DE LA RECHERCHE À L'INDUSTRIE

Caractériser la matière à des pressions extrêmes

DÉCOUVERTE D'UN « CLATHRATE » DE VAN DER WAALS : $(N_2)_6NE_7$

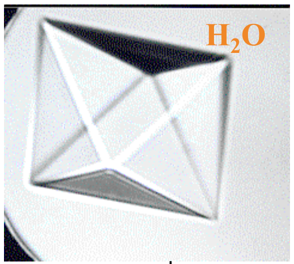
Thomas Plisson, Gunnar Weck, Paul Loubeyre
CEA, DAM, DIF
Seminaire CEA – 2014

16 JUIN 2014

www.cea.fr

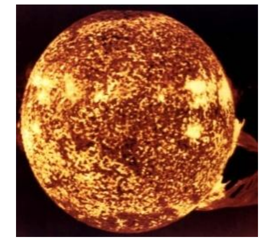
HIGH PRESSURE

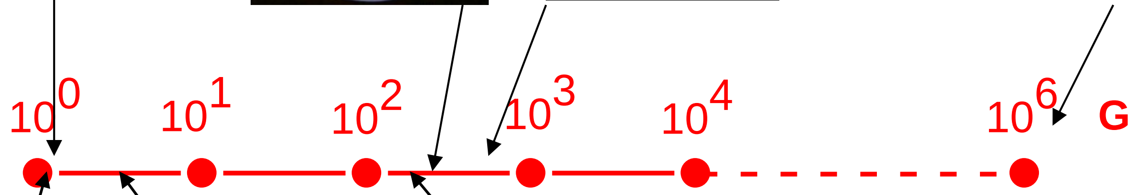
P~1.3 GPa

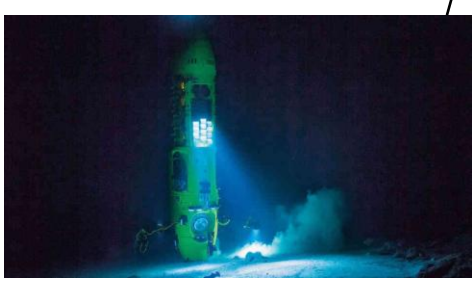


P~380 GPa

P~700 GPa

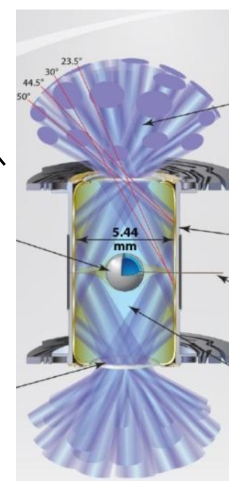






P~0.1 GPa

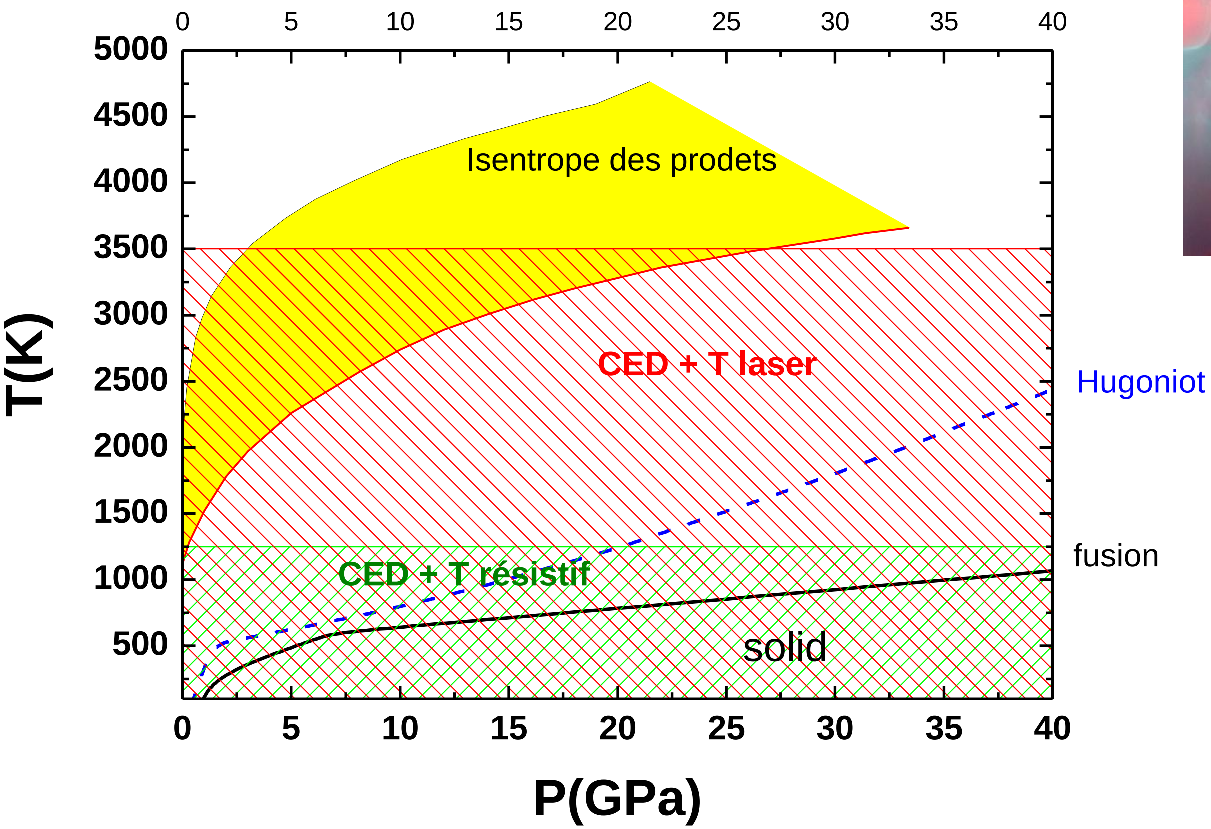
P~6GPa

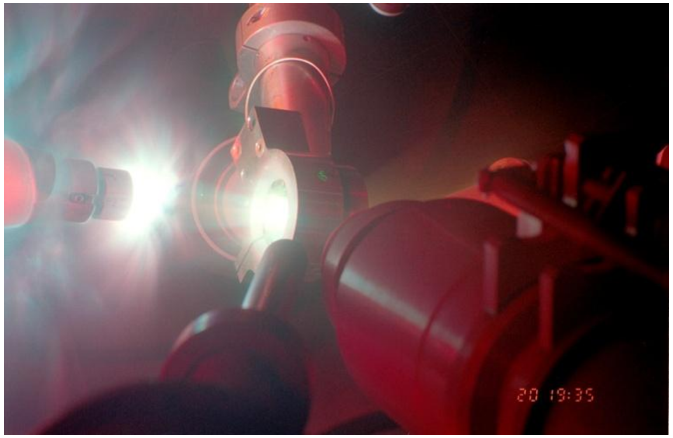


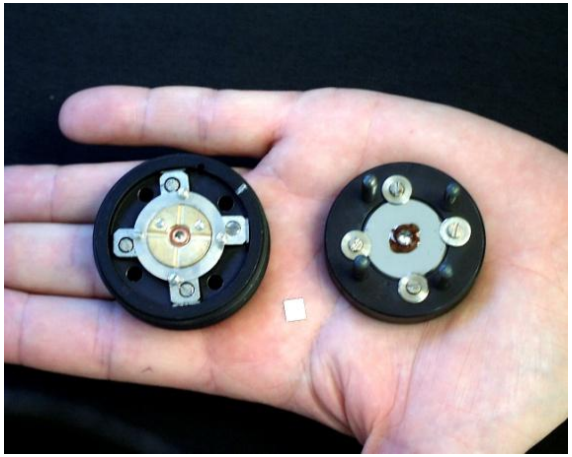
P~200GPa

1 bar = 10^5 Pa
10 kbar = 1 GPa
1 Mbar = 100 GPa

STATIC VS DYNAMIC







EXAMPLES OF APPLICATIONS

Hydrogen and hydrides

Are there new quantum many-body behaviors at high pressure? Metal H ?

Optical studies of solid hydrogen to 320 GPa and evidence for black hydrogen

Paul Loubeyre*, Florent Occelli* & René LeToullec*†

A little bit of lithium does a lot for hydrogen

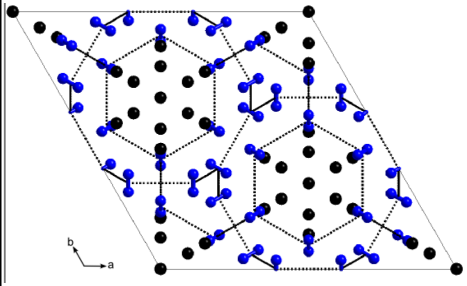
Eva Zurek[a,1], Roald Hoffmann[a,2], N. W. Ashcroft[b], Artem R. Oganov[c,d], and Andriy O. Lyakhov[c]

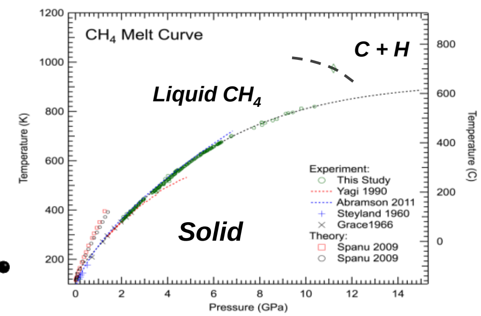
[a]Department of Chemistry and Chemical Biology, Baker Laboratory, and [b]Laboratory of Atomic and Solid State Physics and Cornell Center for Materials Research, Cornell University, Ithaca, NY 14853; [c]Department of Geosciences and New York Center for Computational Science, Stony Brook University, Stony Brook, NY 11794-2100; and [d]Geology Department, Moscow State University, Moscow 119992, Russia

Contributed by Roald Hoffmann, July 28, 2009 (sent for review June 29, 2009)

New materials / High pressure chemistry

100 GPa ~ 1 eV (E of chemical bonding).

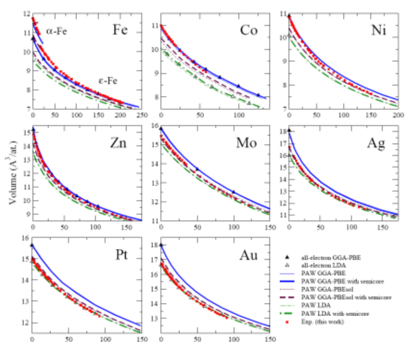




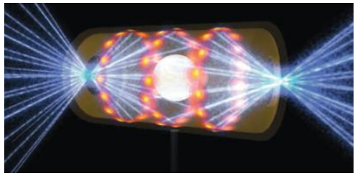
Equations of state

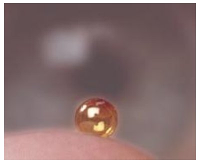
Are ab-initio calculations reliably predictive?

➢ *Metals*



➢ *C-H*





Fluids

PHYSICAL REVIEW B, VOLUME 65, 174105

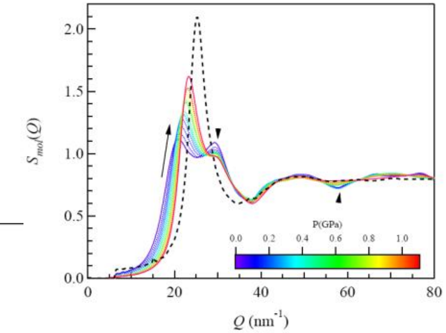
Quantitative structure factor and density measurements of high-pressure fluids in diamond anvil cells by x-ray diffraction: Argon and water

Jon H. Eggert,[1,2] Gunnar Weck,[1] Paul Loubeyre,[1] and Mohamed Mezouar[3]
[1]DIF/DPTA/SPMC, CEA, 91680 Bruyres-le-Châtel, France

NATURE | VOL 403 | 13 JANUARY 2000 | www.nature.com

A first-order liquid–liquid phase transition in phosphorus

Yoshinori Katayama*, Takeshi Mizutani*, Wataru Utsumi*, Osamu Shimomura*, Masaaki Yamakata† & Ken-ichi Funakoshi†



