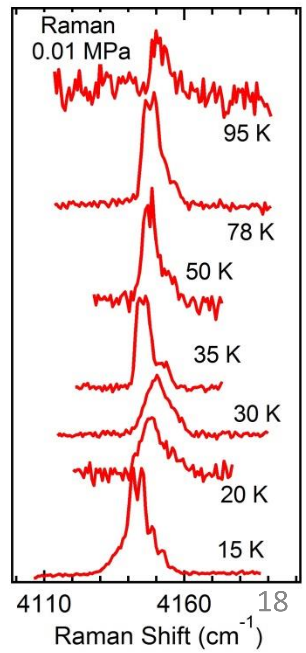
- $Xe(H_2)_8$ can be synthesized from a mixture of Xe and H_2 at 1.2 GPa and 150 K or 4.2 GPa and 300 K.
- Variable H_2 stoichiometry from a mixture of ordered and disordered H_2 molecules proposed.
- This phase can be retrieved to ambient pressure and temperatures as high as 100 K when H_2 release occurs in a single step.











Phys. Rev. B (2015)

Stable Xenon Nitride at High Pressures

Feng Peng[1,2], Yanchao Wang[1], Hui Wang[1], Yunwei Zhang[1], and Yanming Ma[1]*

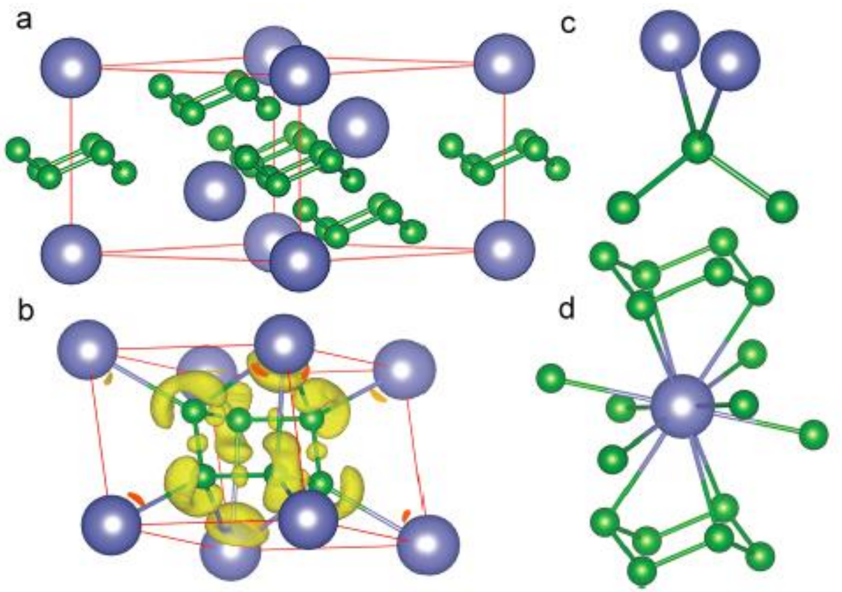


Figure 2. Crystal structure and bonding properties of XeN_6. (a) XeN_6 in an *R*-3*m* structure without showing any Xe-N bonds at 150 GPa where chaired N_6 hexagons are observed. The small green and large purple balls represent N and Xe atoms, respectively. (b) ELF plots at 150 GPa with an isosurface value of 0.83, showing covalent Xe-N bonding polarized towards N. (c) and (d) depict two structural units of 4-fold bonded N (i.e., N in sp^3 hybridization) and 12-fold bonded Xe, respectively.

