Dry High-Pressure Methods

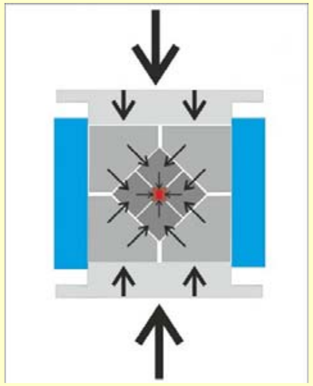
Chemistry at the Earth's surface at ~100 kPa
Chemistry in the Universe at hight pressures and temperatures - deep within the planets and stars

Laboratory:
Pressures up to 770 GPa (static), 2 TPa (ns), 100 TPa (shock wave)
High temperatures ~7000 °C
1 bar = 100 kPa   1 Mbar = 100 GPa

p-V work during compression to 1 Mbar equivalent to approx. 1 eV
~ chemical bond energy

In-situ observations by diffraction, spectroscopy to probe chemical reactions, structural transformations, crystallization, amorphization, phase transitions

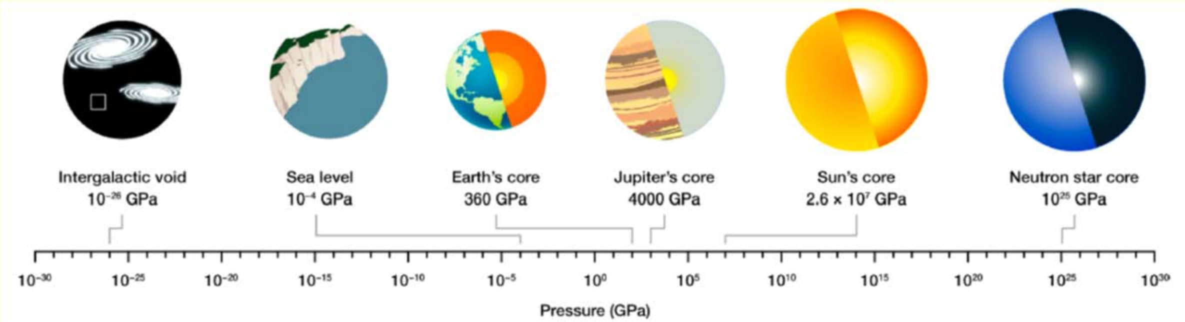
Methods of obtaining high pressures
- **Diamond anvils, tetrahedral and octahedral**
- **Shock waves (km s^{-1})**
- **Laser compression (10 ns)**
- **Explosions, projectiles**
- **Go to another planet: Jupiter (H_2 is metallic at 100 Gbar)**

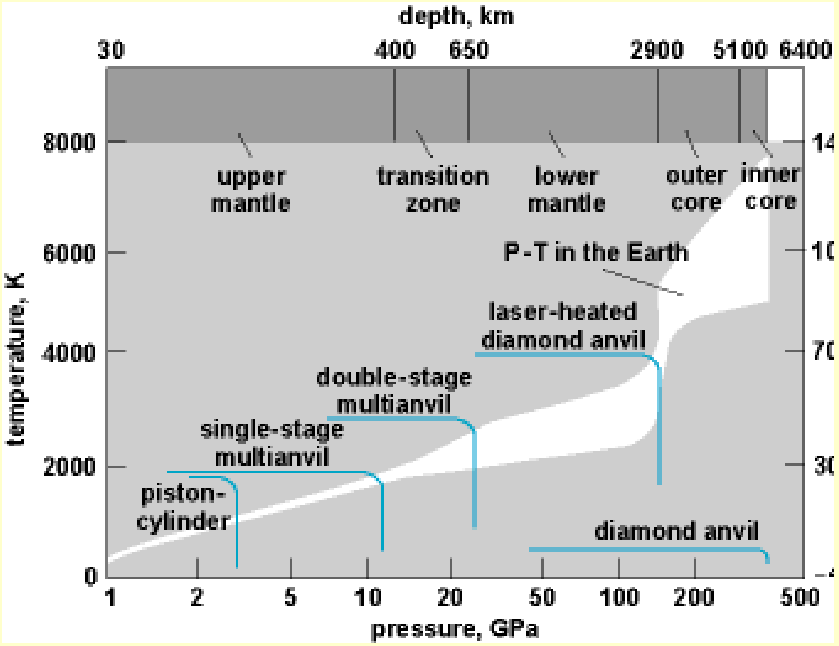


Pressure Scale

Pressure bar	System
	1 Mbar = 100 GPa
10^{-12}	high vacuum chamber
1	atmospheric pressure
1.5	kitchen pressure cooker
2.0	car tire
50	a lady in stilleto heels
60	breakdown of human nervous system - divers
73.8	critical pressure of CO_2
150	autoclave (safety burst disc)
221.2	critical pressure of H_2O
10^3	pressure at the bottom of the ocean (11 km)
2.10^3	LDPE
10^4	Earth crust (30 km)
10^5	synthetic diamond production
$3.4\ 10^6$	pressure at the center of the Earth (6378 km)
10^7	Saturn, Jupiter, metallic hydrogen
10^8	neutron stars

50 orders of magnitude





Earth

Core 3.4 Mbar = 340 GPa,   6000 K

ε-Fe hcp

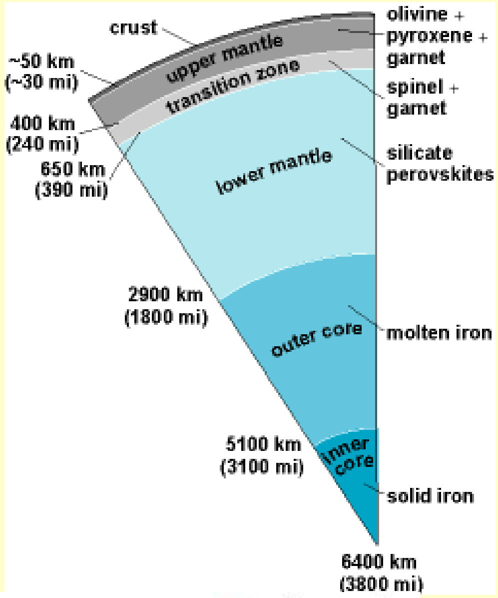
$MgSiO_3$ most abundant silicate mineral within our planet !

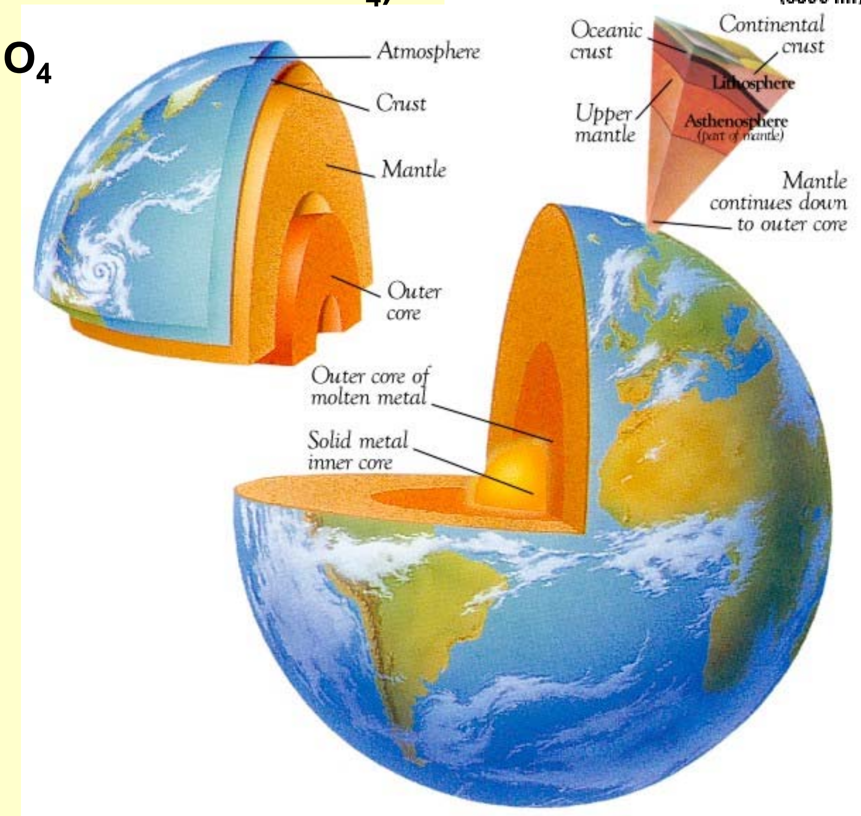
Olivine Mg_2SiO_4 (orthosilicate = nesosilicate = isolated SiO_4)

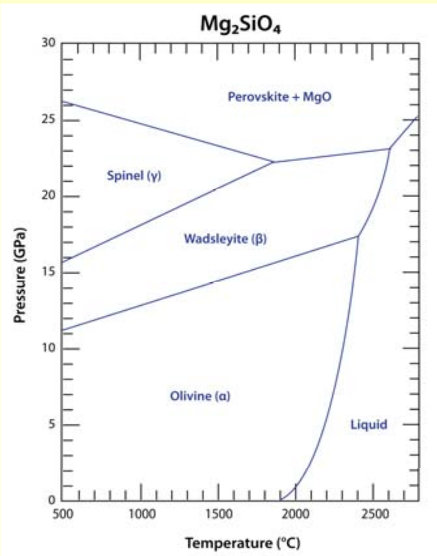
pyroxene (silicate chains) > spinel Mg_2SiO_4

ilmenite > garnet (HT) >

perovskite $MgSiO_3$ - Si CN = 6







Dry High-Pressure Methods

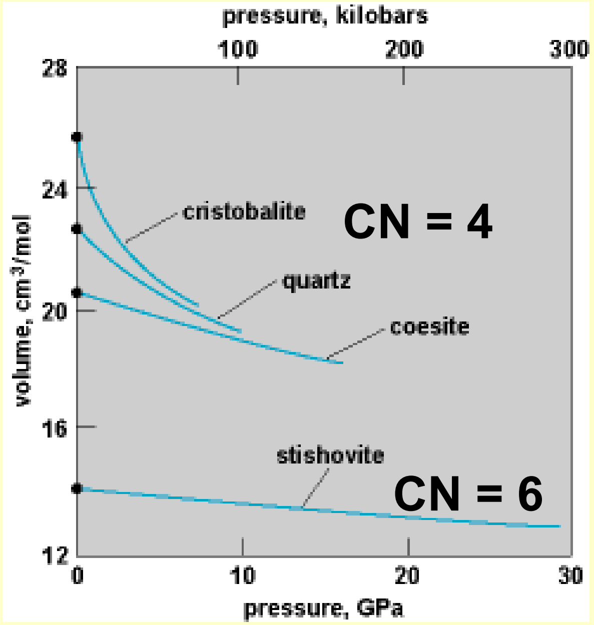
Pressure techniques useful for synthesis of unusual structures