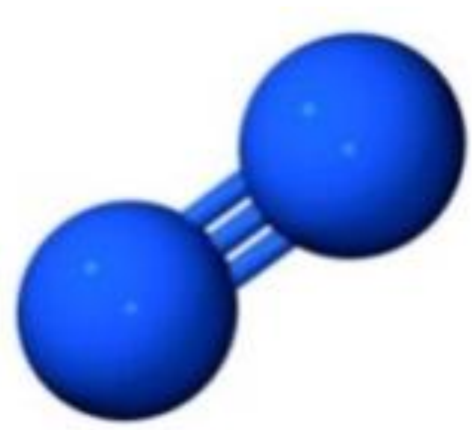
26 APRIL 2013 VOL 340 SCIENCE

Melting of Iron at Earth's Inner Core Boundary Based on Fast X-ray Diffraction

S. Anzellini,[1]* A. Dewaele,[1] M. Mezouar,[2] P. Loubeyre,[1] G. Morard[3]

NITROGEN

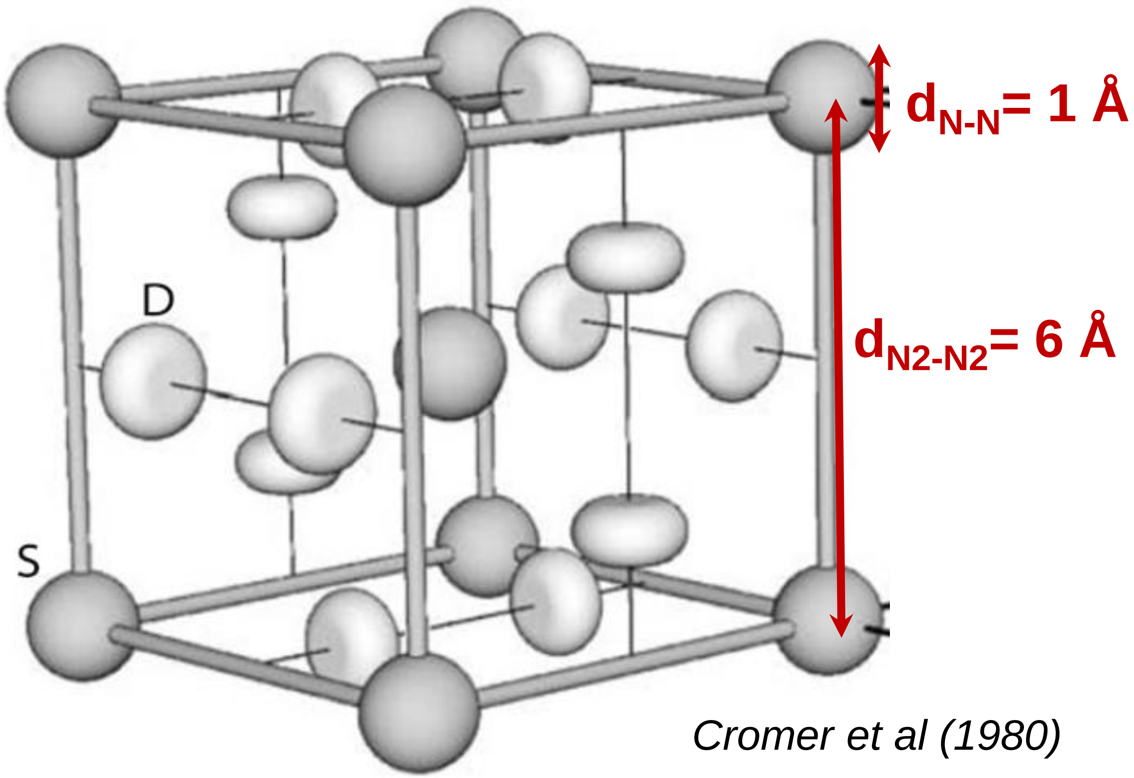
N_2



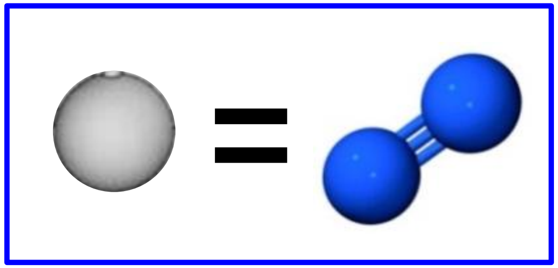
N_2 triple bond : 9.8 eV/atom

NITROGEN

Structure of solid nitrogen at 4.9 GPa / 300 K = cubic (Pm-3n)



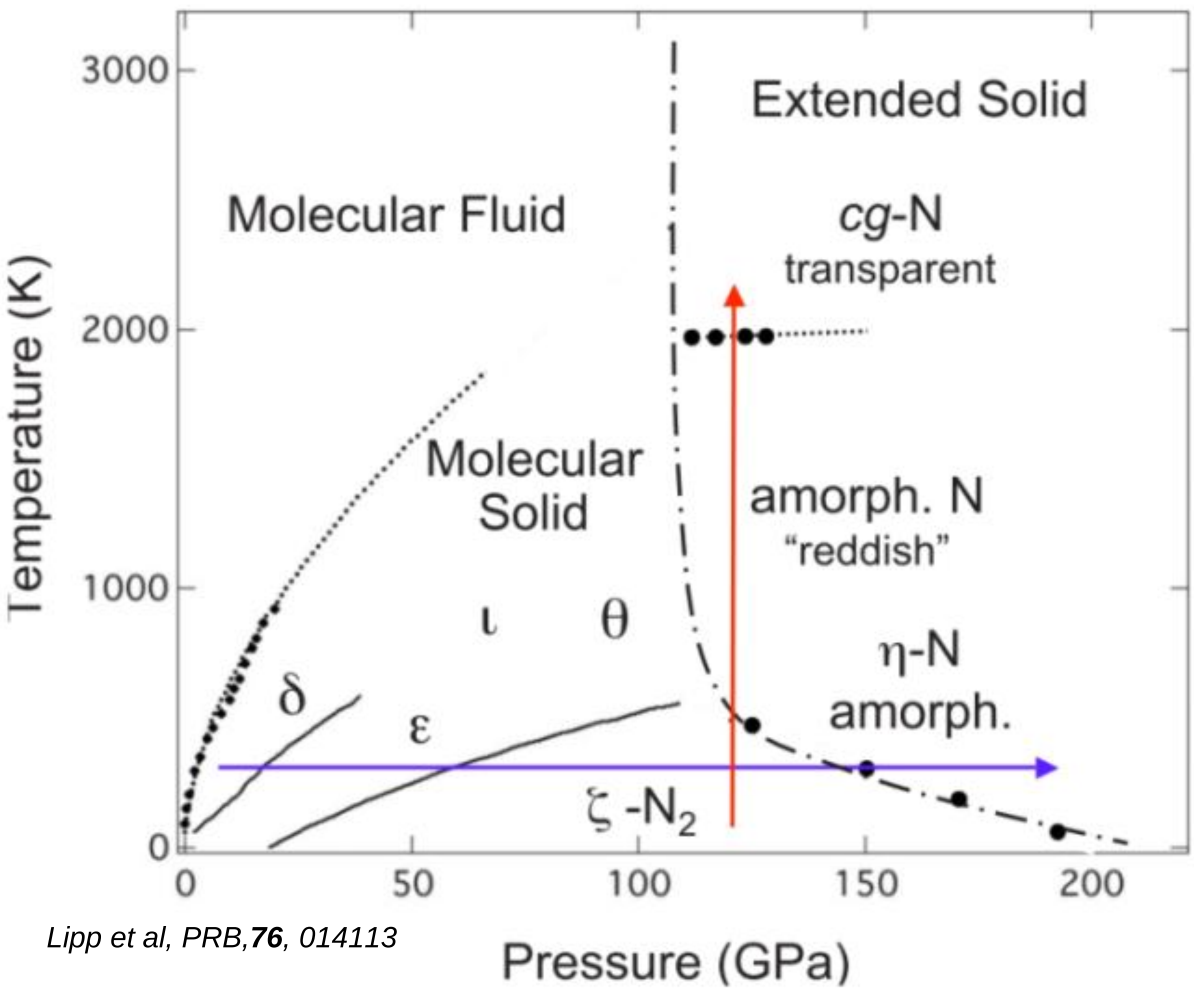
Cromer et al (1980)



«van der Waals solid» = Molecules bonded by (weak) van der Waals forces

POLYMERIC NITROGEN

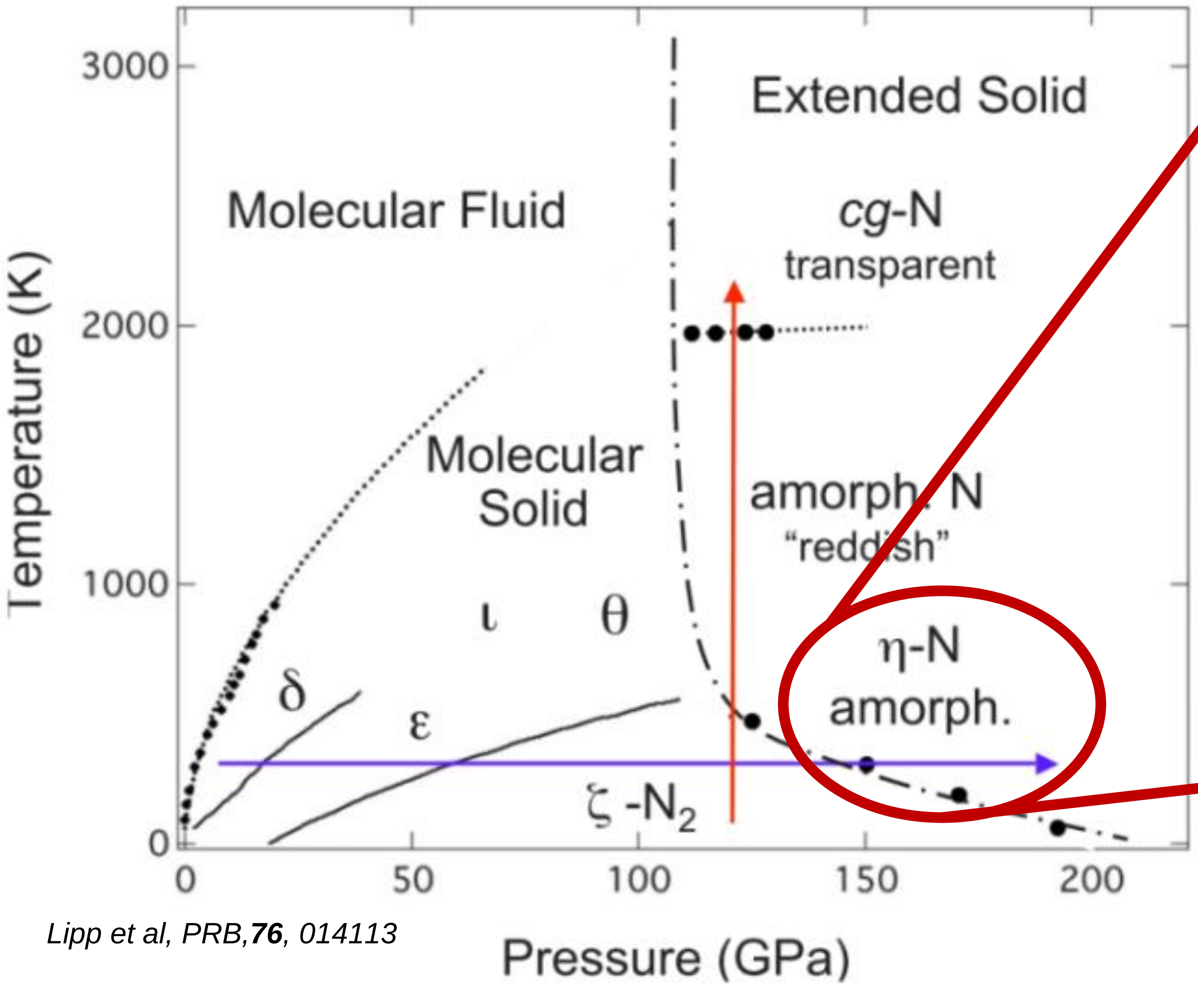
Evolution under pressure



*Lipp et al, PRB,**76**, 014113*

POLYMERIC NITROGEN

Evolution under pressure

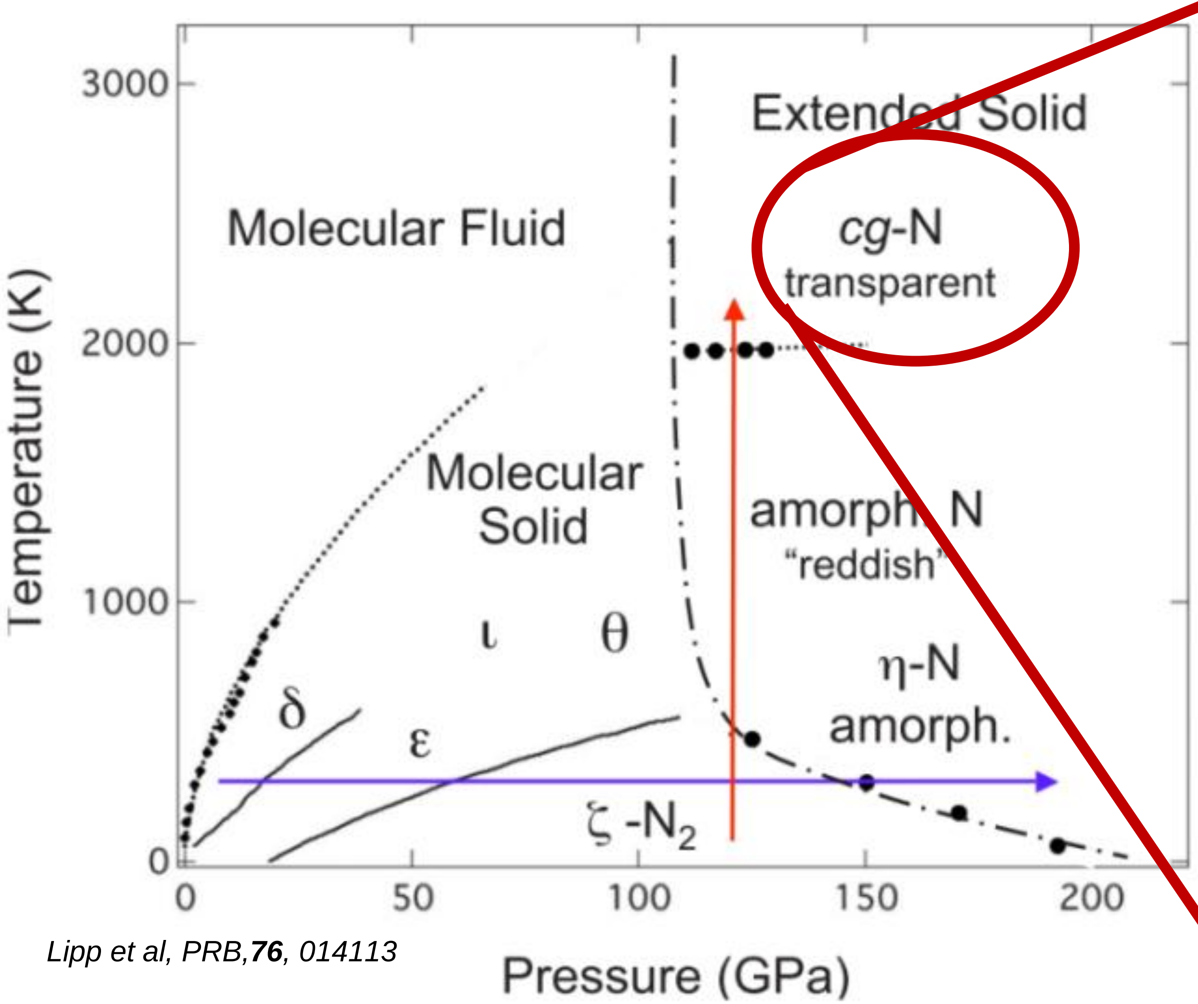


*Lipp et al, PRB,**76**, 014113*

Amorphisation of N_2 at ambient temperature
(Goncharov et al, 2000)