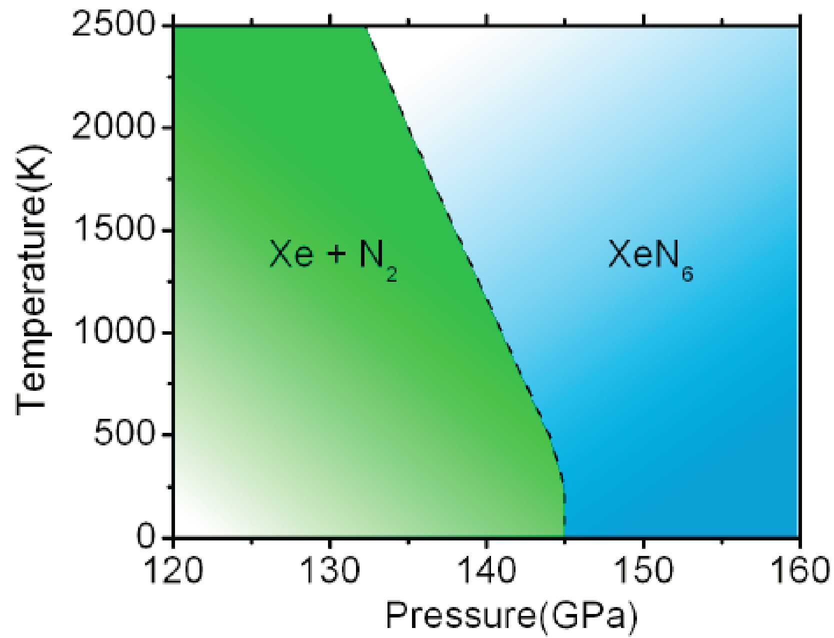
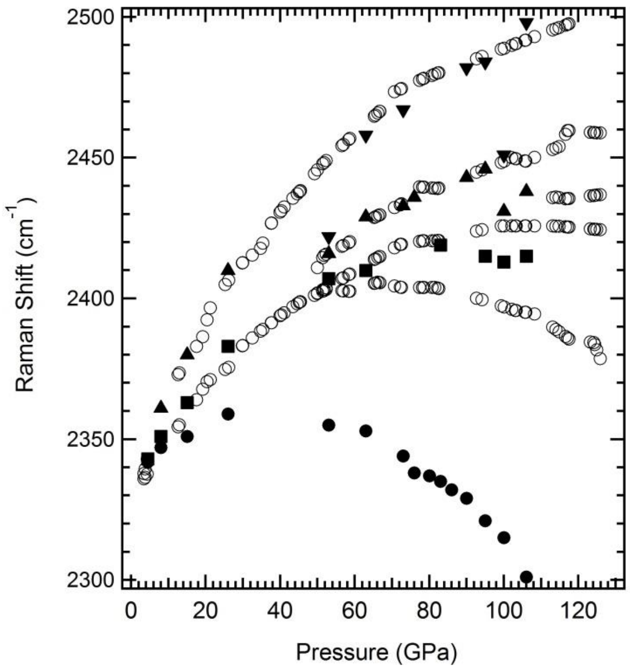


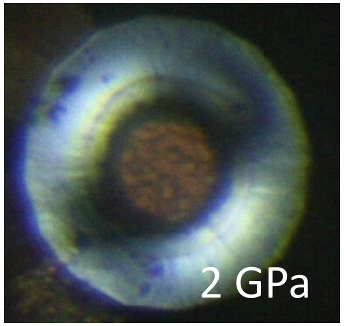
Figure 5. Phase diagram of Xe-N_2 system. The dashed line separates the Xe-N_2 mixture (left and green region) and the stable XeN_6 compound (right and blue region).