A redistribution of the electronic density

TD metastable yet kinetically stable when pressure released
= pressure and temperature quenching

Reconstructive transformation hindered at low temperature
insufficient thermal energy for bond-breaking

- **high pressure phases**
- **higher density**
- **enhanced intermolecular interactions**
- **bonds shorten with increasing *p***
- **higher coodination number (longer bonds)**
- **higher symmetry**
- **band broadening and mixing**
- **transition to from nonmetal to metal**



Bond Distances at High Pressure

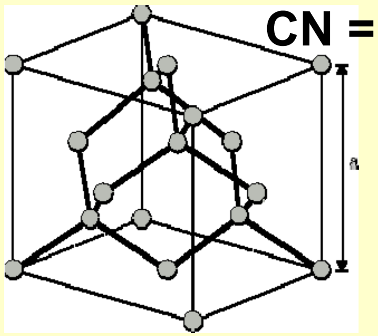
Decrease of bond lengths with increasing pressure

Pressure/Coordination Number Rule:
increasing pressure → transition to higher CN

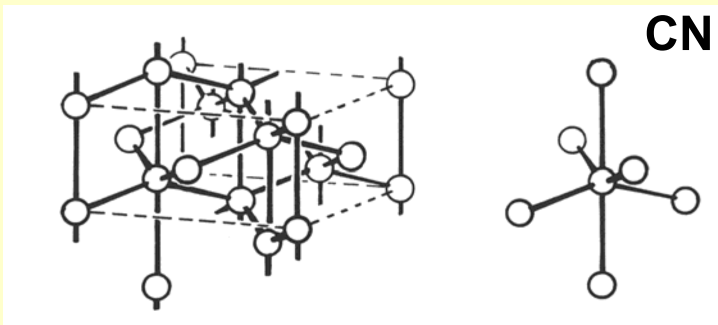
Pressure/Distance Paradox: increasing pressure – longer bonds

Gray Sn (diamond type, stable below 13 °C, semiconductor)
Coordination number 4, Sn-Sn bond length 281 pm, a = 6.4892 Å, dens = 5.57 g/cm^3

White Sn (metallic)
Coordination number 6, Sn-Sn bond lengths 302 and 318 pm,
a = 5.8316 Å, c = 3.1815 Å, dens = 7.31 g/cm^3



CN = 4

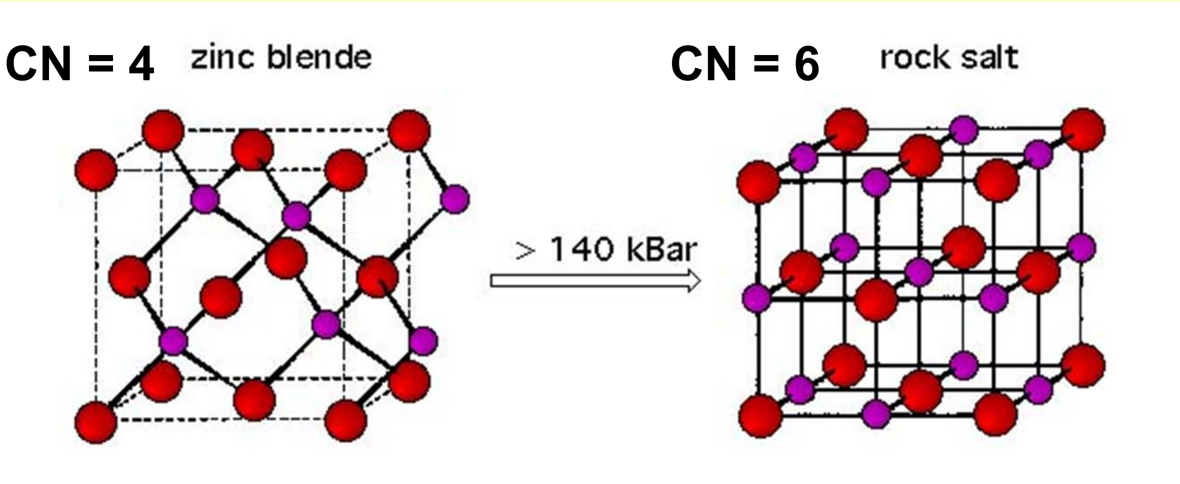


CN = 6

Dry High-Pressure Methods

Examples of high pressure polymorphism for some simple solids

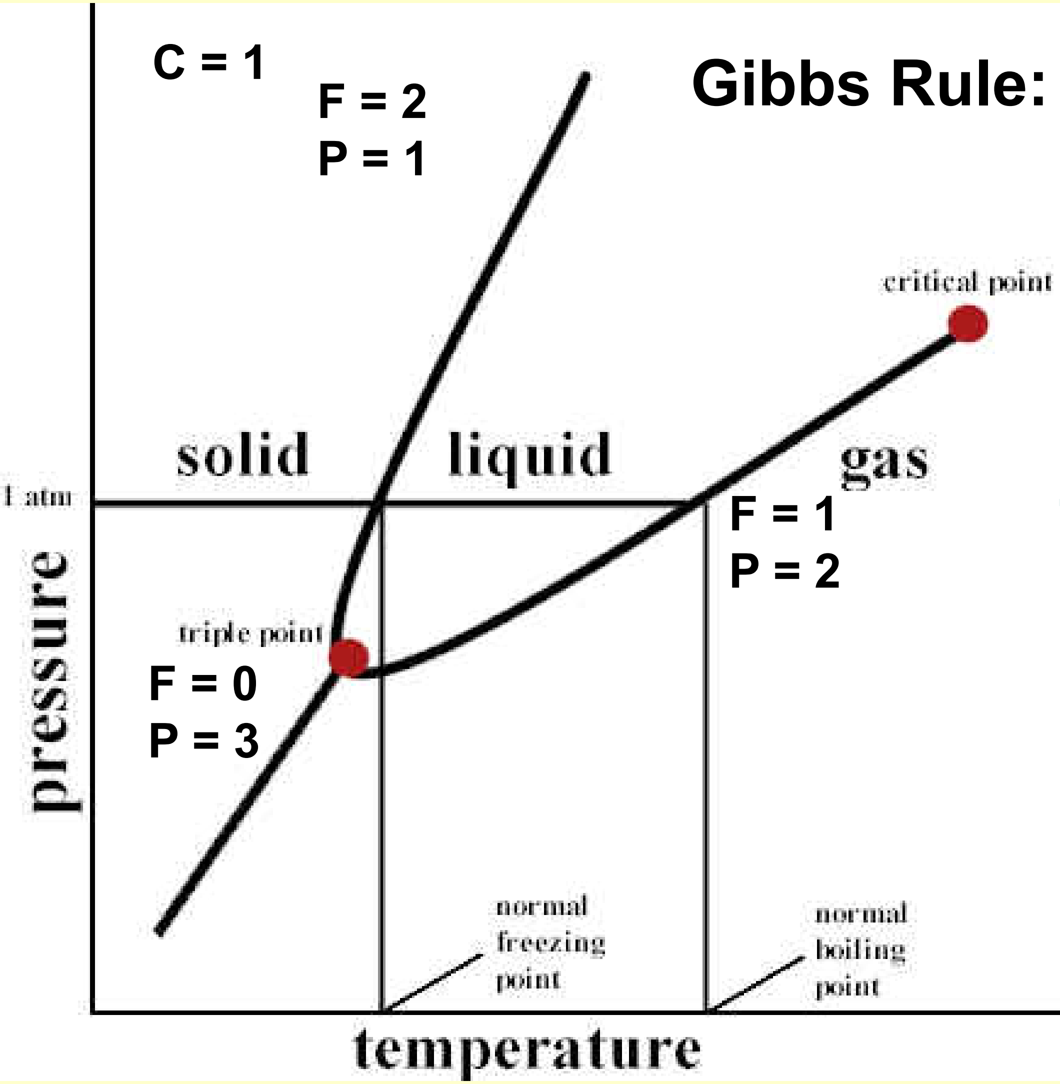
Solid	Normal structure	Transf. P (kbar)	Transf. T (^{o}C)	High pressure structure
C	Graphite 3	130	3000	Diamond 4
CdS	Wurtzite 4:4	30	20	Rock salt 6:6
KCl	Rock salt 6:6	20	20	CsCl 8:8
SiO_2	Quartz 4:2	120	1200	Rutile 6:3 (stishovite)
Li_2MoO_4	Phenacite 4:4:3	10	400	Spinel 6:4:4
$NaAlO_2$	Wurtzite 4:4:4	40	400	Rock salt 6:6:6