- **Interpretation in terms of a "non-molecular" but amorphous phase**

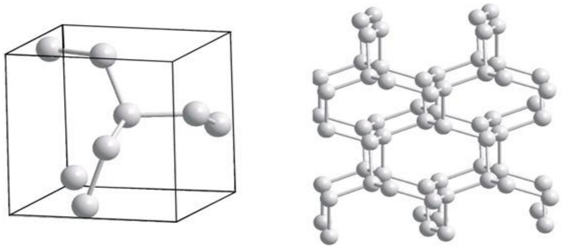
Evolution under pressure



*Lipp et al, PRB,**76**, 014113*

Synthesis of the cristalline form
(Eremets et al, 2004)

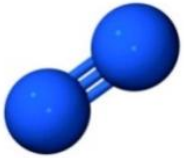
- **P = 110 GPa et T>2000 K**
- **« cg-N » structure**



- **Metastable at ambient temperature down to 42 GPa**

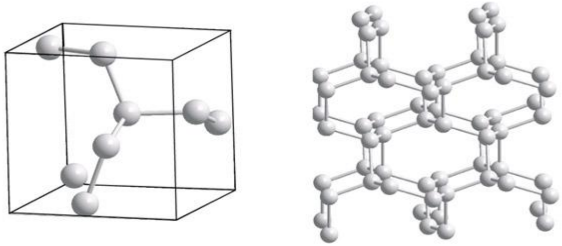
A HIGH ENERGY DENSITY MATERIAL

- **N_2 triple bond : 9.8 eV/atom**



- **N-N (polymeric) single bond : 1.7 eV/atom**

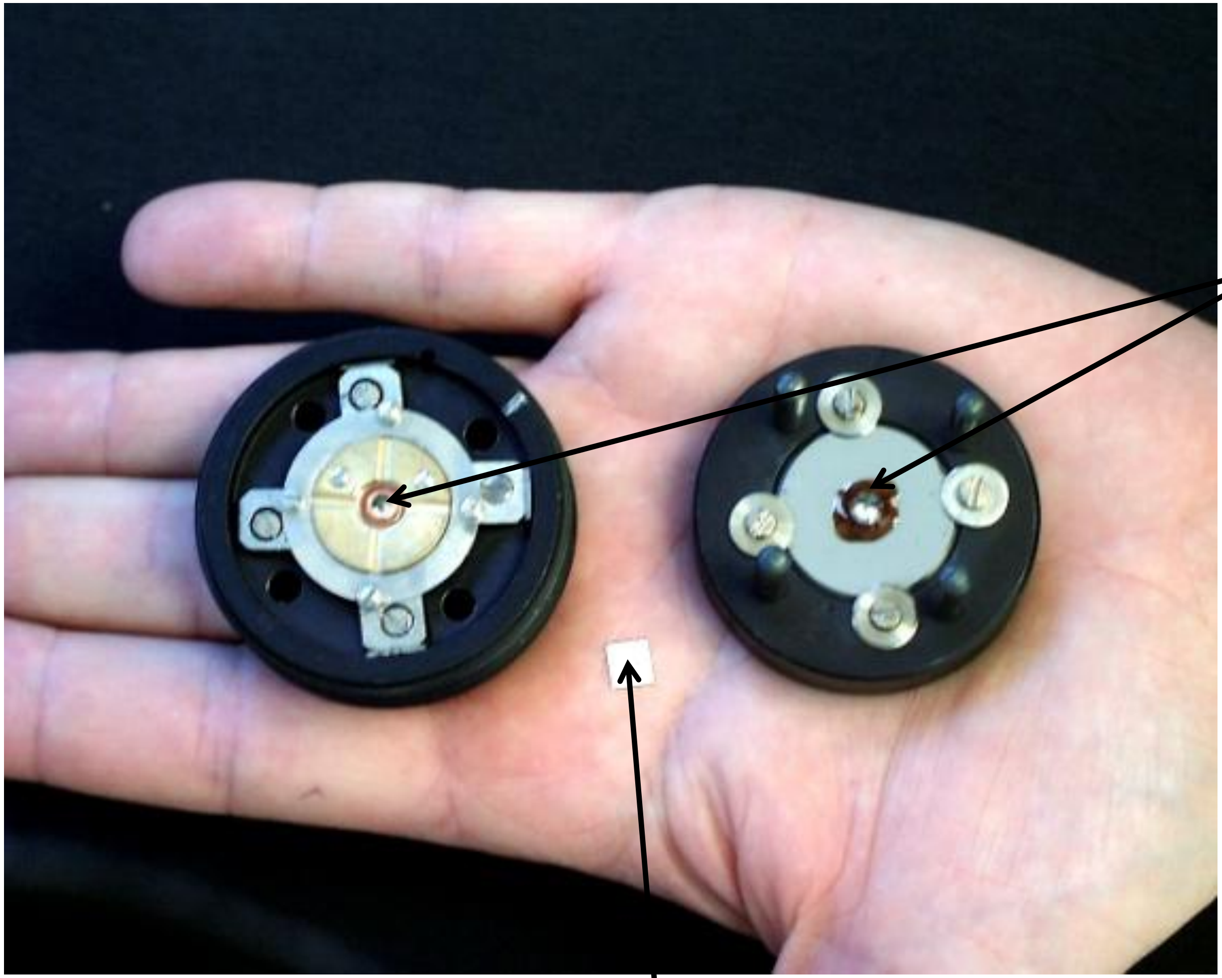
Cg-N



*Eremets et al, Nature Mat., **3**, 558 (2004)*

- **N-polymere : 64 MJ/L**
- **Diesel : 36 MJ/L**
- **TNT : 7.6 MJ/L**
- **O_2-H_2 : 2.7 MJ/L**
- **(Uranium : 1.5 10^9 MJ/L)**

THE DIAMOND ANVIL CELL



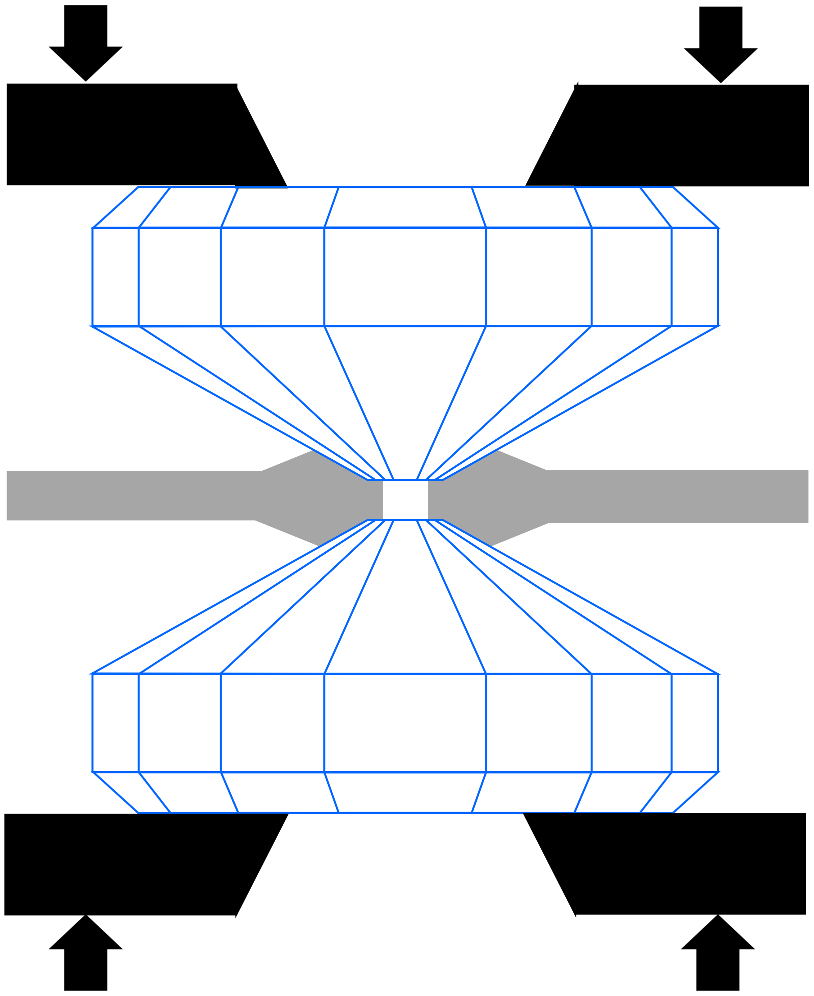
Diamonds

Metallic gasket

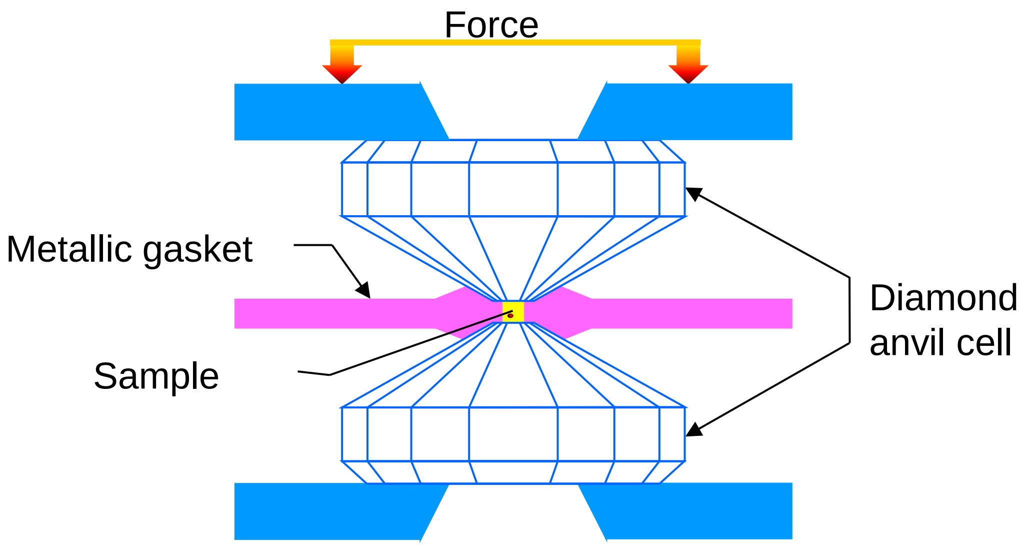
THE DIAMOND ANVIL CELL

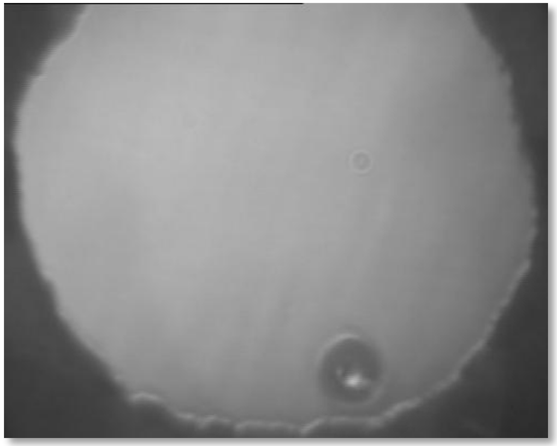
100 bars on the membrane (S~cm^2)

1Mbar in the sample (S~100µm x 100µm)