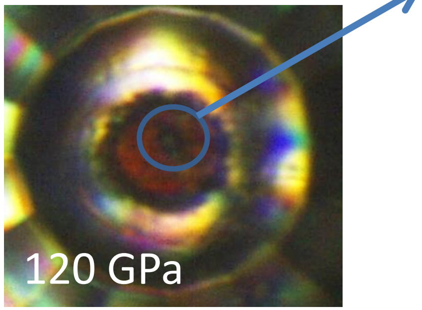
Xenon – Nitrogen system

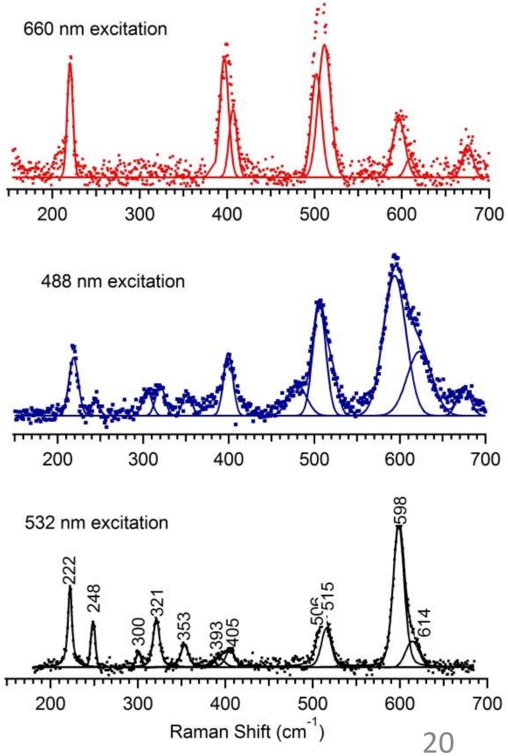
- vdW compound identified as $Xe(N_2)_4$ synthesized at 9 GPa and at RT.
- $Xe(N_2)_4$ is stable even at 150 GPa. Turns dark and becomes completely opaque above 120 GPa.
- Xe_xN_y forms when this compound is heated to T > 1500 K for all pressures above 110 GPa



Empty symbols – pure N_2; filled symbols – $Xe(N_2)_4$





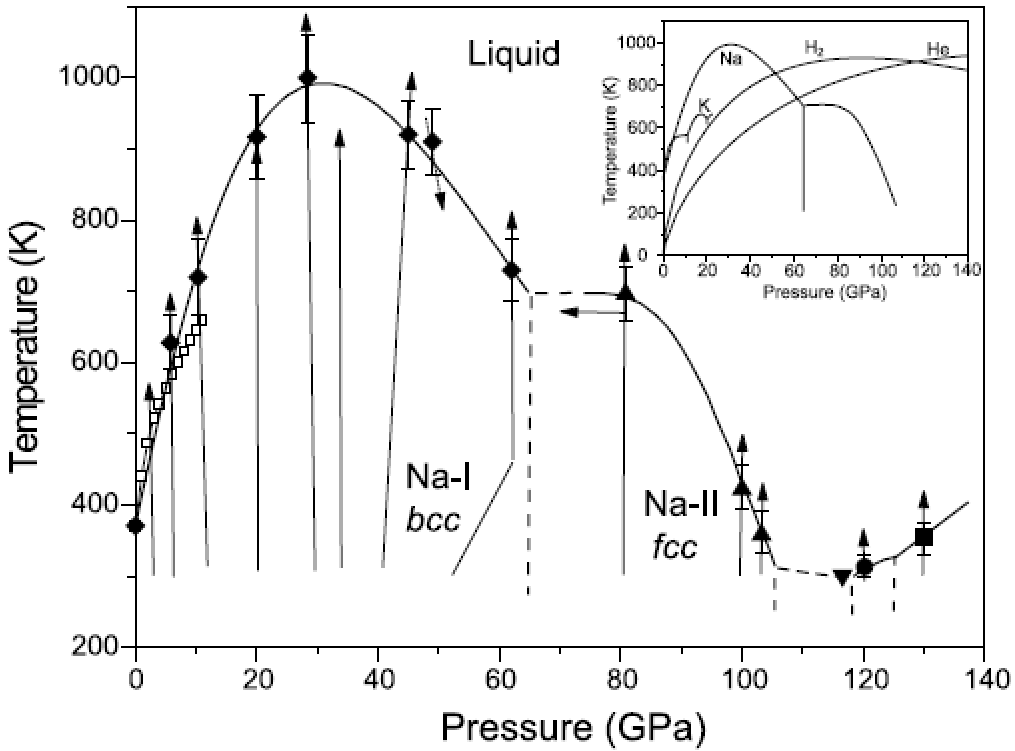


High Pressure Alkali Chemistry

PRL 94, 185502 (2005) PHYSICAL REVIEW LETTERS week ending 13 MAY 2005

Melting of Dense Sodium

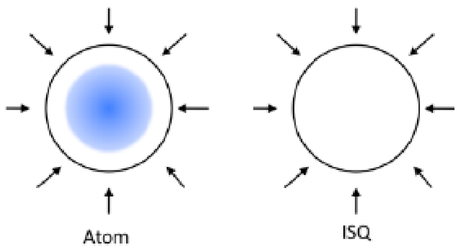
Eugene Gregoryanz,[1] Olga Degtyareva,[1] Maddury Somayazulu,[2] Russell J. Hemley,[1] and Ho-kwang Mao[1]