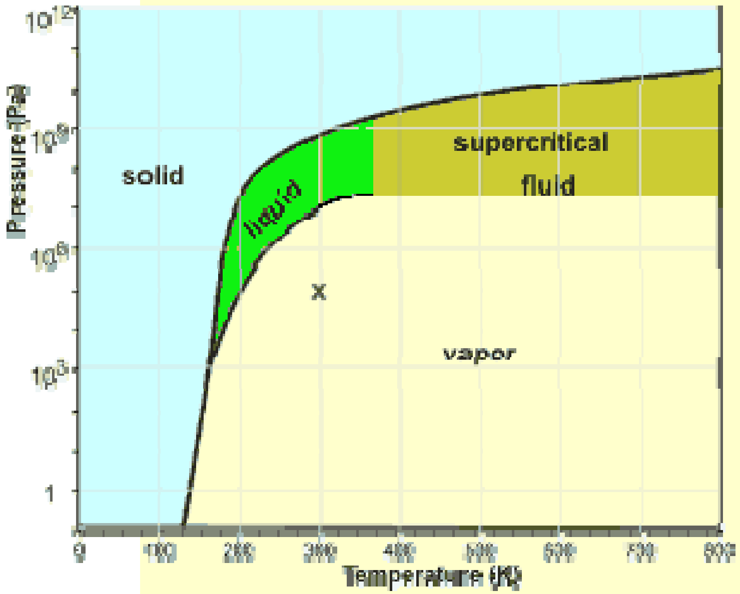


p-T Phase Diagrams

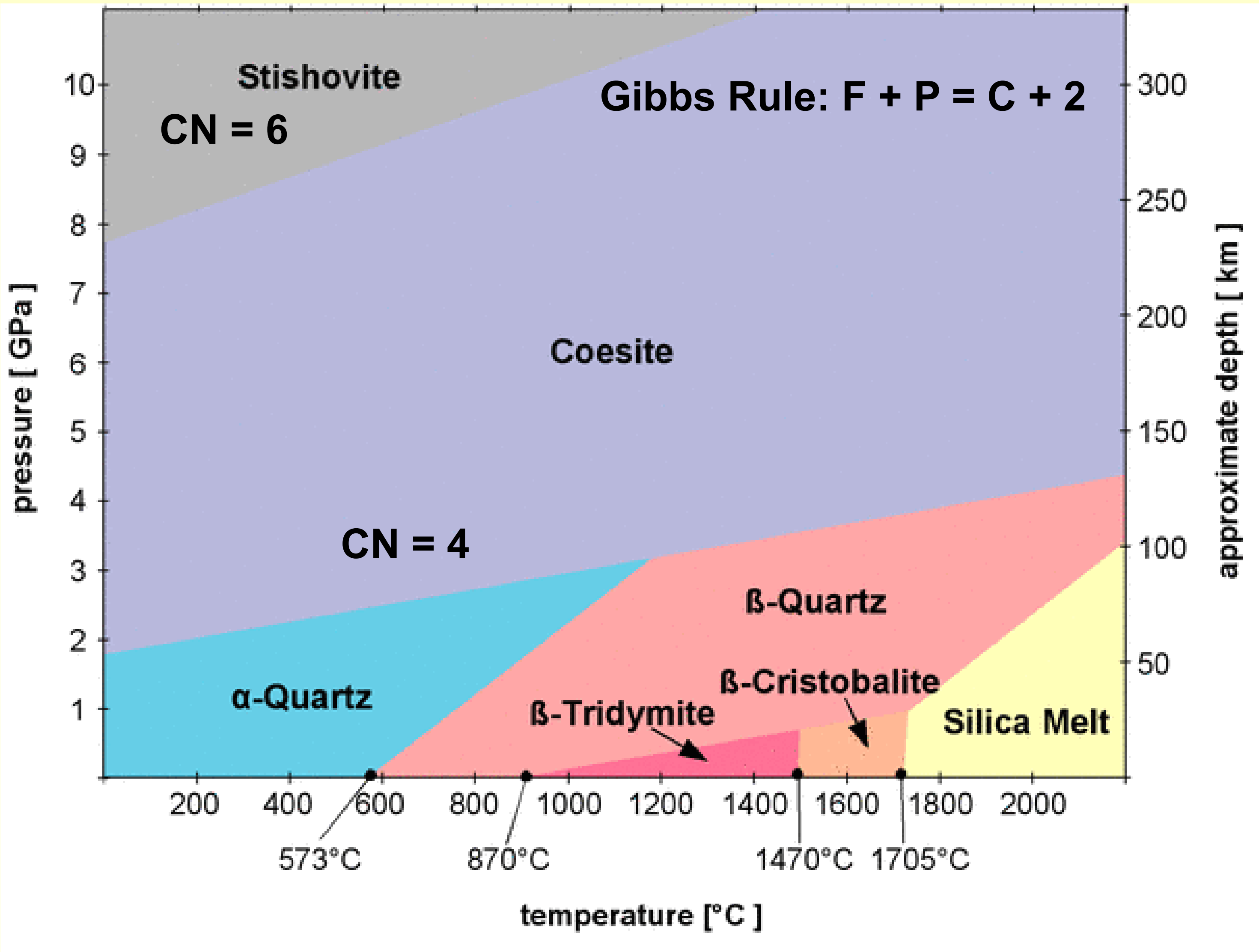
Gibbs Rule: F + P = C + 2

F = degree of freedom
P = number of phases
C = number of components





p-T Phase Diagram of SiO_2

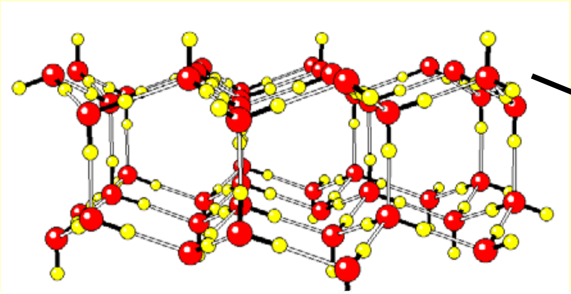


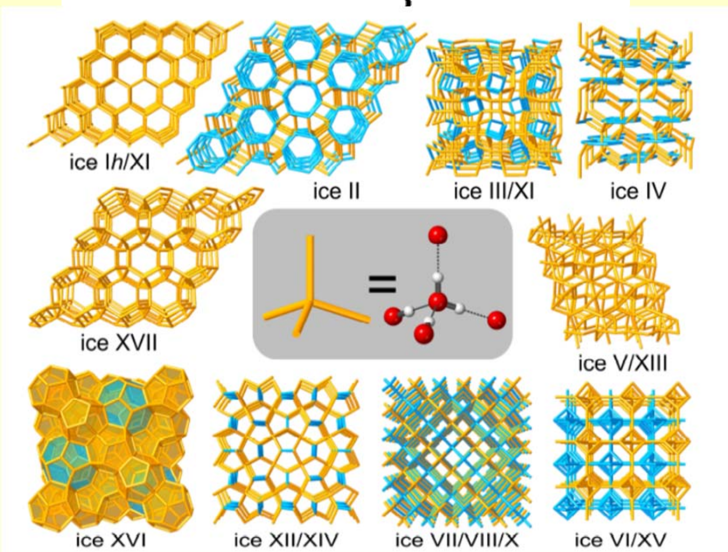
p-T Phase Diagram of Ice

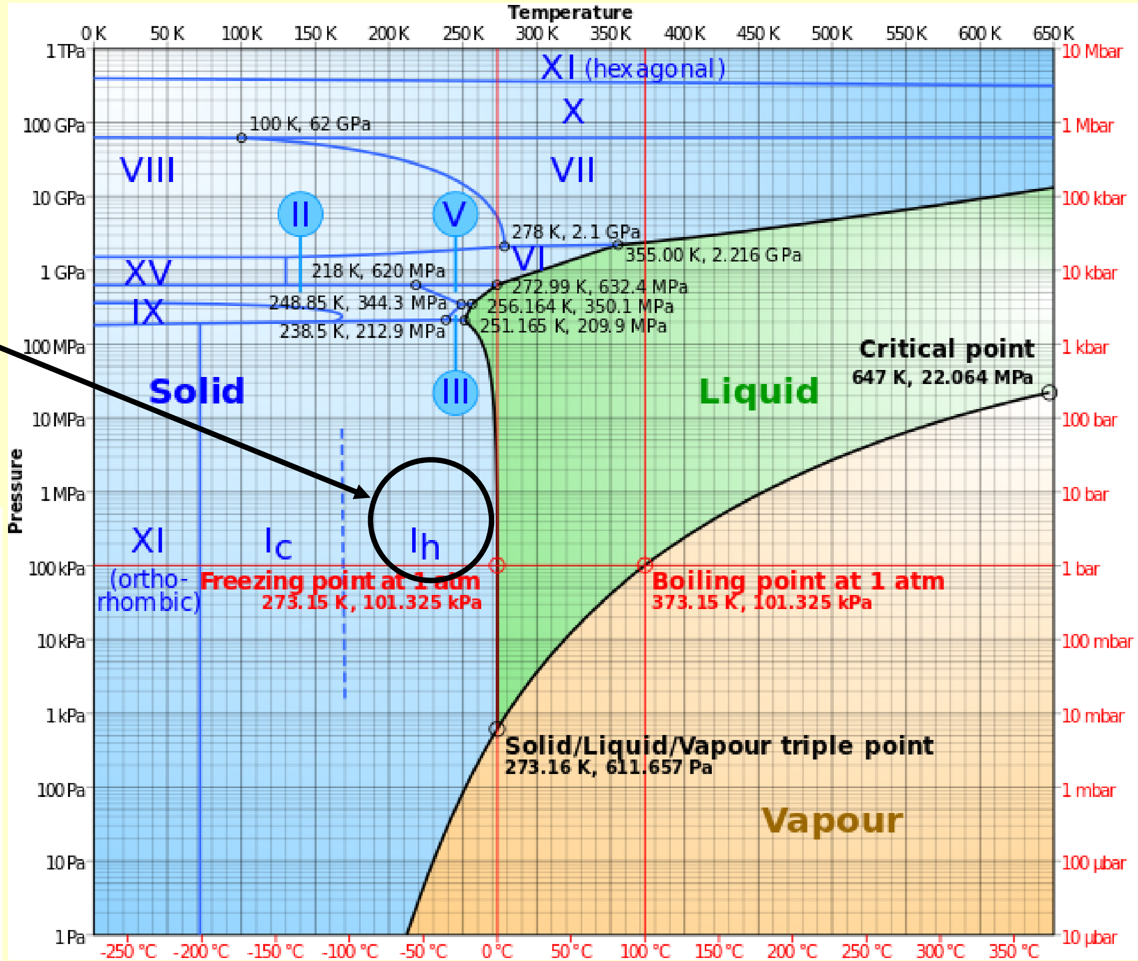
Ice

17 solid phases

Hexagonal Ice







High-Pressure Phases

Water

17 phases of ice

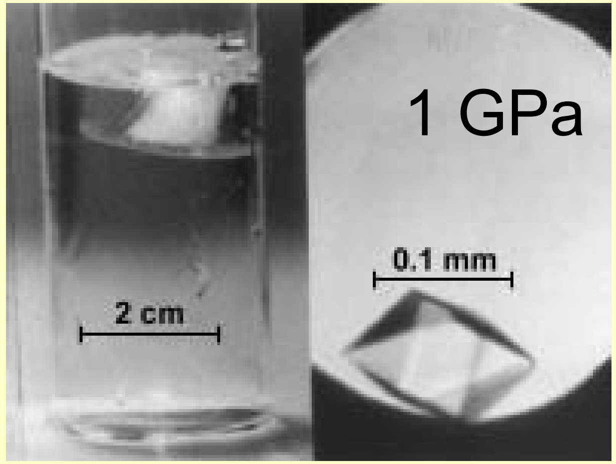
Ice-VII m.p. 100 °C

Ice-X fluorite, ionically conductive above 10 GPa

Equalization of O-H covalent

and hydrogen bonds above 60 GPa

Max. pressure attained for water 210 GPa



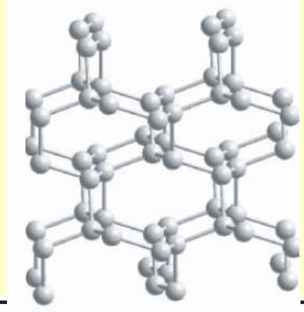
floats sinks

Ca

ccp at ambient pressure

bcc (!) above 20 GPa 4s-3d mixing, Ca become a transition metal

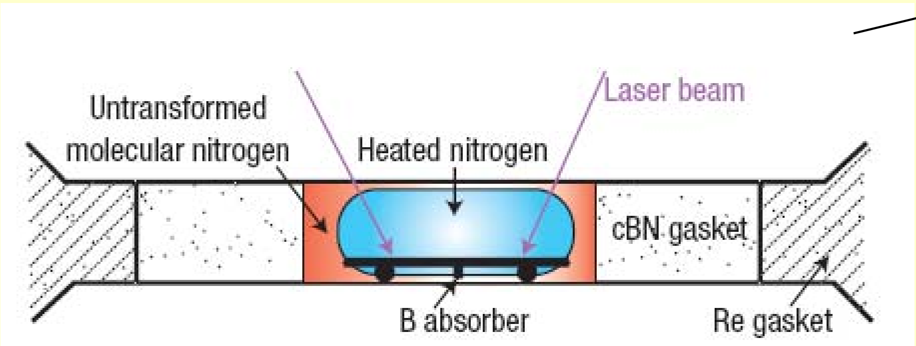
Condensed Gases

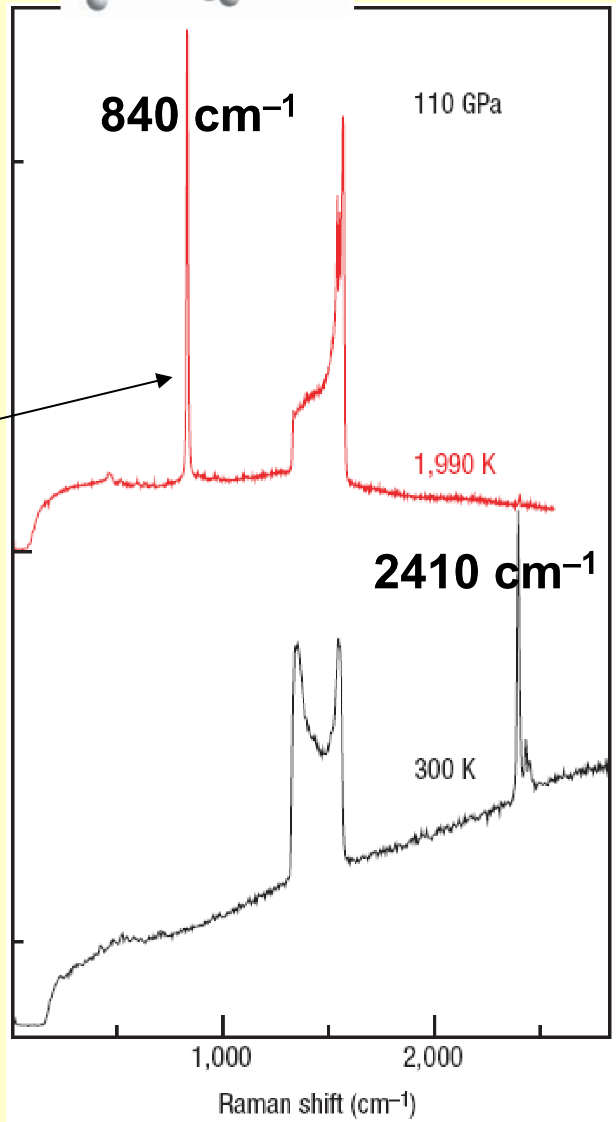