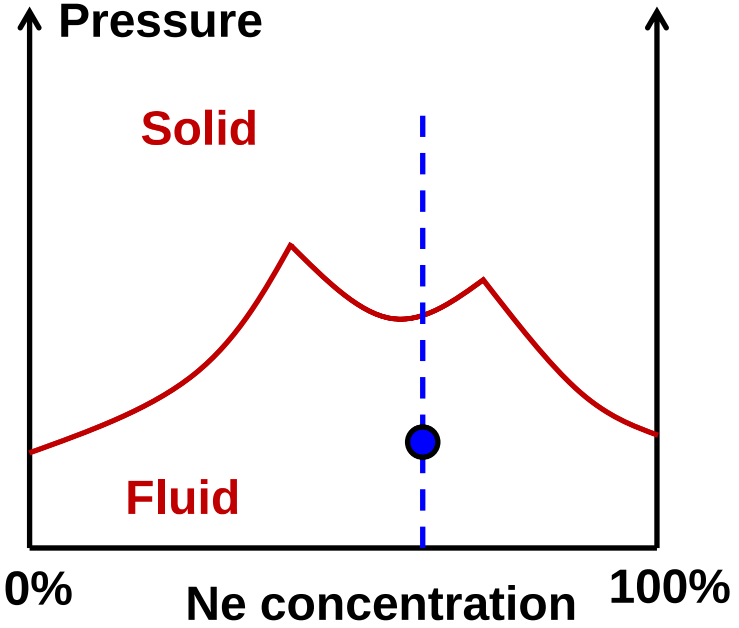


EVOLUTION UNDER PRESSURE

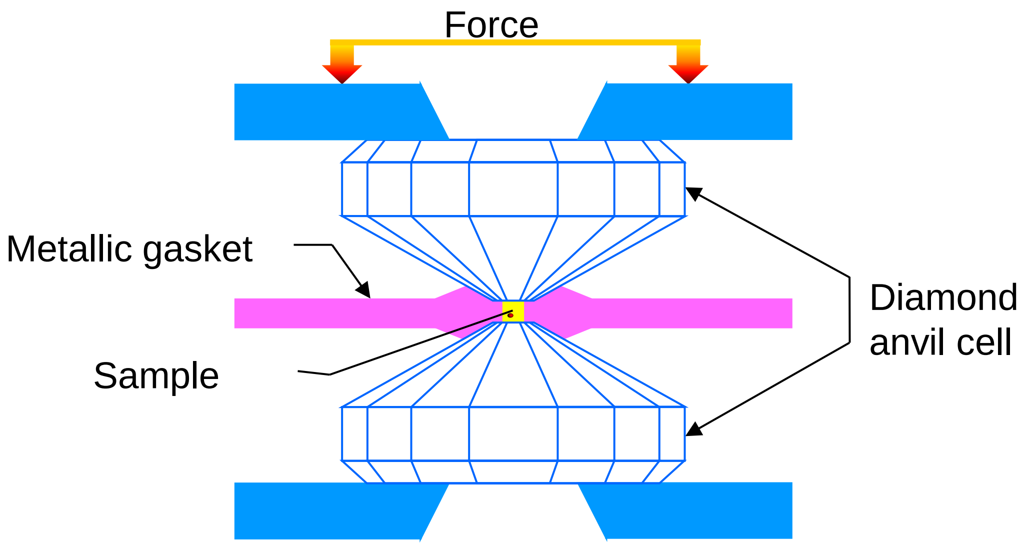


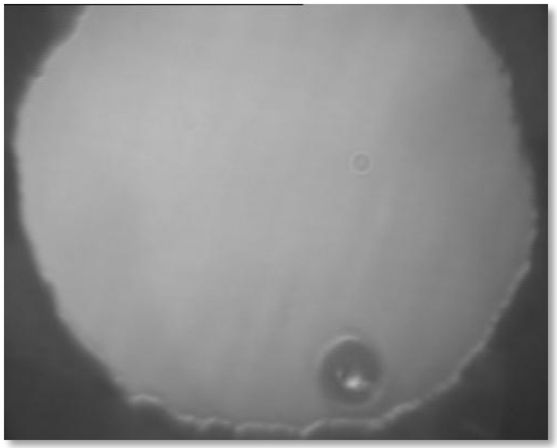


State : homogeneous fluid

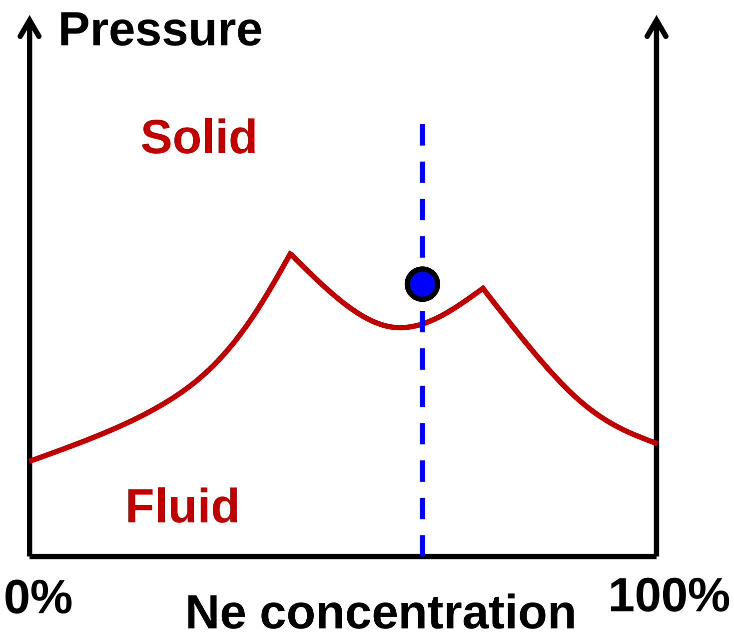


EVOLUTION UNDER PRESSURE

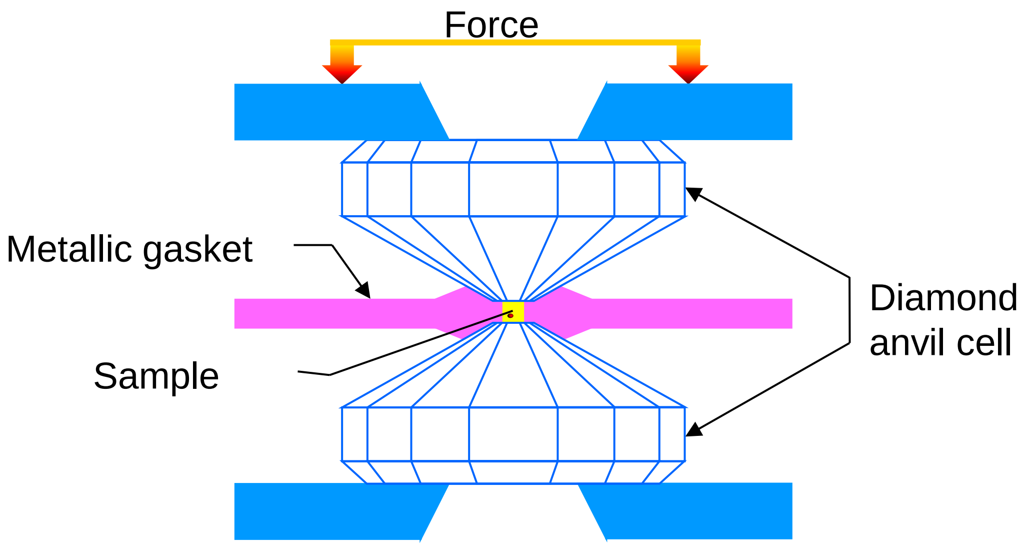




State : Over-pressured fluid

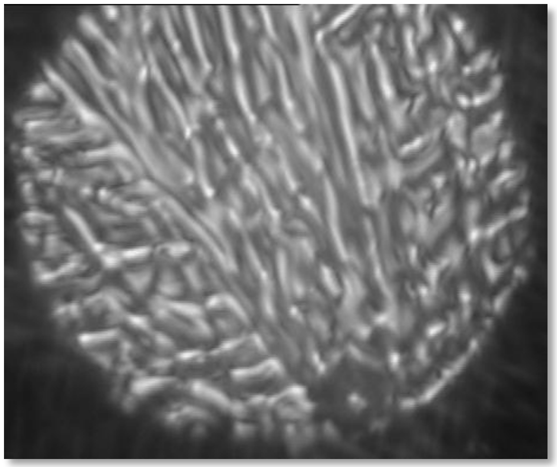


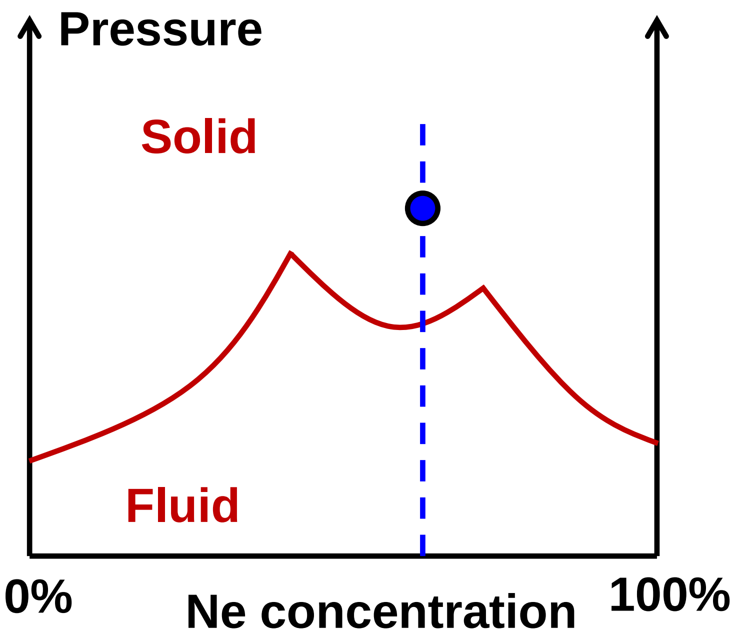
EVOLUTION UNDER PRESSURE



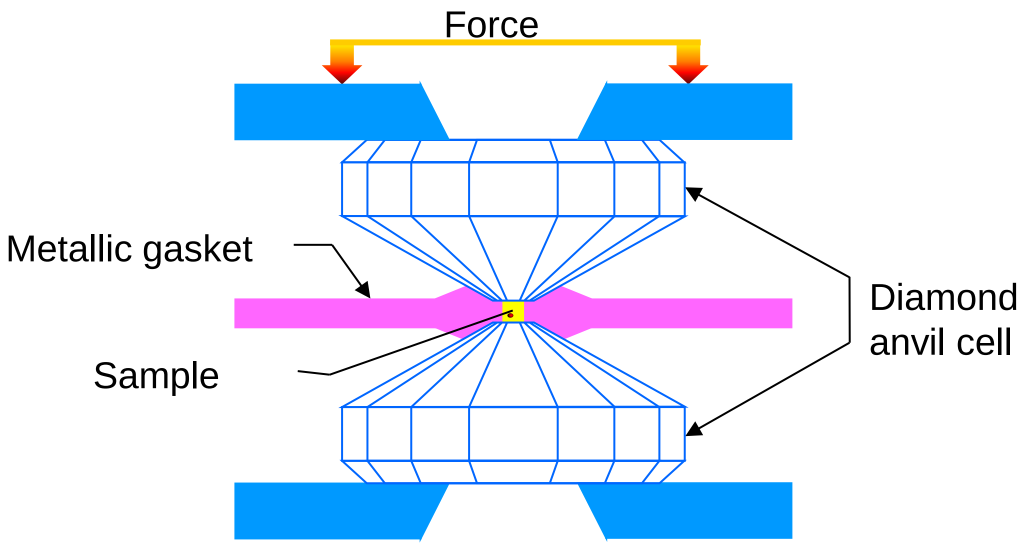
State : Phase separation

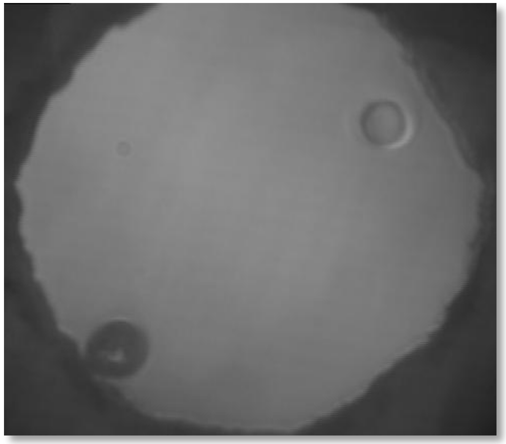
Powder or polycristal





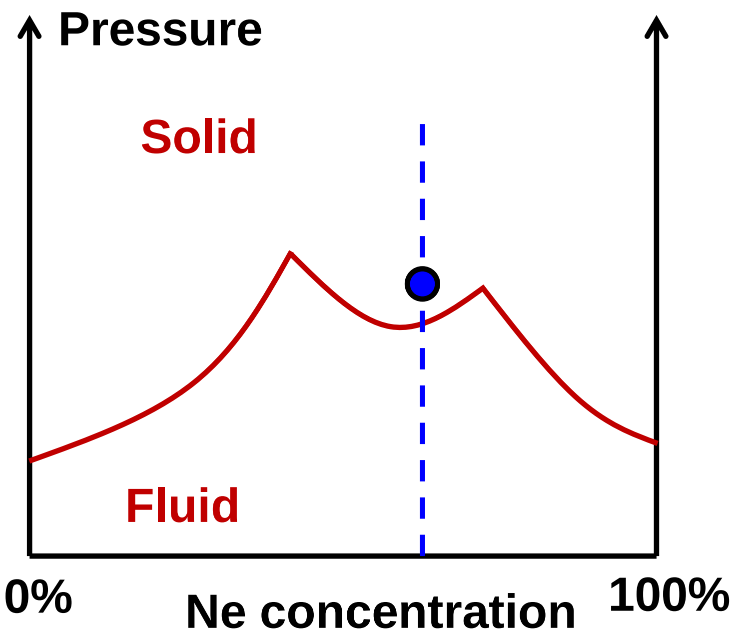
EVOLUTION UNDER PRESSURE



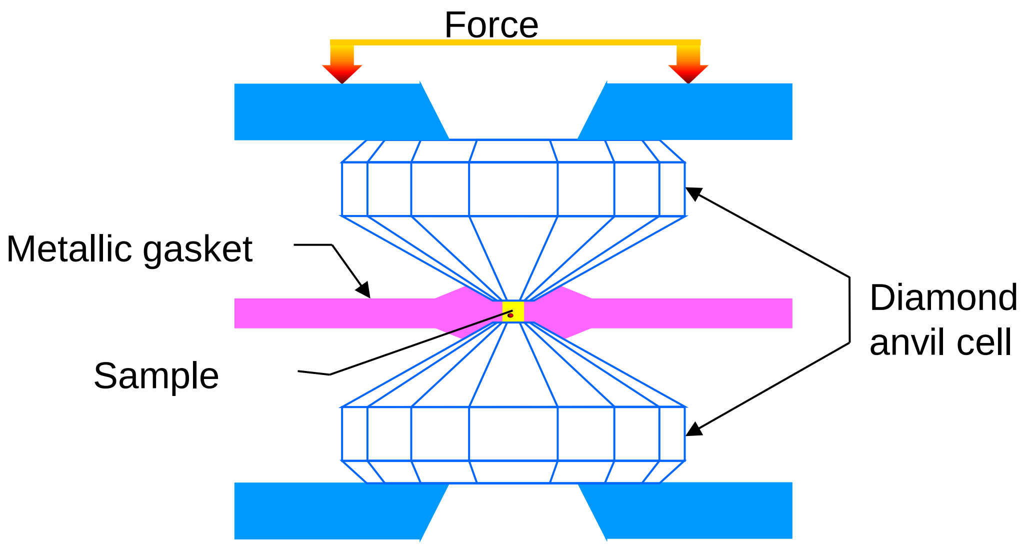


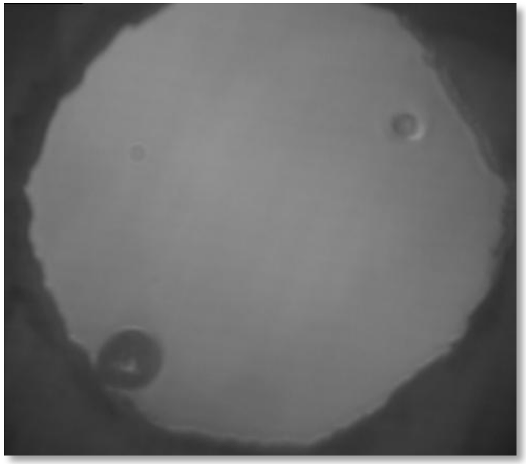