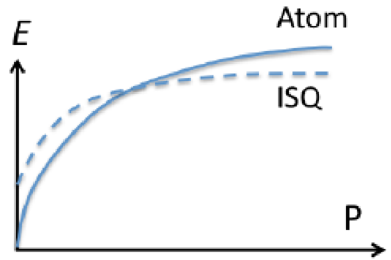


From Metals to Insulators and Back

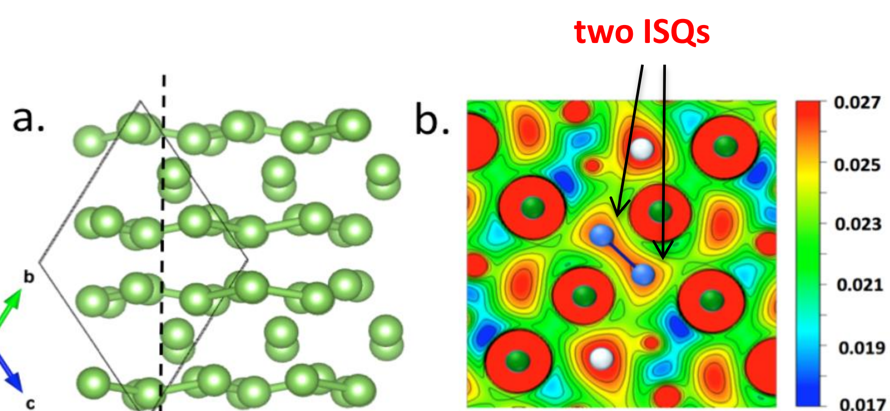
Formation of Quasimolecules in Insulating States

Interstitial quasiatoms and quasimolecules form when the valence *p* electrons move down relative to s electrons: Li, Na, Mg, Al…



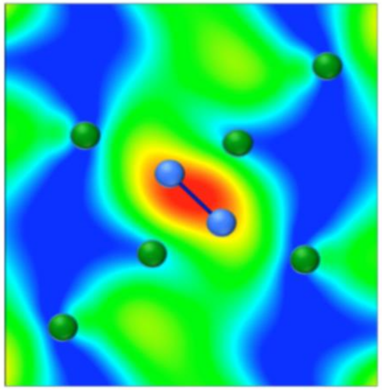


Two nearest ISQ's in *Aba*2-Li form a "molecule"within the structure

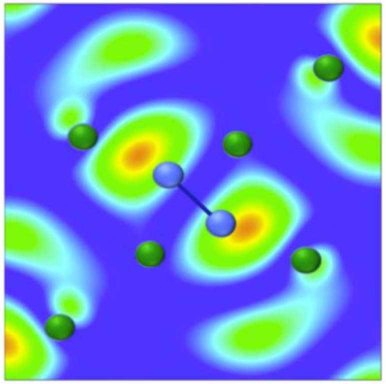


Like two H atoms, two ISQs can form both bonding and antibonding orbitals

Charge density for bonding orbital



Charge density for antibonding orbital



The "molecular" orbitals can be understood as maximally localized Wannier functions