$NO_2 + N_2O$ $NO^+ NO_3^-$ calcite

N_2 semiconducting oligomers $(\text{-N-})_x$ at 100-240 GPa

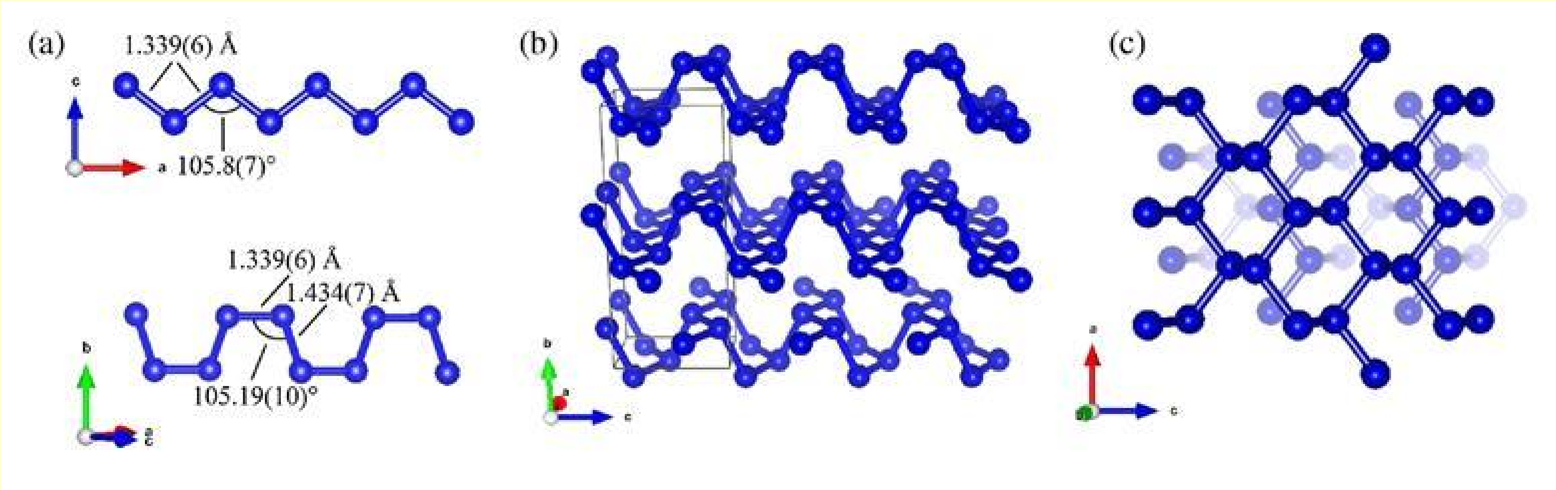
cubic diamond 110 GPa, 2000 K





Heating: 1-μm B plate (absorber of laser radiation rests on c-BN pieces that thermally insulate the plate from the bottom anvil. The sample squeezed between the anvils is surrounded by the c-BN/epoxy gasket followed by the metallic (Re) supporting ring

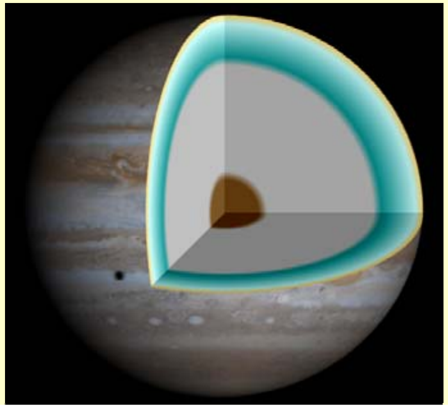
Black Nitrogen



A transparent and crystalline allotrope = black phosphorus
a diamond anvil cell, 140 GPa, heating with a laser to 4000 K

1 D Laniel et al, Phys. Rev. Lett, 2020, DOI: 10.1103/PhysRevLett.124.216001
2 C Ji et al, Sci. Adv, 2020, DOI: 10.1126/sciadv.aba9206

Phase Diagram of Hydrogen

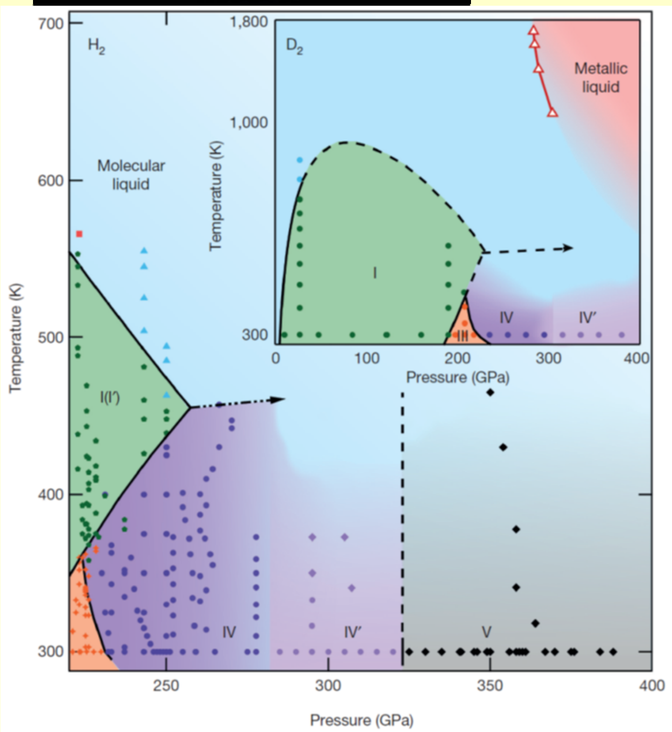


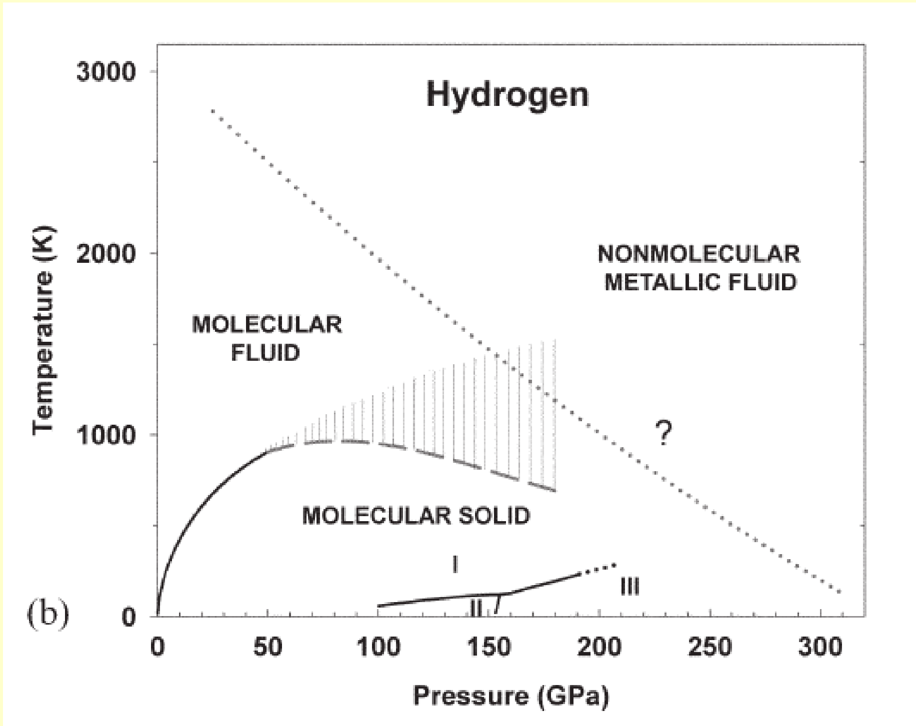
H–H bond 0.74 Å, bond dissociation energy of 4.52 eV