State : Solid-fluid equilibrium

Single – crystal

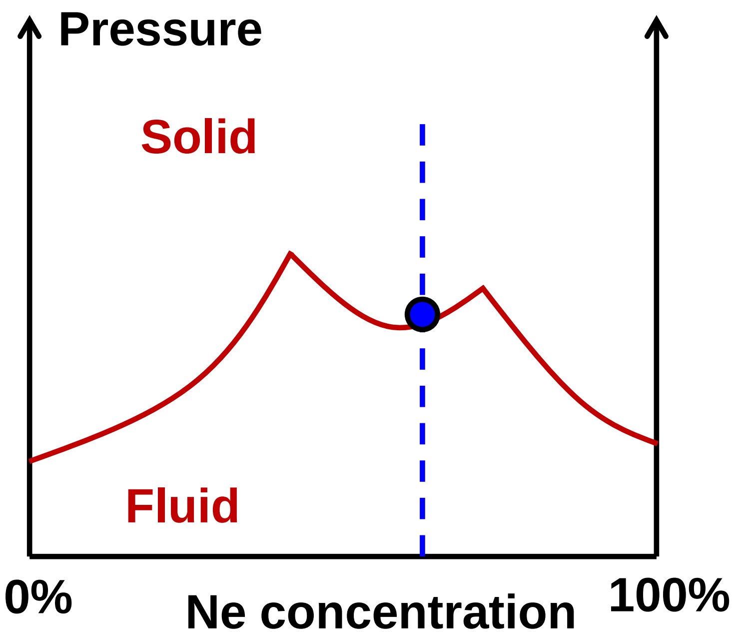


EVOLUTION UNDER PRESSURE

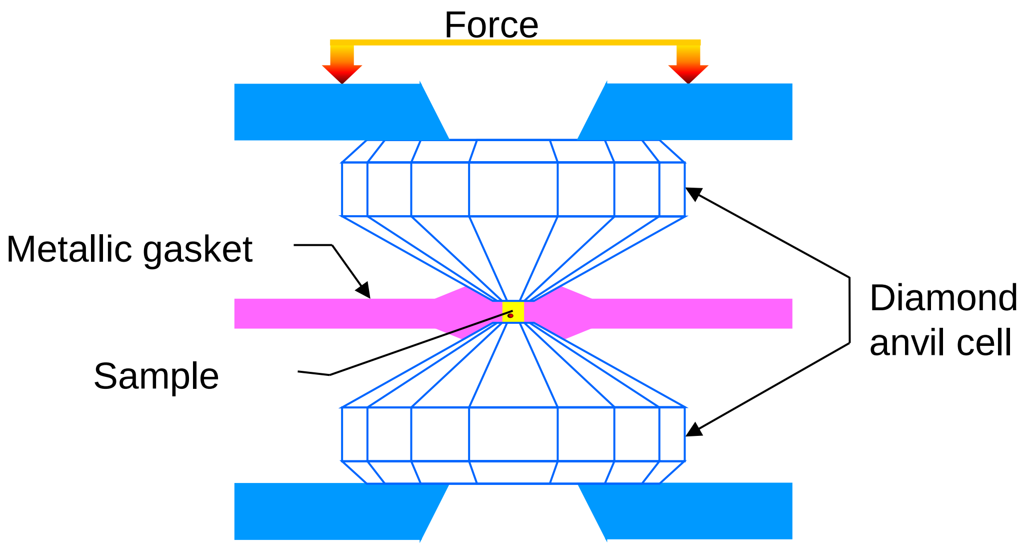


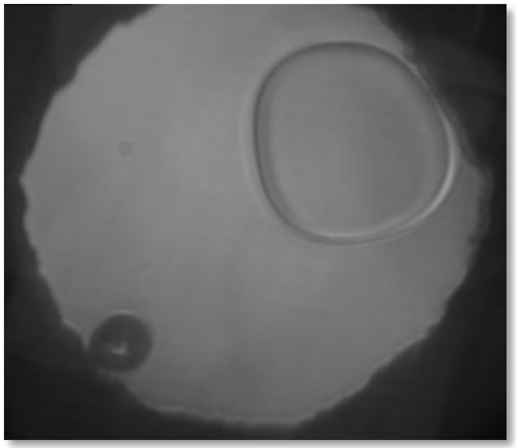


State : Solid – fluid equilibrium
Threshold of disappearance of the single-crystal = Liquidus

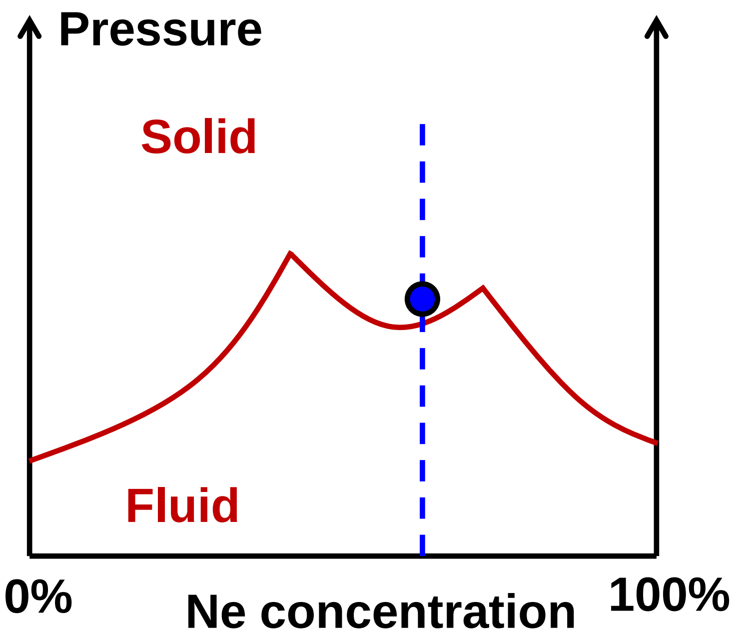


EVOLUTION UNDER PRESSURE

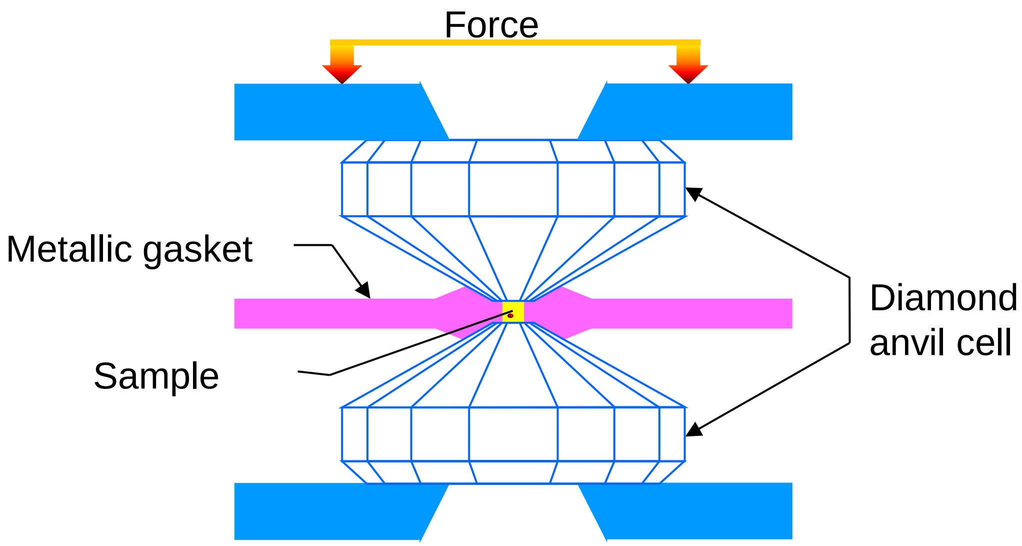




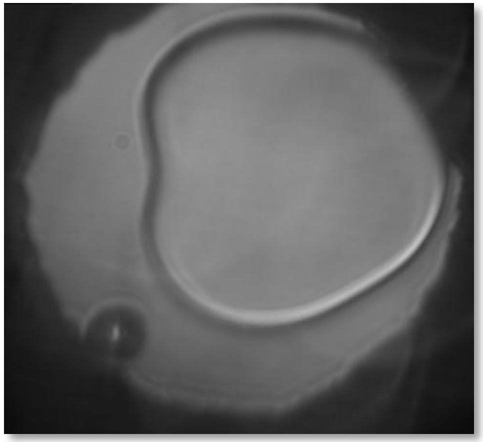
State : Solid – fluid equilibrium
Single-crystal growth

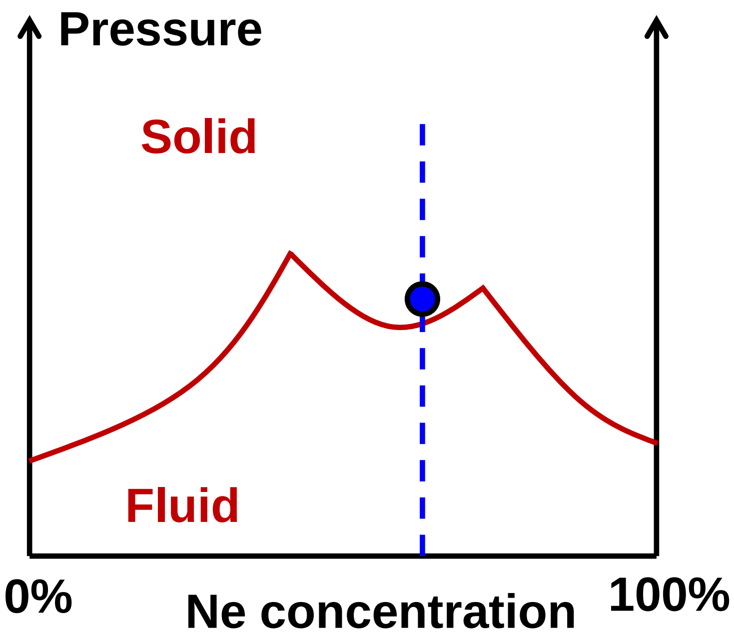


EVOLUTION UNDER PRESSURE

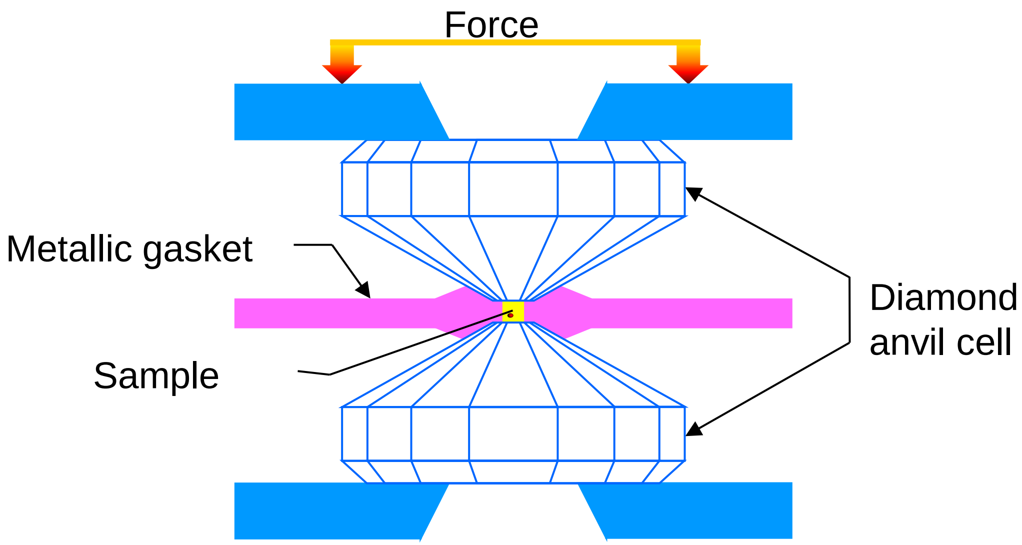


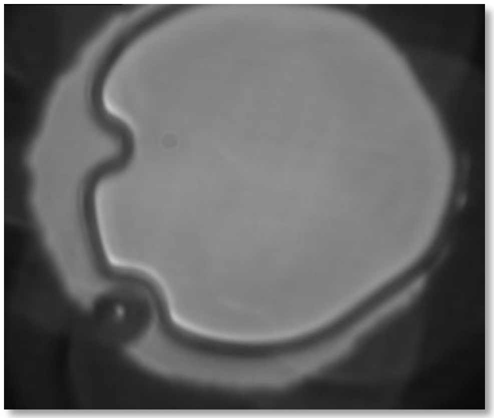
State : Solid – fluid equilibrium
Single-crystal growth