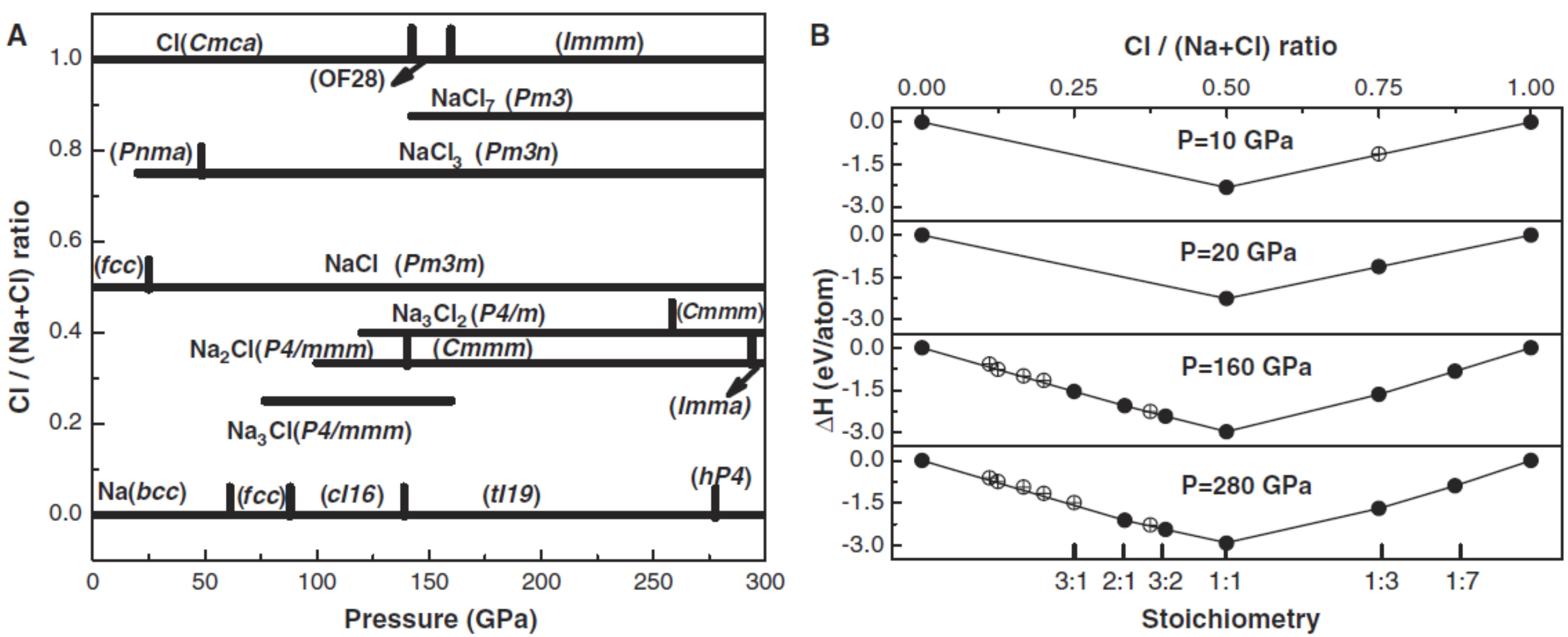
isosurface=±2.5

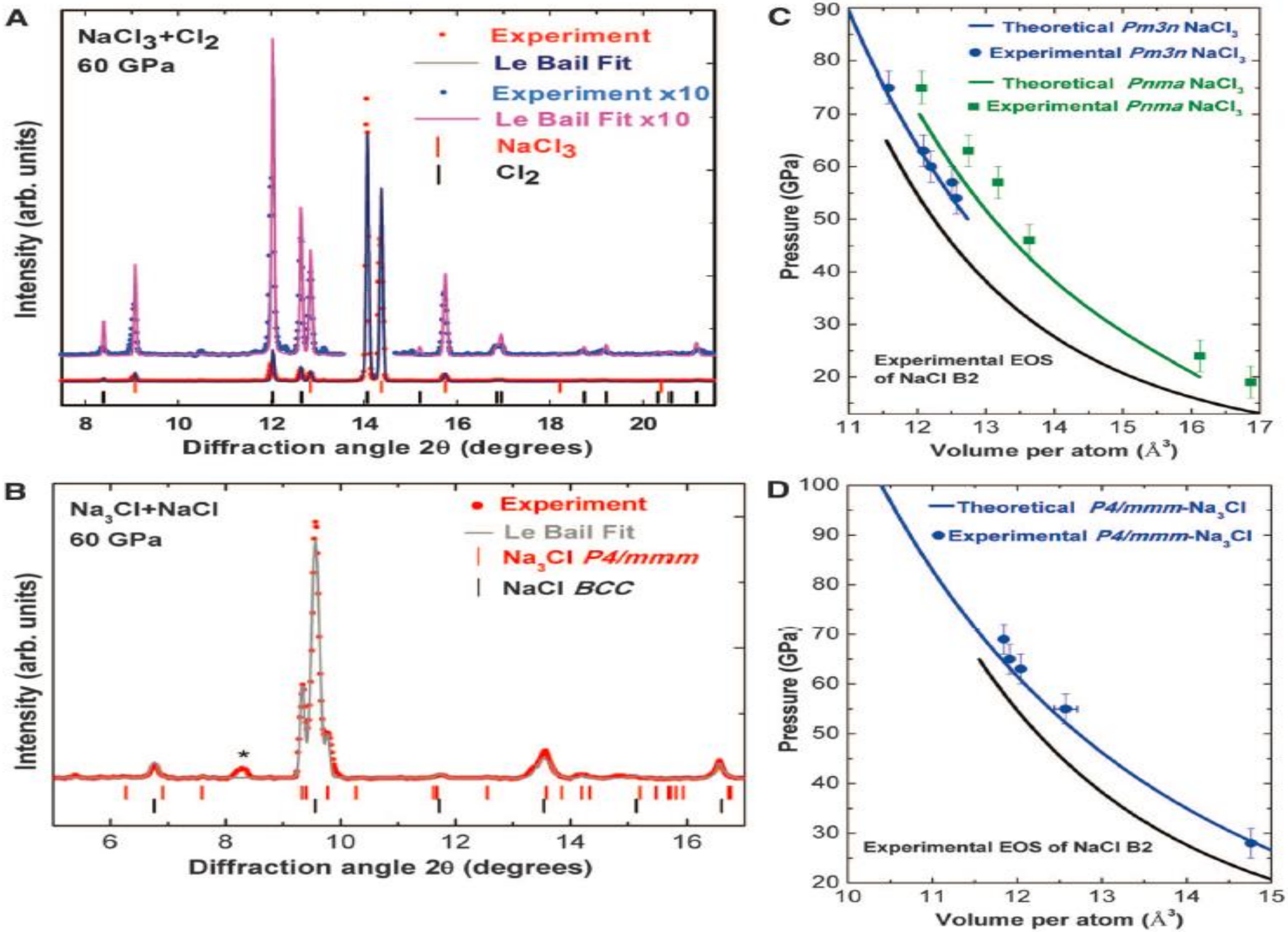
[Miao, Naumov, Hoffmann, & Hemley, *submitted*]

Unexpected Stable Stoichiometries of Sodium Chlorides

20 DECEMBER 2013 VOL 342 **SCIENCE**

Weiwei Zhang,[1,2]*† Artem R. Oganov,[2,3,4]*† Alexander F. Goncharov,[5,6] Qiang Zhu,[2] Salah Eddine Boulfelfel,[2] Andriy O. Lyakhov,[2] Elissaios Stavrou,[5] Maddury Somayazulu,[5] Vitali B. Prakapenka,[7] Zuzana Konôpková[8]




A
NaCl3+Cl2
60 GPa
Experiment
Le Bail Fit
Experiment x10
Le Bail Fit x10
NaCl3
Cl2
Intensity (arb. units)
Diffraction angle 2θ (degrees)
B
Na3Cl+NaCl
60 GPa
Experiment
Le Bail Fit
Na3Cl P4/mmm
NaCl BCC
Intensity (arb. units)
Diffraction angle 2θ (degrees)
C
Theoretical Pm3n NaCl3
Experimental Pm3n NaCl3
Theoretical Pnma NaCl3
Experimental Pnma NaCl3
Experimental EOS of NaCl B2
Pressure (GPa)
Volume per atom (Å3)
D
Theoretical P4/mmm-Na3Cl
Experimental P4/mmm-Na3Cl
Experimental EOS of NaCl B2
Pressure (GPa)
Volume per atom (Å3)

Suggested beamline enhancements focused on CDAC science -

1. Tighter focus and smaller ‘tail effects’ (GSECARS offers better grid search)
2. Higher flux for light element studies and faster data acquisition of heavier elements
3. Better detectors to yield better resolution (PETRA detector shows better resolution and uses CRLs to focus that allows longer focal length)
4. Ability to combine Raman spectroscopy with XRD very crucial in these studies
5. Other LH geometries to allow radial diffraction and possibly with ramped P-T