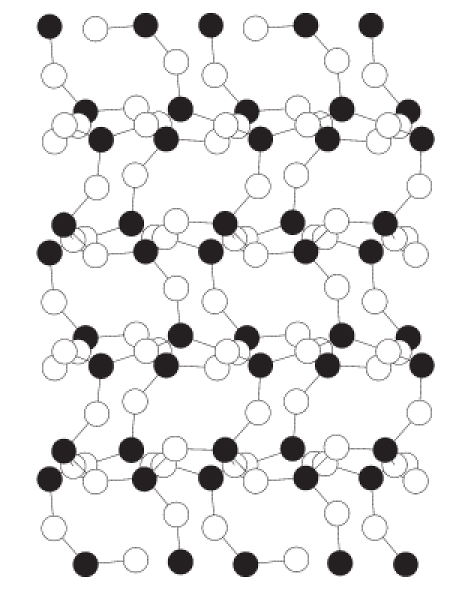
Prediction: at 25 GPa - non-molecular (atomic and metallic)

Solid H_2 at 5.5 GPa or at 14 K - phase I = disordered orientationally freely rotating H_2 molecules in hcp

H_2 metallic conductivity in dense fluid hydrogen H_2^+ H_2^-







Phase Diagram of CO_2

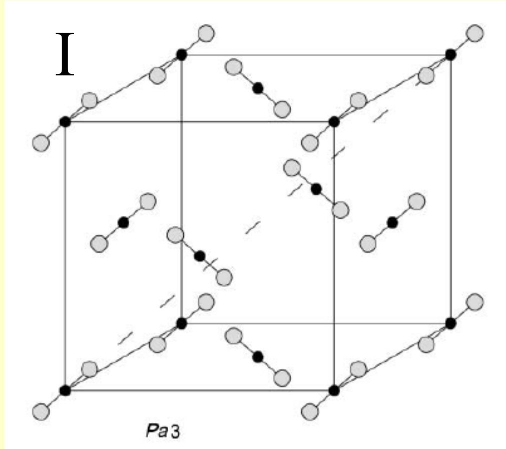
CO_2-V
Quartz
superhard

CO_2 heating at 10-20 GPa

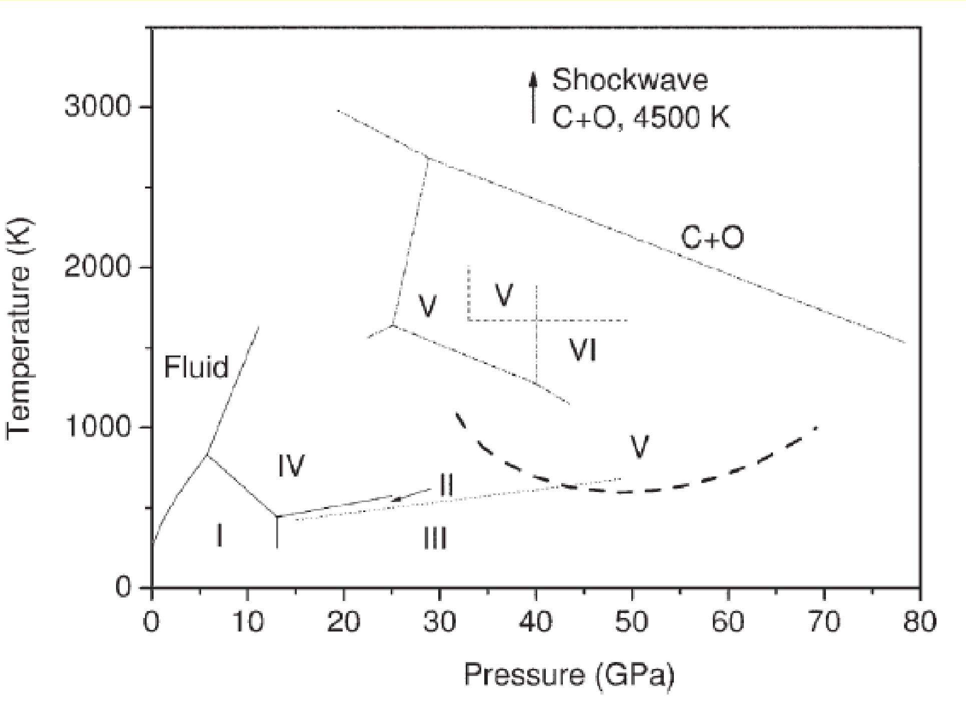
sp^3 bonded CO_4

cristobalite, tridymite

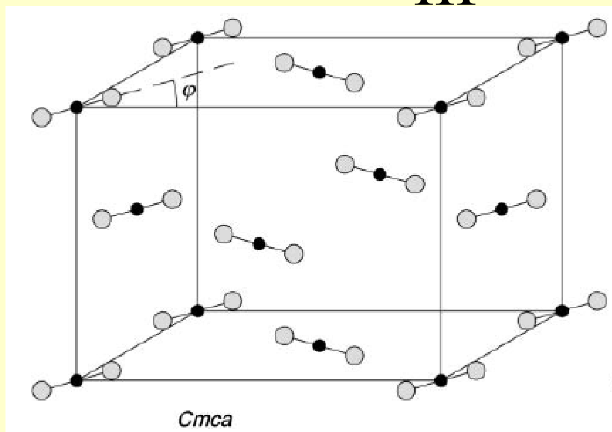
40 GPa quartz
(noncentrosymmetric)



fcc



III



Reaction Equlibrium and Pressure

The reaction volume ΔV^0 = the volume difference between the products (C) and the reactants (A)

A $\rightleftarrows$ C

$$K = \frac{[C]_{eq}}{[A]_{eq}}$$

$$\Delta G^0 = -RT \ln K \quad \longrightarrow \quad \left(\frac{\partial RT \ln K}{\partial P}\right)_T = -\Delta V^0$$

Associative type = negative ΔV^0 ($V_C < V_A$)

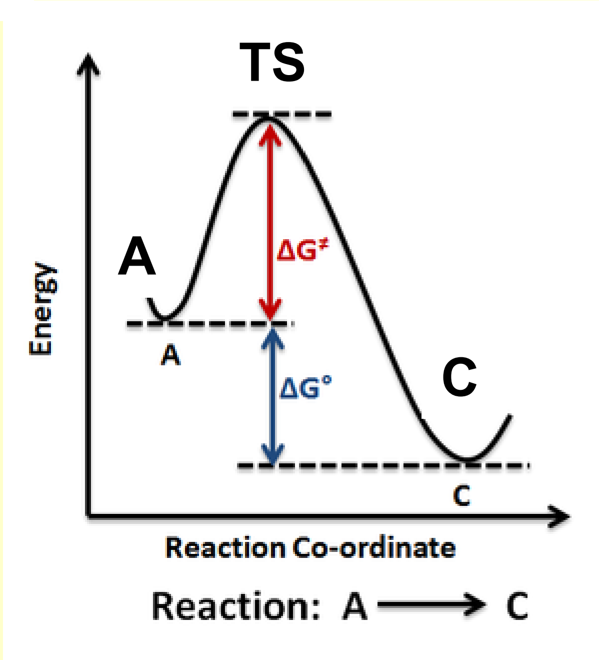
K increases with increasing pressure

A $\rightarrow$ C

Dissociative type = positive ΔV^0 ($V_C > V_A$)

K decreases with increasing pressure

A $\leftarrow$ C

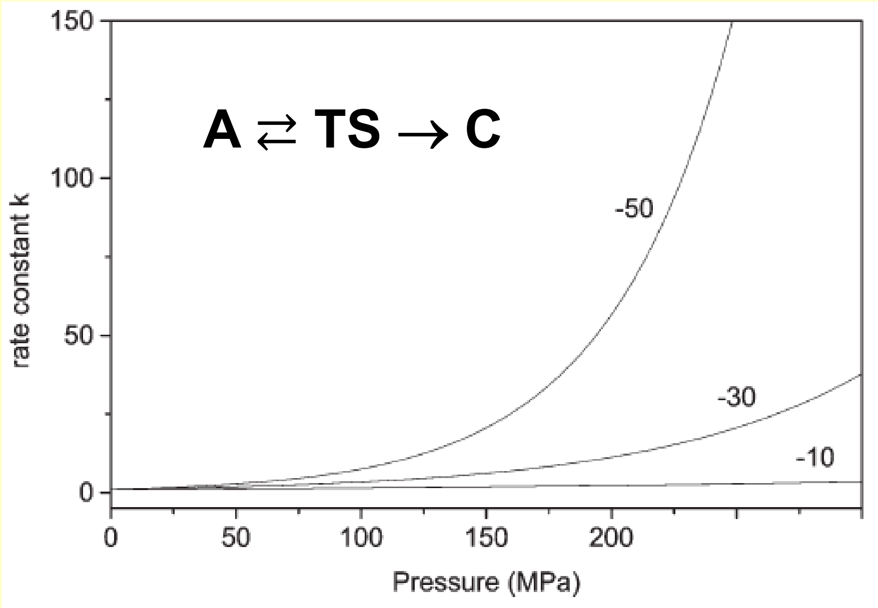


Reaction Kinetics and Pressure

The activation volume $\Delta V^{\neq}$ = the volume difference between the transition state complex (TS) and the reactants (A)

$$\left(\frac{\partial \ln k}{\partial T}\right)_P = -\frac{E_a}{RT}$$

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^{\neq}}{RT}$$



Room-temperature pressure dependence of the rate constant for different activation volume $\Delta V^{\neq}$ values (in $cm^3\ mol^{-1}$)

Associative type = the rate determining step involves the formation of a covalent bond