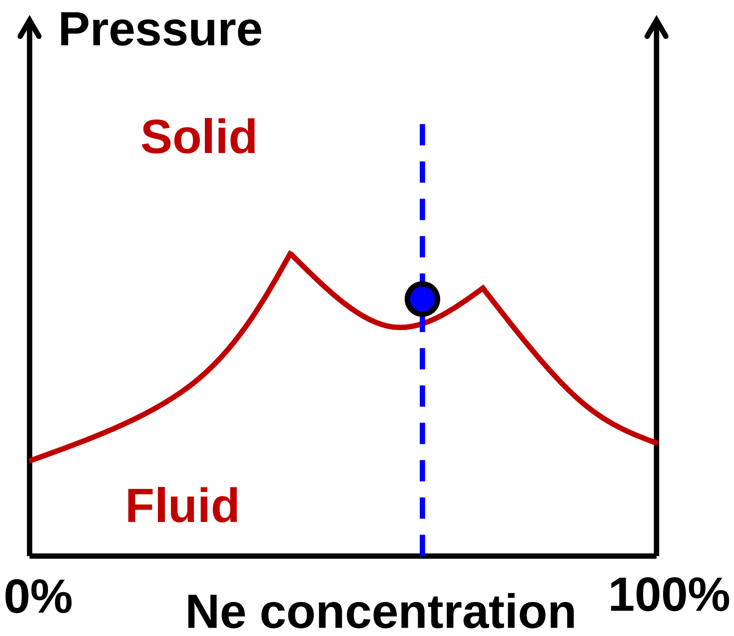


EVOLUTION UNDER PRESSURE

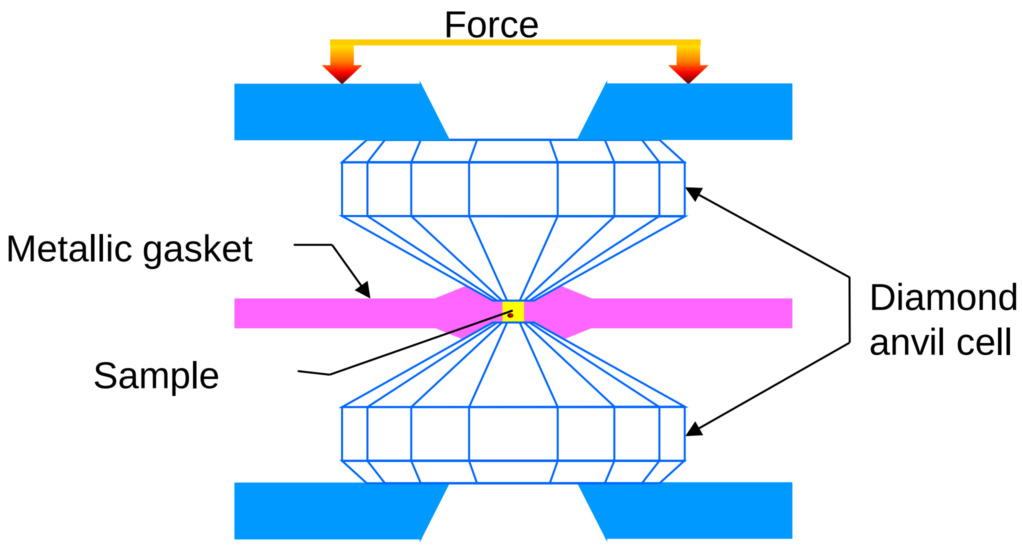


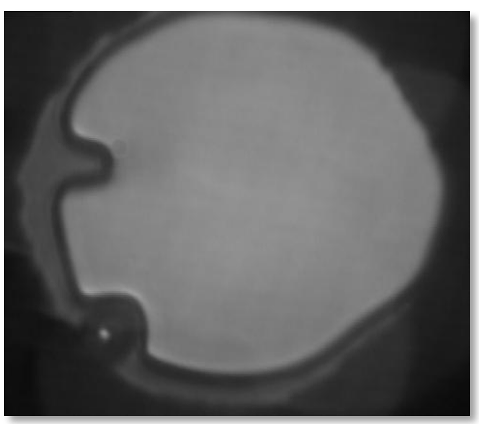


State : Solid – fluid equilibrium
Single-crystal growth

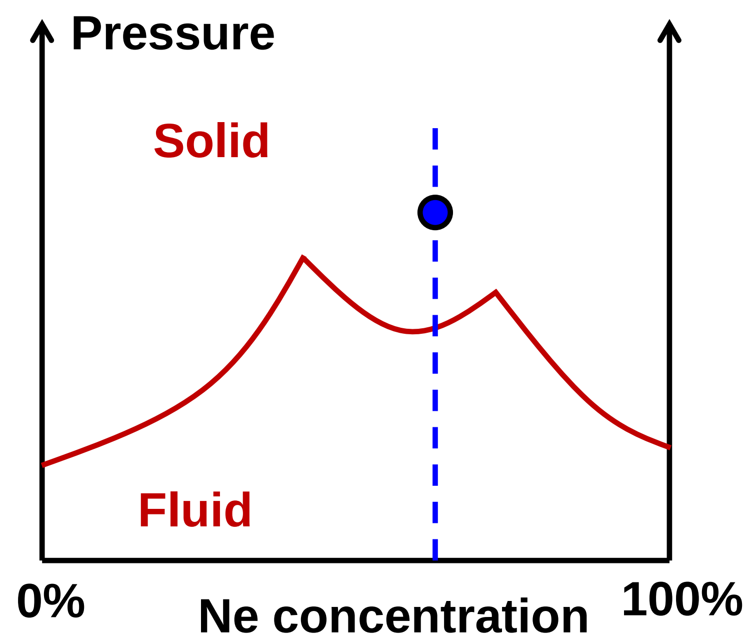


EVOLUTION UNDER PRESSURE

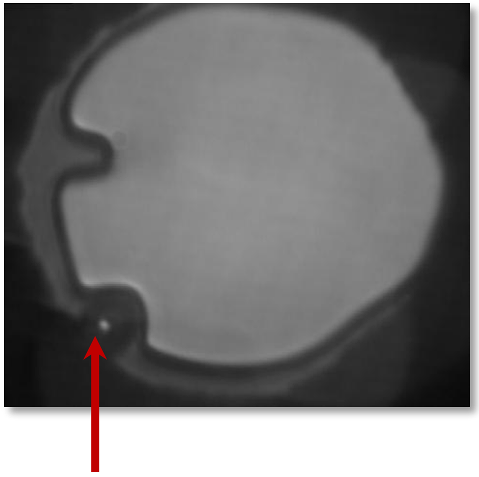




State : Phase separation

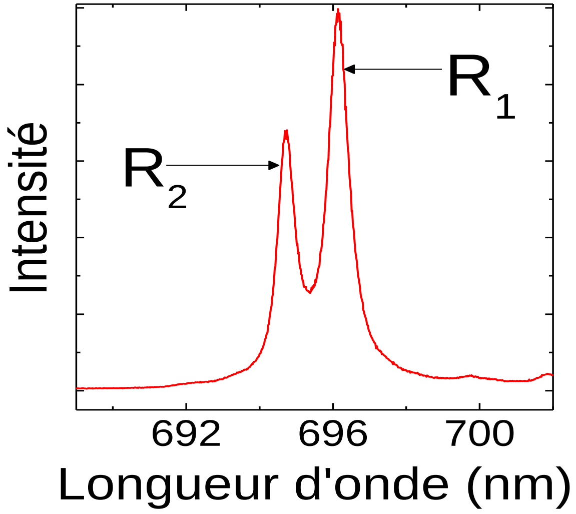


PRESSURE MEASUREMENT



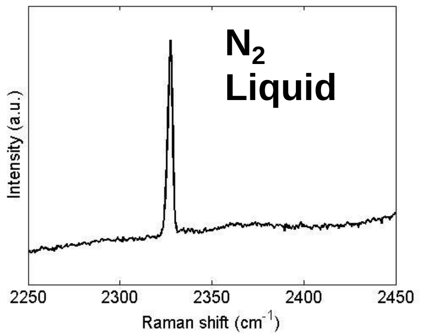
Ruby

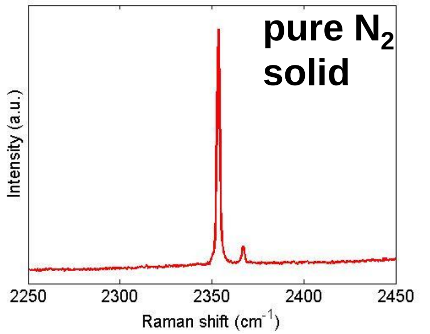
Ruby fluorescence spectrum

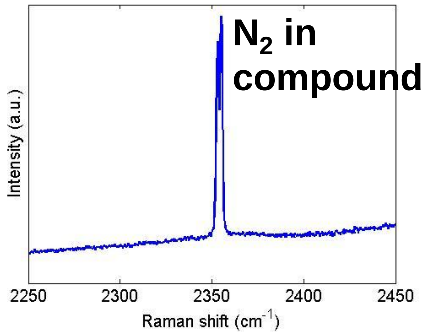


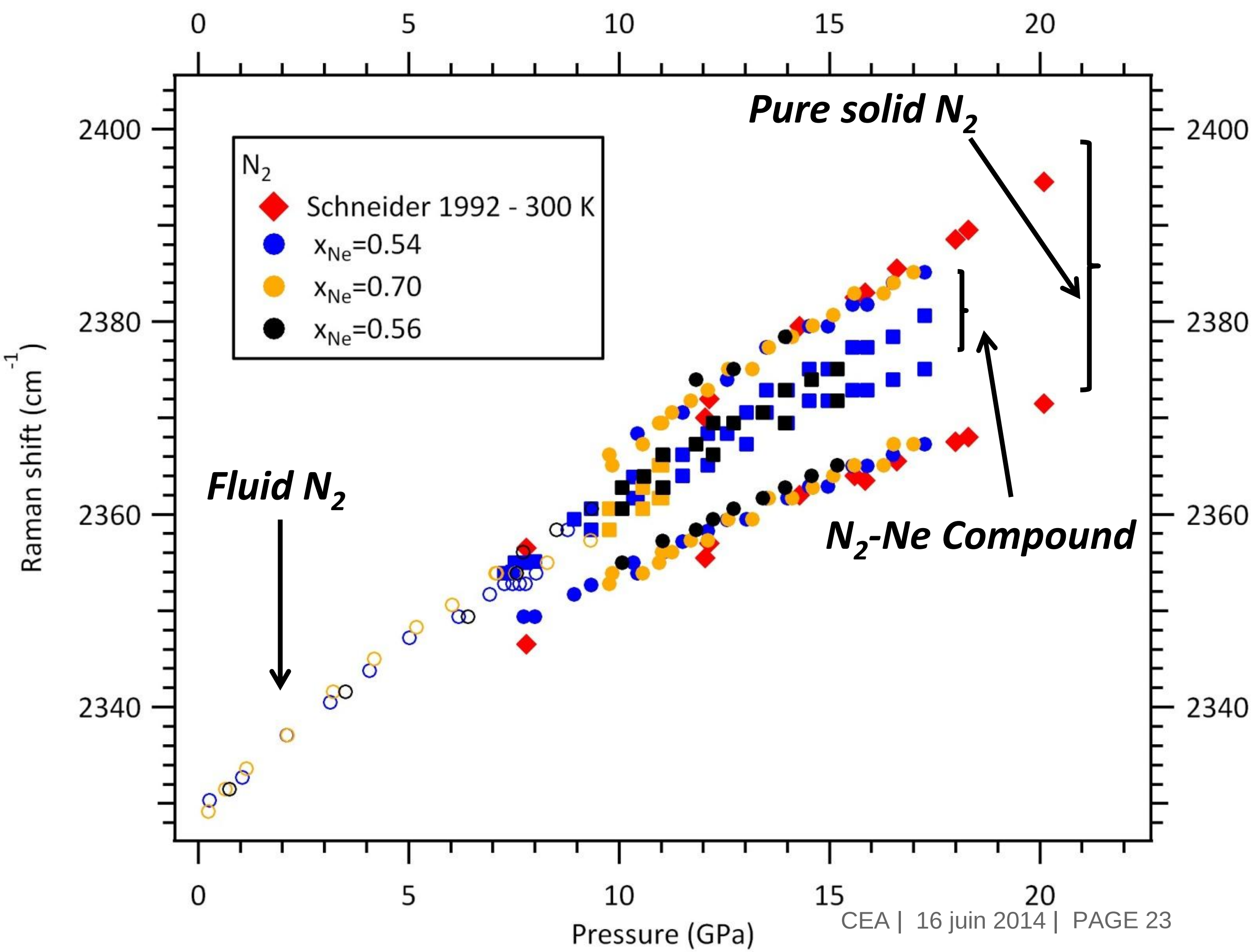
PHASE CHARACTERIZATION

Raman spectroscopy : *vibrational modes of the N_2 molecule*

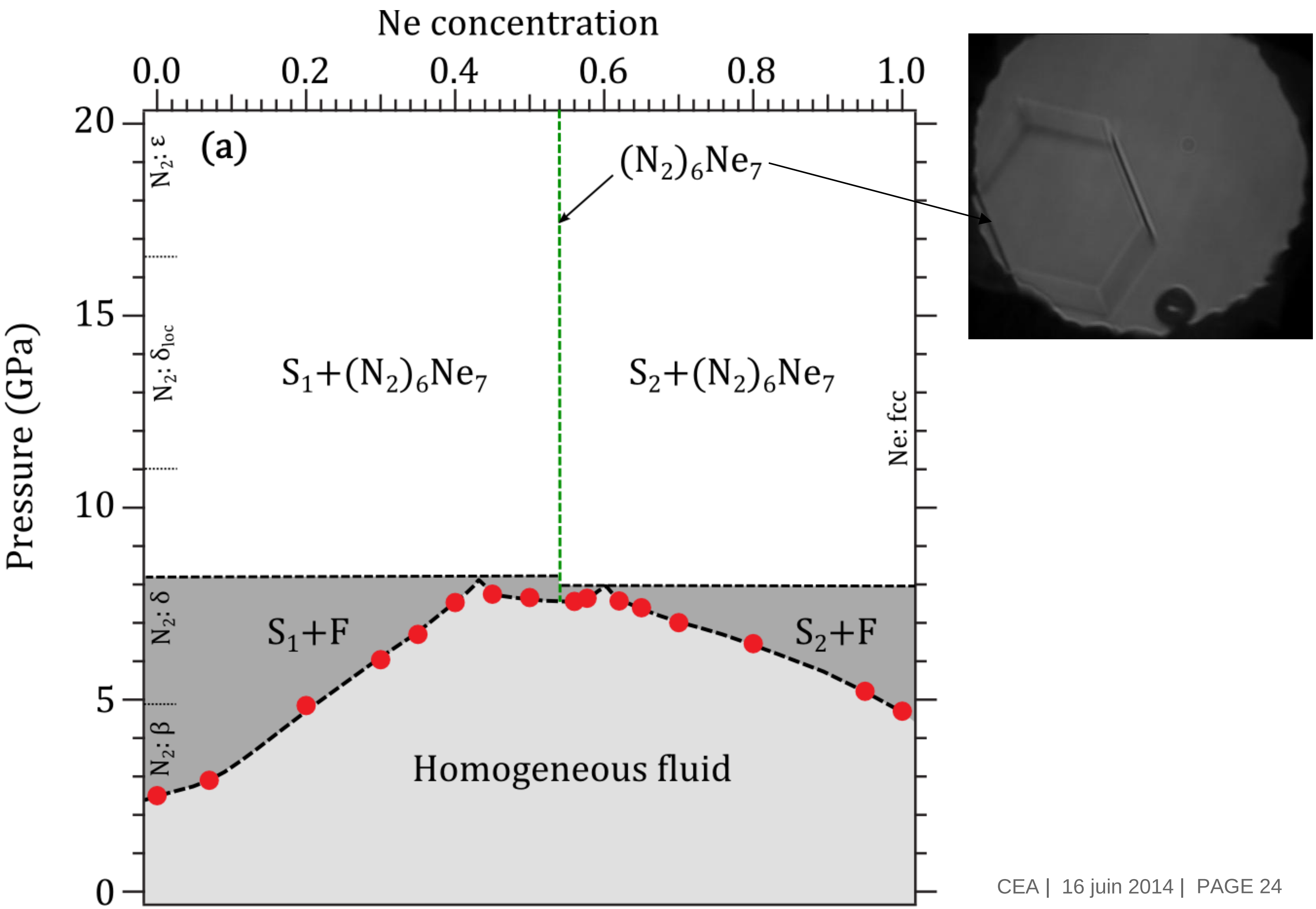






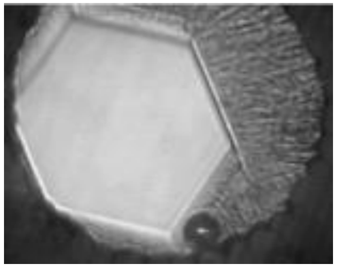


N_2 – NE BINARY DIAGRAM



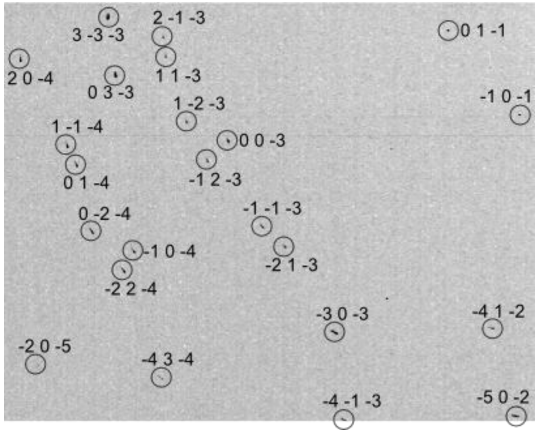
STRUCTURE OF THE COMPOUND

N_2-Ne
Single crystal



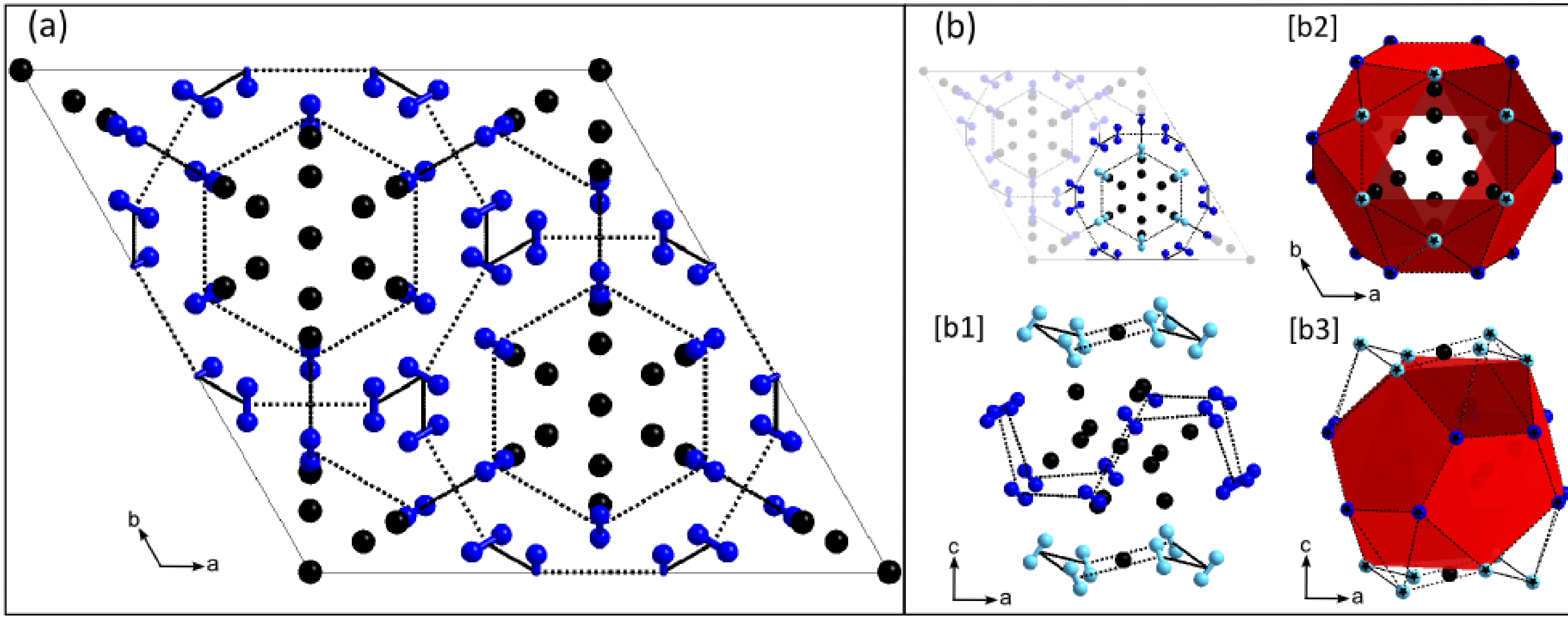
Synchrotron (ESRF, Grenoble)

Image plate