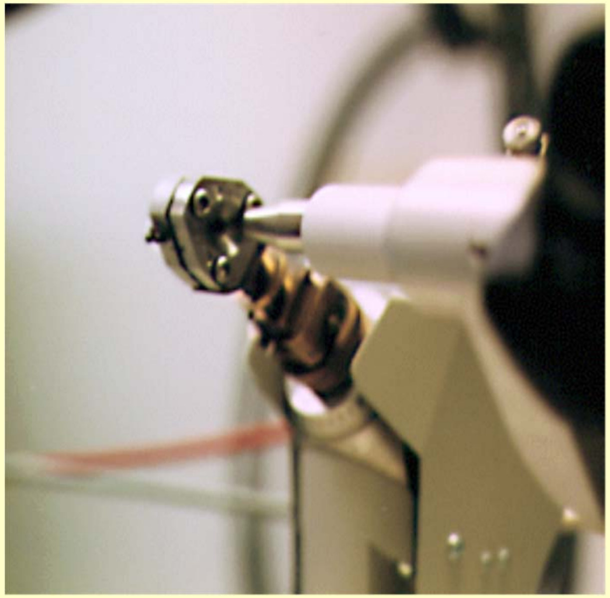
negative $\Delta V^{\neq}$ ($V_{TS} < V_A$) → reaction rate increases with increasing pressure

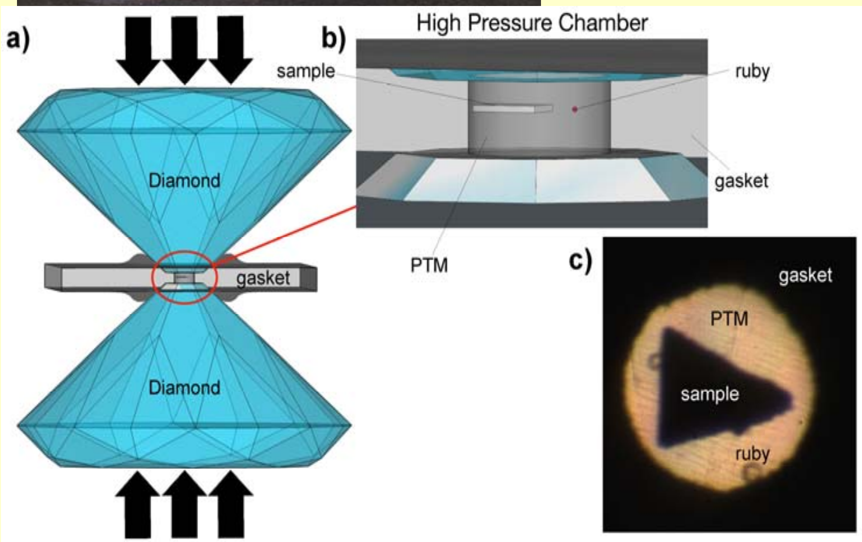
Dissociative type = the breaking of a covalent bond

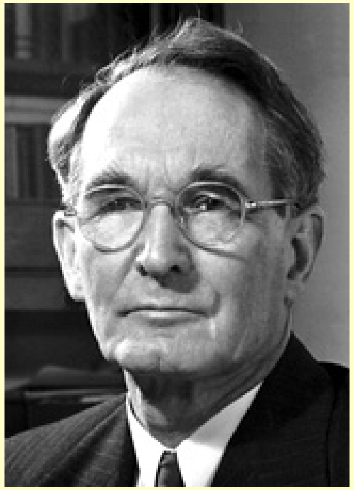
positive $\Delta V^{\neq}$ ($V_{TS} > V_A$) → reaction rate decreases with increasing pressure

Diamond Anvil Cell

- **hydraulic press**
- **anvils**
- **sample assembly**







Percy Williams Bridgman
(1882 – 1961, NP in Physics 1946)

Diamond Anvil Cell

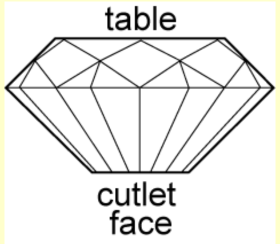
Diamond anvil cell (DAC)

p = F/A

p = 40 GPa

A_{table} / A_{culet} = 10 : 1

A_{culet} = 100-200 µm



Nanocrystalline anvils

Re or steel gasket

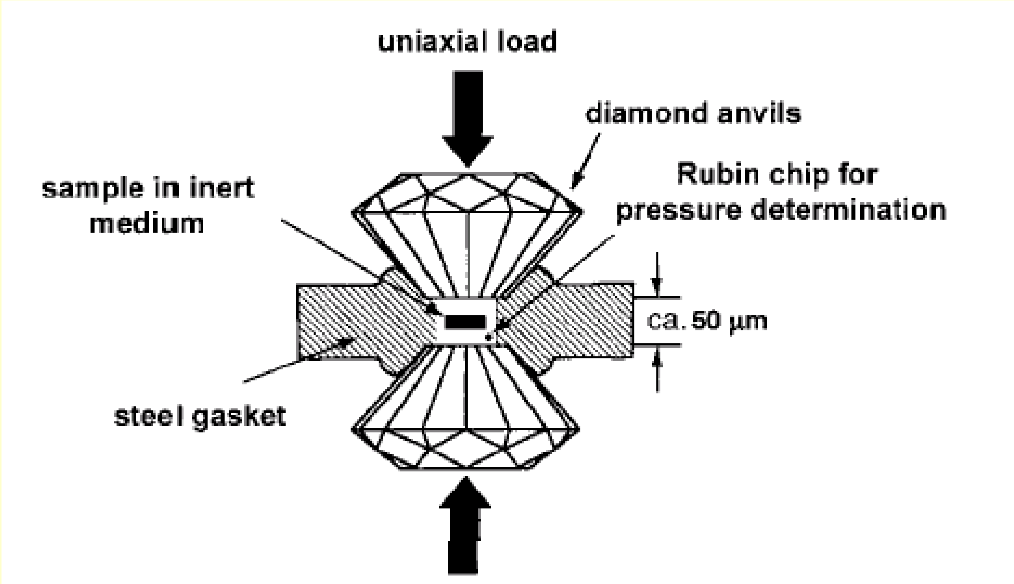
Pressure transmitting medium:

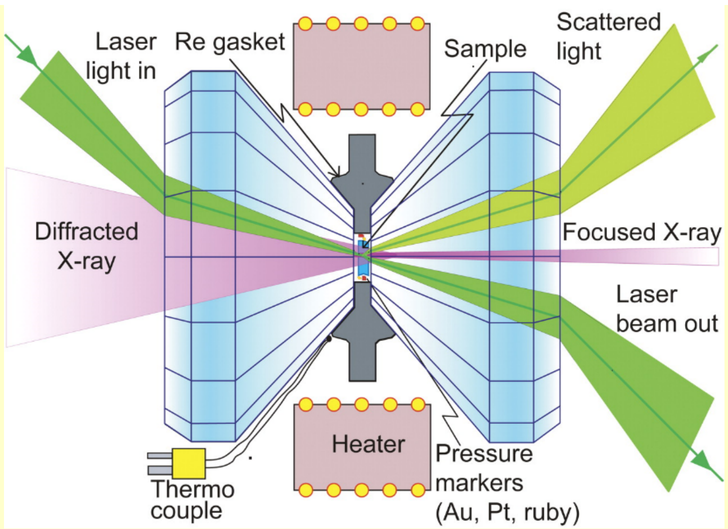
BN, MgO, NaCl, AgCl, He, Ne, N_2, Ar, methanol:ethanol 4:1

Diamond transparent to radiation from IR to X-ray

Laser heating T > 2500 °C

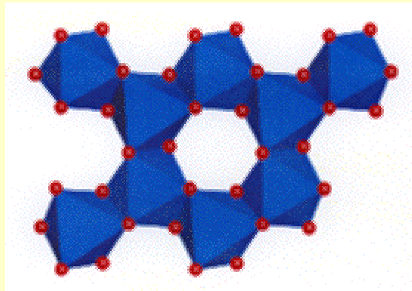
Resistive heating



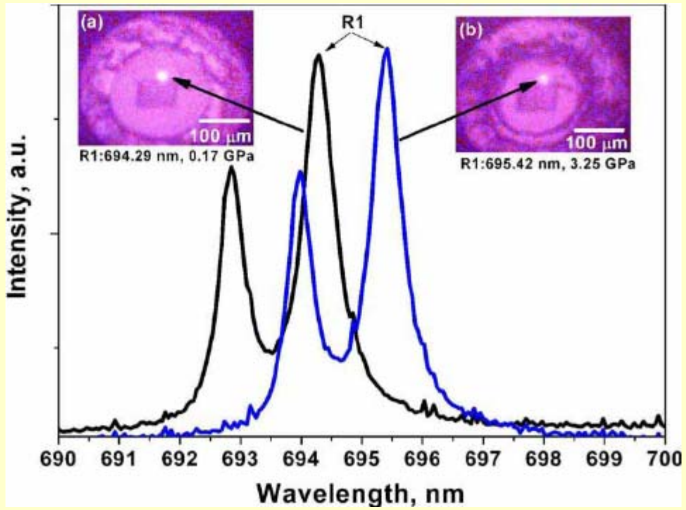


Diamond Anvil Cell

Calibrating a high pressure diamond anvil cell



• Ruby (0.5 wt %Cr doped corundum) - fluorescence transition, up to 400 °C, Sm:YAG, $SrBO_4$
• Bi, Pb, Tl, Ba pressure induced phase transition
• Cu, Ag, Au, Pt, and NaCl - the unit cell size from the equation of state



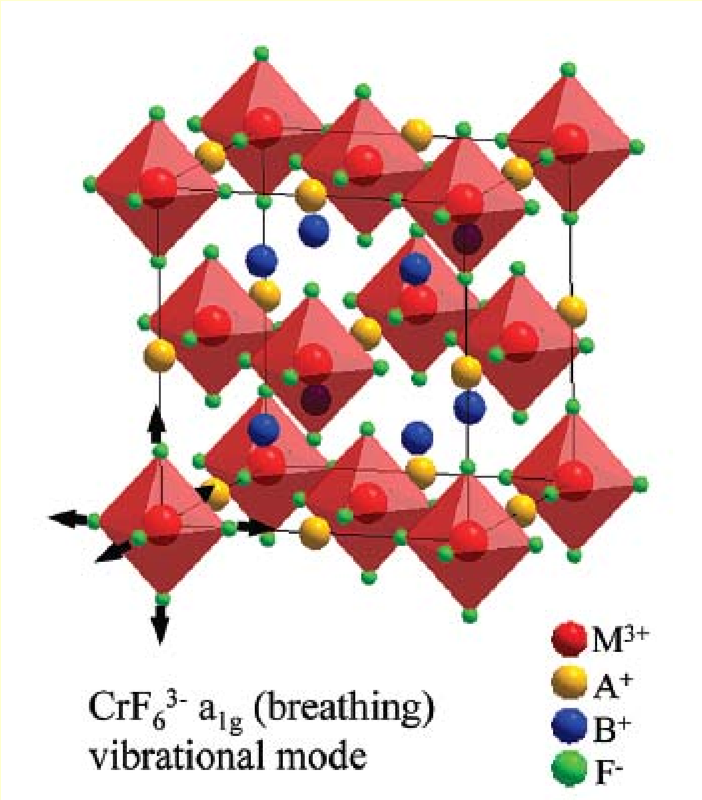
Temperature measurement
Raman - the Stokes and anti-Stokes vibrational excitations

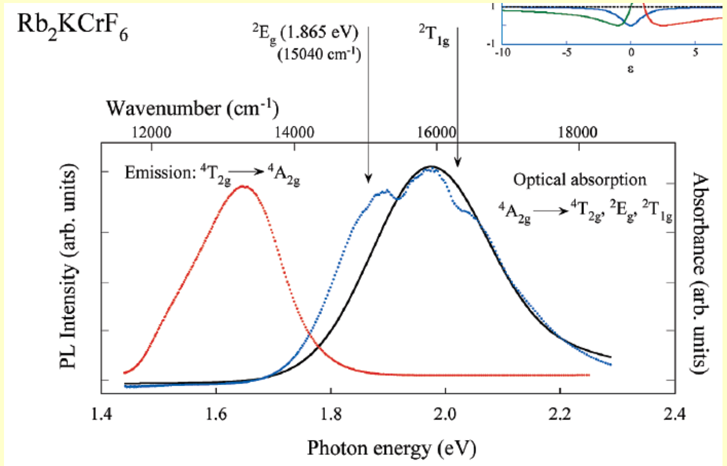
Measurements in DAC

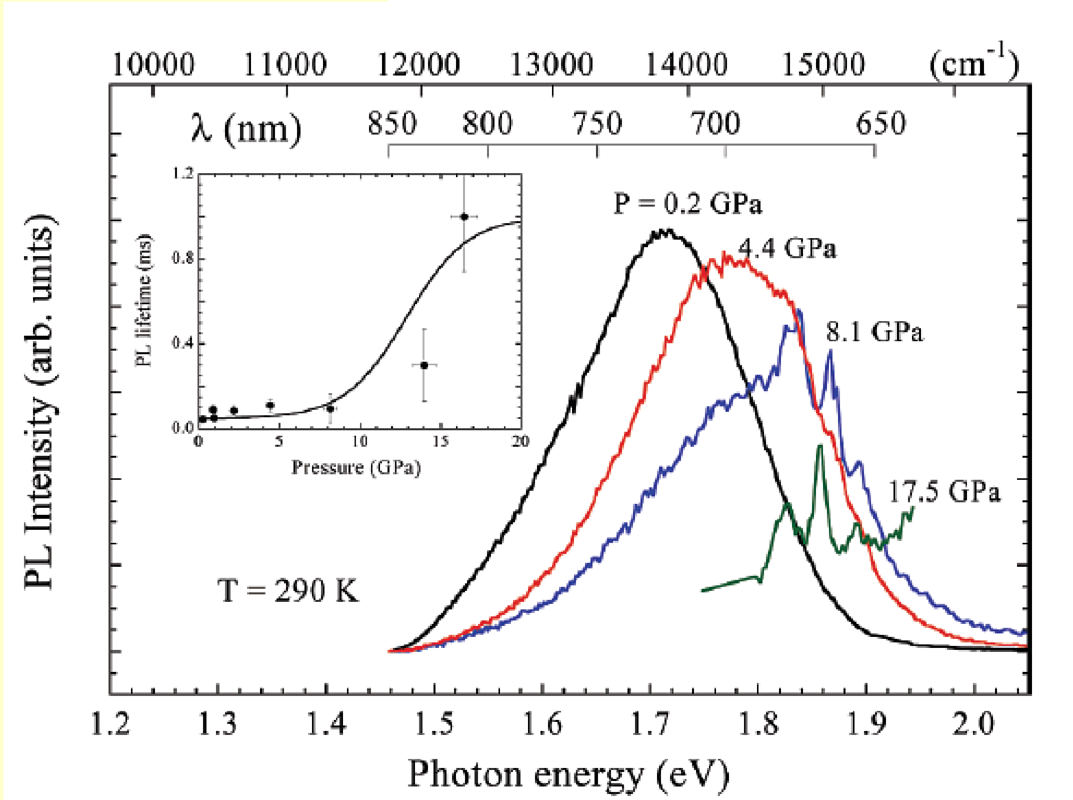
X-ray diffraction (synchrotron)
Optical, UV, IR and Raman spectroscopies
Magnetic measurements
Electric conductivity
Ultrasonic interferometry

Rb_2KCrF_6

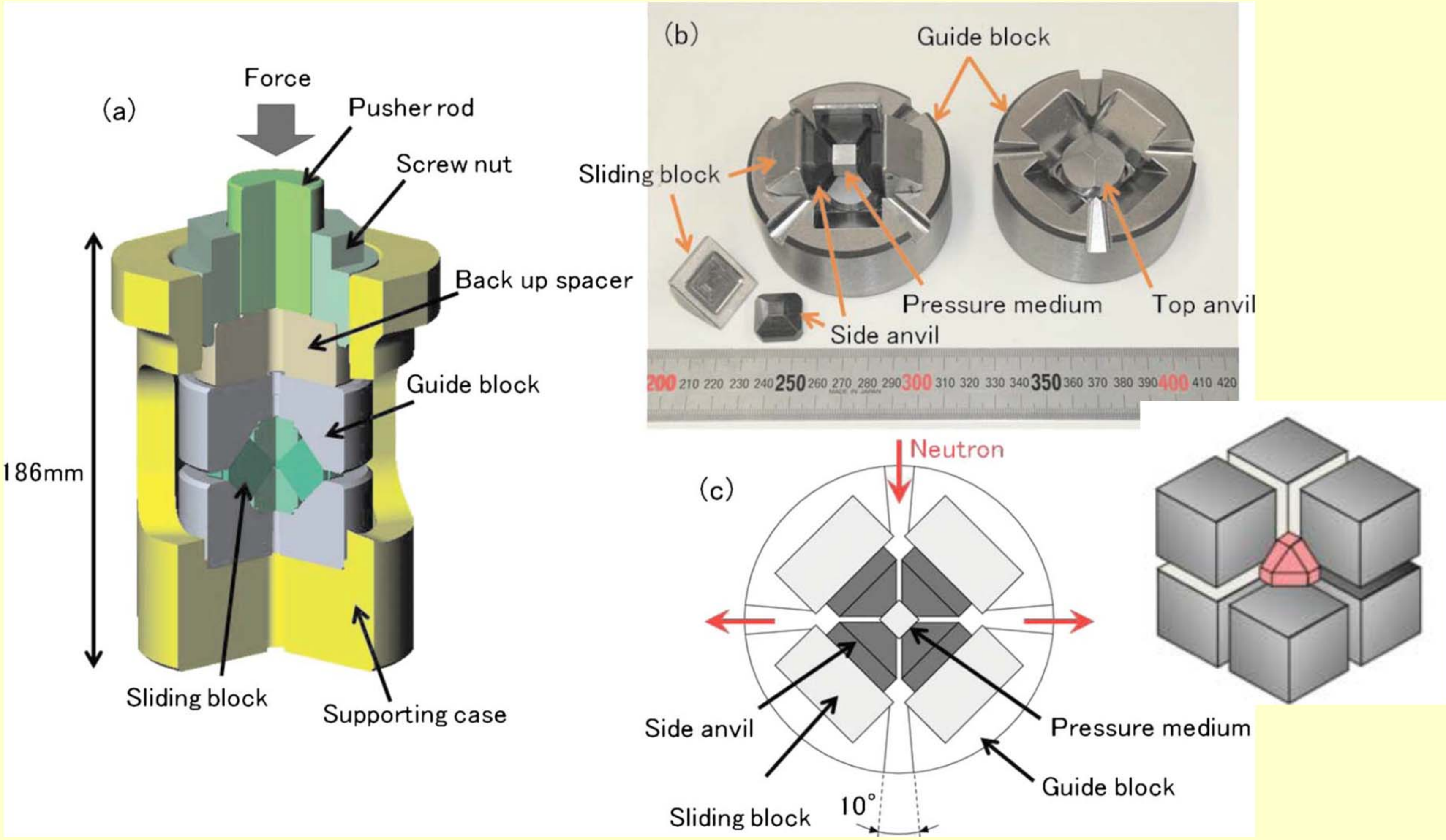
Optical, UV, IR and Raman spectroscopies



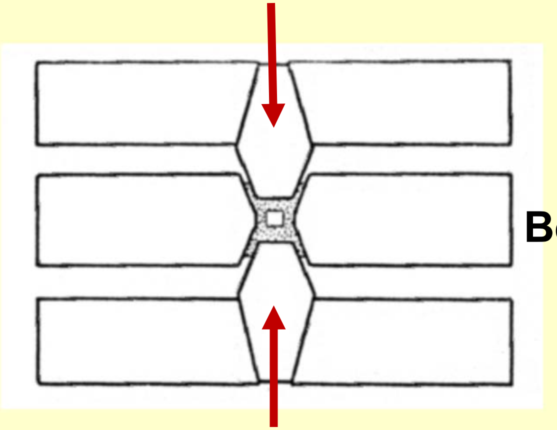




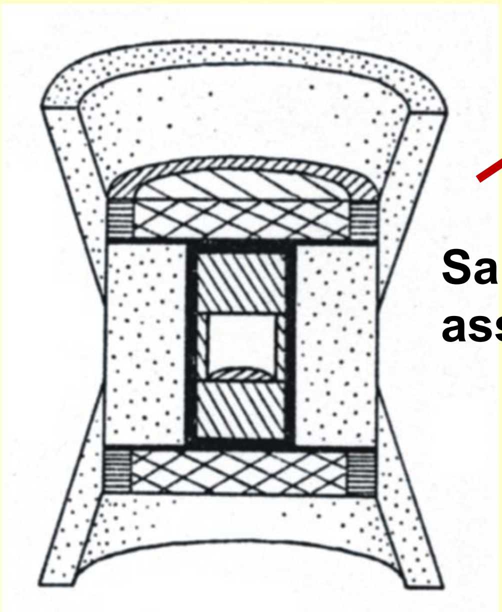
Cubic Anvil Cell



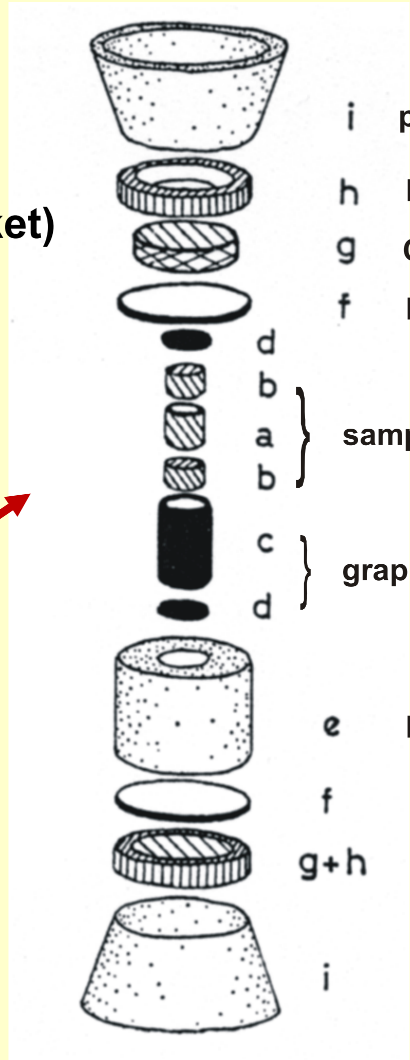
High Pressure Two-Die Belt-Type Apparatus