+ Direct methods in crystallography

STRUCTURE OF THE COMPOUND

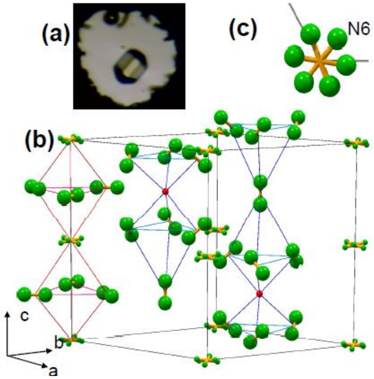


$(N_2)_6Ne_7$

Hexagonal / R$\bar{3}$m

a=b=14.4 Å, c=8.09 Å @ 8 GPa

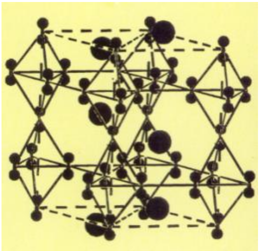
AN ORIGINAL VAN DER WAALS COMPOUND



He$(N_2)_{11}$

Structures of $(N_2)_{11}$He compound to 175 GPa: a close relationship with pure N_2

S. Ninet,[1,2] G. Weck,[2] P. Loubeyre,[2] and F. Datchi[1]

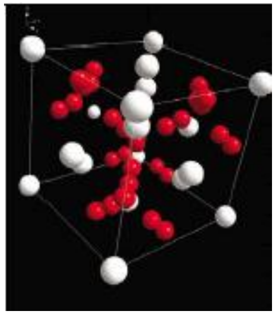


Ar$(H_2)_2$

VOLUME 72, NUMBER 9 PHYSICAL REVIEW LETTERS 28 FEBRUARY 19

Compression of Ar$(H_2)_2$ up to 175 GPa: A New Path for the Dissociation of Molecular Hydrogen

Paul Loubeyre, René Letoullec, and Jean-Pierre Pinceaux



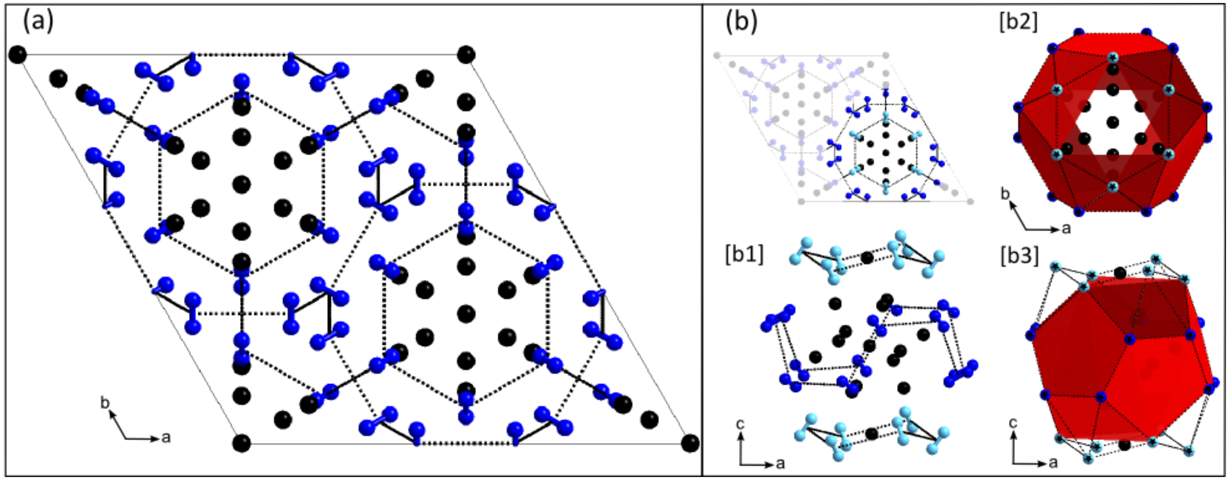
Xe$(0_2)_2$

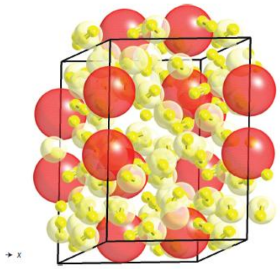
PHYSICAL REVIEW B 82, 014112 (2010)

Oxygen/noble gas binary phase diagrams at 296 K and high pressures

Gunnar Weck, Agnès Dewaele, and Paul Loubeyre
CEA, DAM, DIF, F-91297 Arpajon, France

(Received 17 May 2010; published 28 July 2010)





del structure of Xe$(H_2)_7$. The xenon atoms are surrounded by

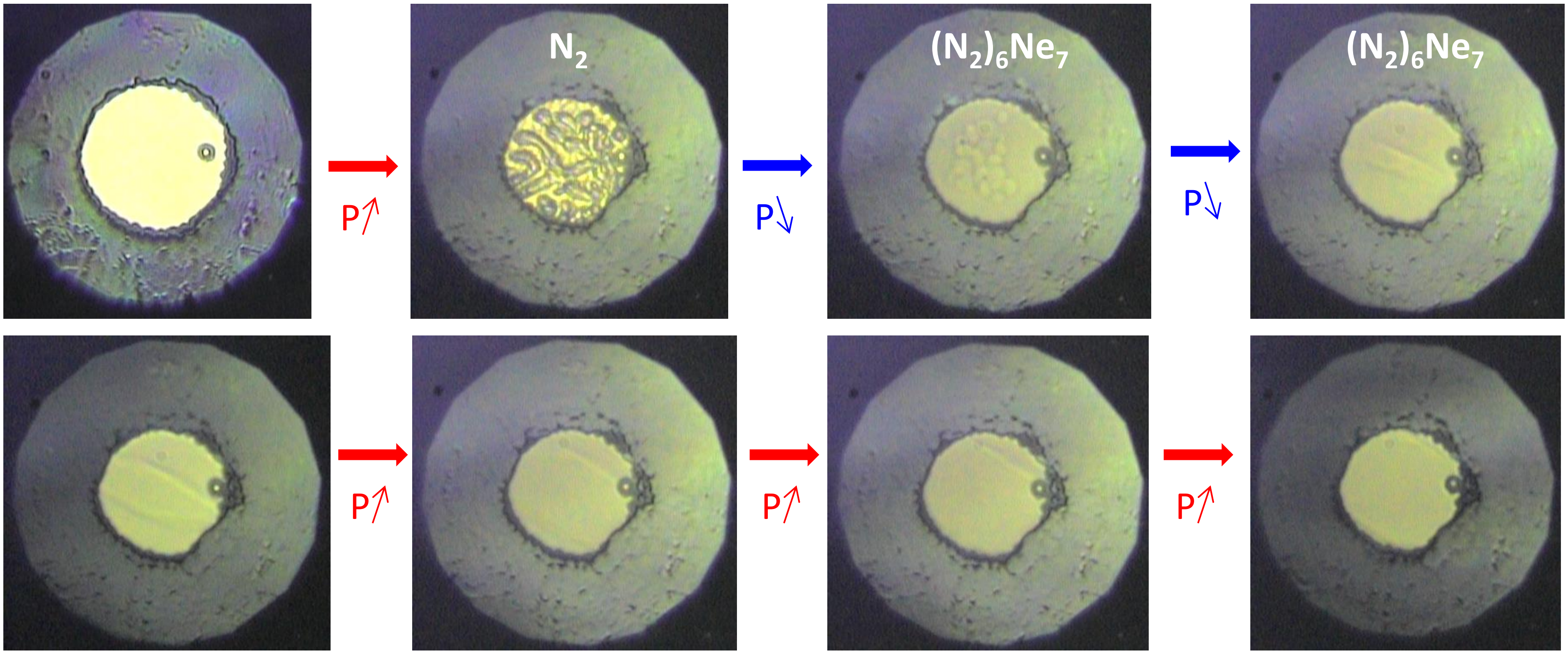
Xe(H2)7

Pressure-induced bonding and compound formation in xenon–hydrogen solids

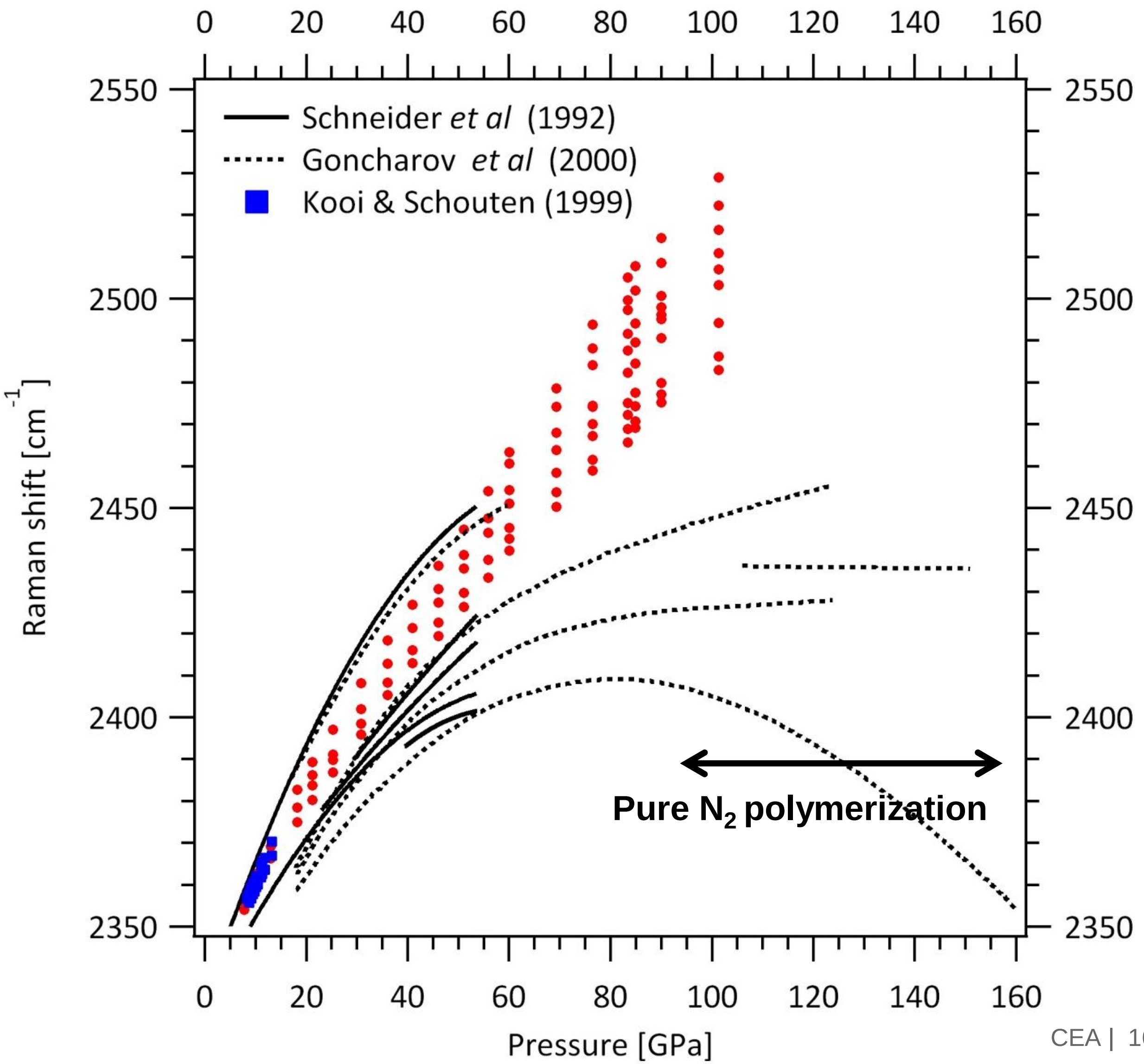
Maddury Somayazulu[1*], Przemyslaw Dera[2], Alexander F. Goncharov[1], Stephen A. Gramsch[1], Peter Liermann[3], Wenge Yang[3], Zhenxian Liu[1], Ho-kwang Mao[1,3] and Russell J. Hemley[1]

HIGH PRESSURE BEHAVIOR

- Diamonds with 100 µm diameter
- Raman characterization

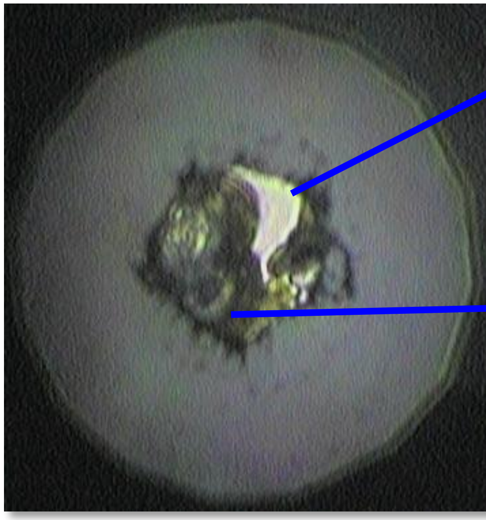


HIGH PRESSURE BEHAVIOR

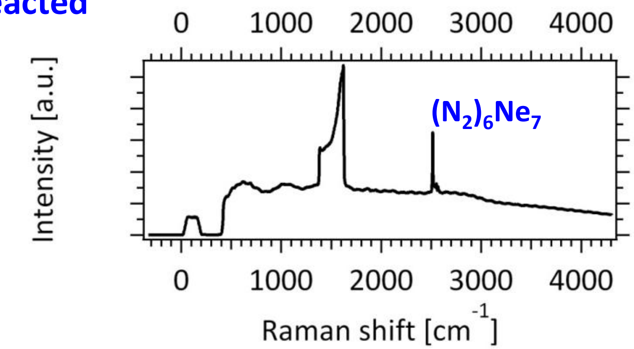


HIGH PRESSURE BEHAVIOR

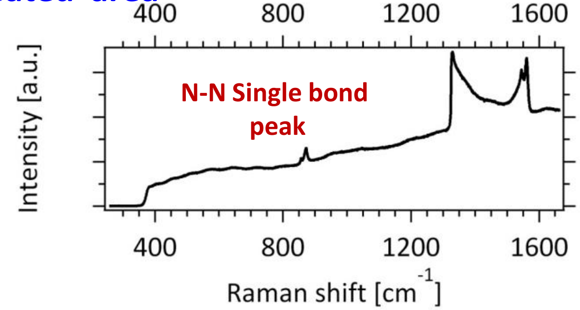
Laser heating at 130 GPa (YAG)



Non-reacted area

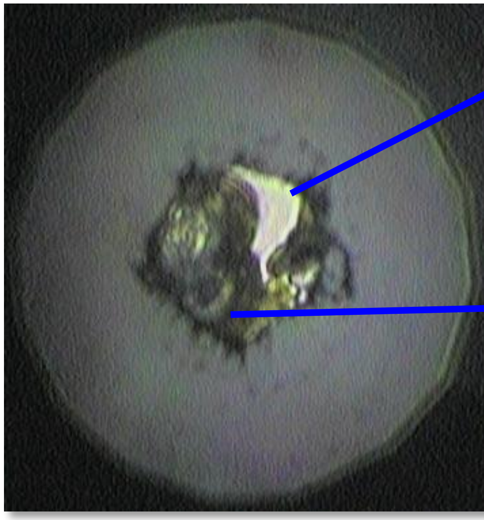


Strongly heated area

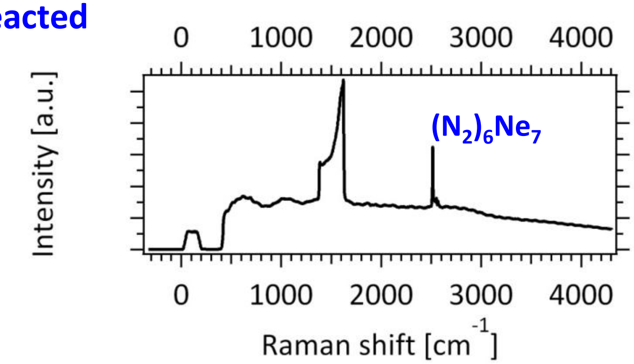


HIGH PRESSURE BEHAVIOR

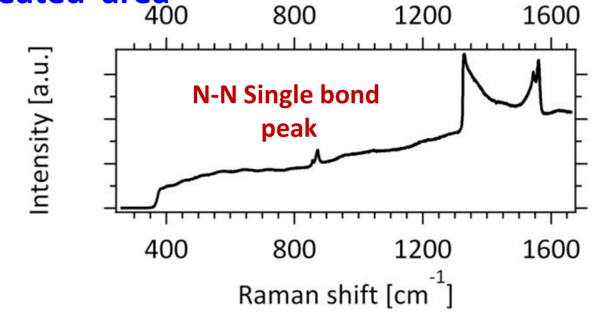
Laser heating at 130 GPa (YAG)

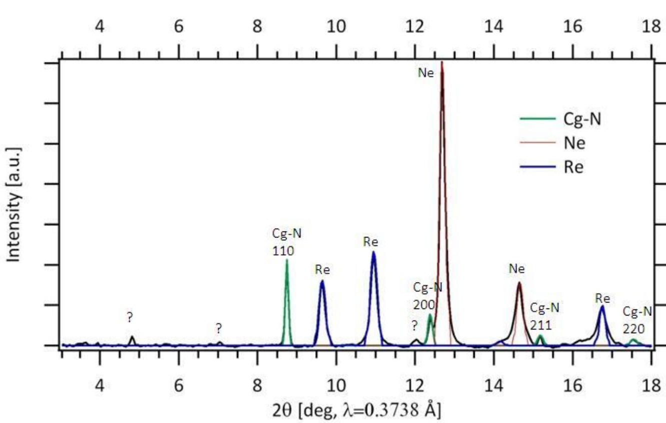


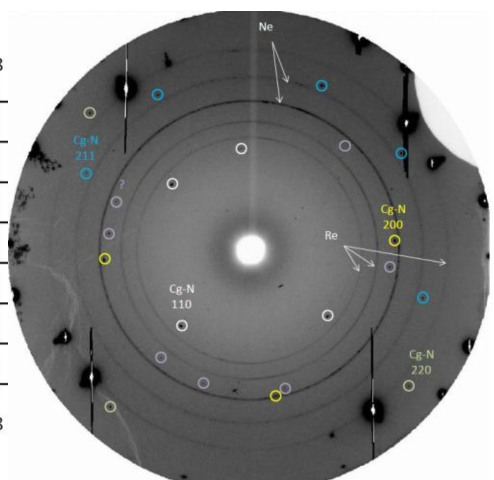
Non-reacted area



Strongly heated area







Phase separation under heating

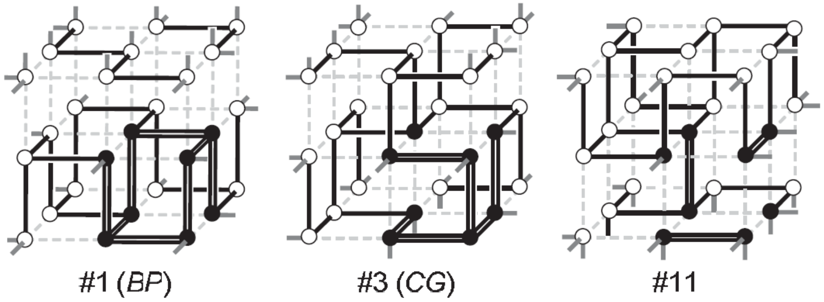
Recrystallisation of cg-N
Neon stays as a powder

OUTLOOK

New perspectives opened by numerical simulations

- Numerical simulations predict a lower polymerization pressure (65 GPa) than the experimental one (110 GPa)

*Pickard et al, PRL **102**, 125702 (2009)*
*Erba et al , PRB **84**, 012101 (2011)*



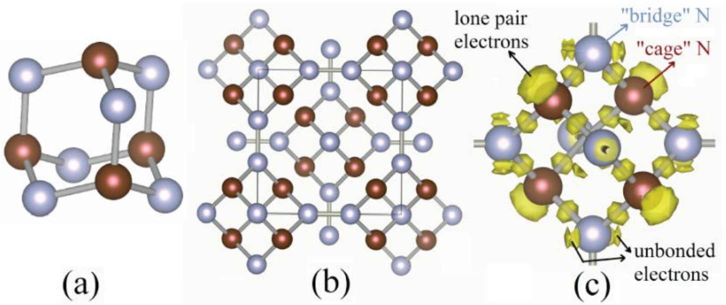
Zahariev et al

- Atomic phases of nitrogen are distortion of simple cubic ; different structures predicted

*Zahariev et al , PRL, **97** 155503 (2006)*
*Pickard et al, PRL **102**, 125702 (2009)*

- Exotic phases predicted : diamondoid N_{10}

*Wang et al, PRL, **109**, 175502 (2012)*



Wang et al

Binary mixtures will provide geometrical constraints and / or nano-structuration with phase separation