Belt (gasket)



Sample assembly



i pressure - transmitting medium

h Fe ring (electrical connection)

g Corundum disc (thermal insulation)

f Mo disc (electrical connection)

b, a, b: sample container + lids

c, d: graphite heating mantle

e pressure - transmitting medium

High Pressure Synthesis

High pressures required to access new compounds or high-pressure phases

Some remain stable (metastable) after decompression back to ambient conditions - intact after the pressure and temperature are quenched, a subset of these compounds can persist indefinitely – e.g., diamond

- Delocalization of d-electrons

- Stabilization of high oxidation states (perovskite $CaFeO_3$, $BaNiO_3$)

- Suppression of ferroelectric displacement

- Change in site preferences (Zn: $4 \rightarrow 6$)

MnO_2 + ZnO $\rightarrow$ $ZnMnO_3$ Ilmenite at high pressure, CN = 6:6

Zn[ZnMn]O_4 spinel at normal pressure

High Pressure Synthesis

- **Suppression of $6s^2$ core polarization in Tl^+, Pb^{2+}, Bi^{3+}**

$SnO_2 + Pb_2SnO_4 \rightarrow 2\ PbSnO_3$ perovskite at 7 GPa, 400 °C
At ambient pressure, the reaction provides only SnO_2 and PbO

- **Faster kinetics - $LnFeO_3$, $LnRhO_3$, $LnNiO_3$ – few hours at h.p., at normal pressure need heating for days, $LnFeO_3$, $LnRhO_3$ not formed**

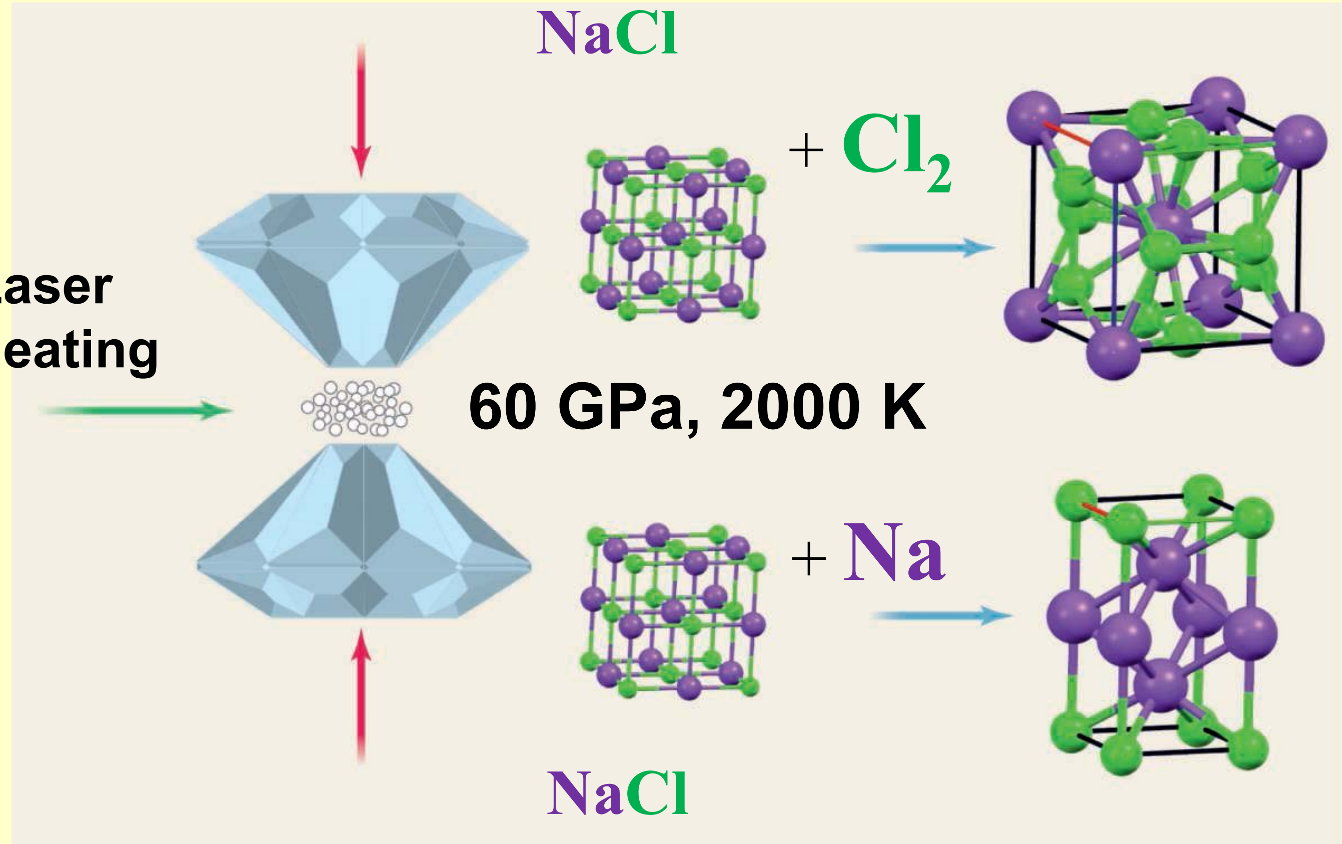
- **Stabilization of new bonds**

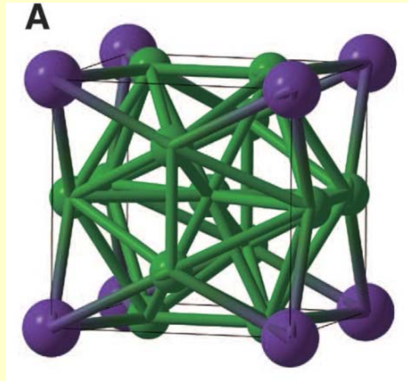
Fe-Bi - no stable intermetallic compounds at ambient pressure
No Fe−Bi bonds known (perovskite $BiFeO_3$: Bi-Fe nonbonding)
Phase diagram - complete immiscibility, even as molten liquids

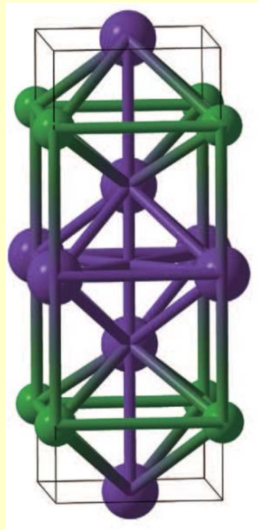
$Fe + Bi \rightarrow FeBi_2$ at 1400 K, 32 GPa

d(Fe−Bi) = 2.72 Å at 30 GPa

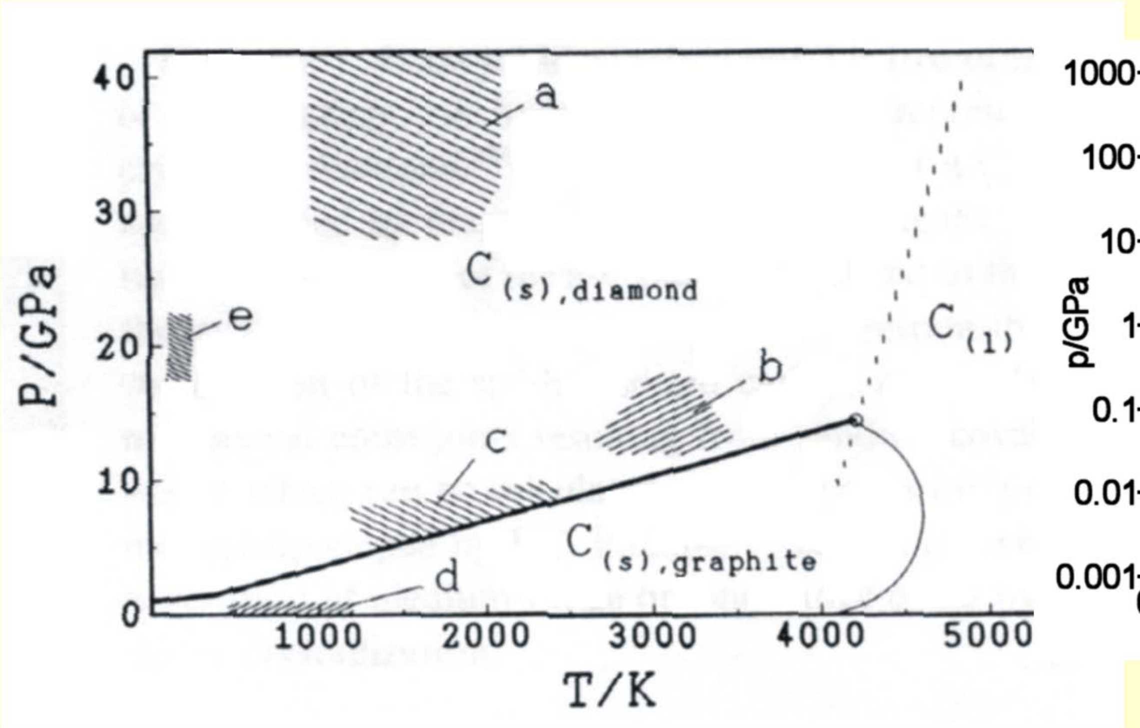
Unusual Stoichiometries under High-Pressure

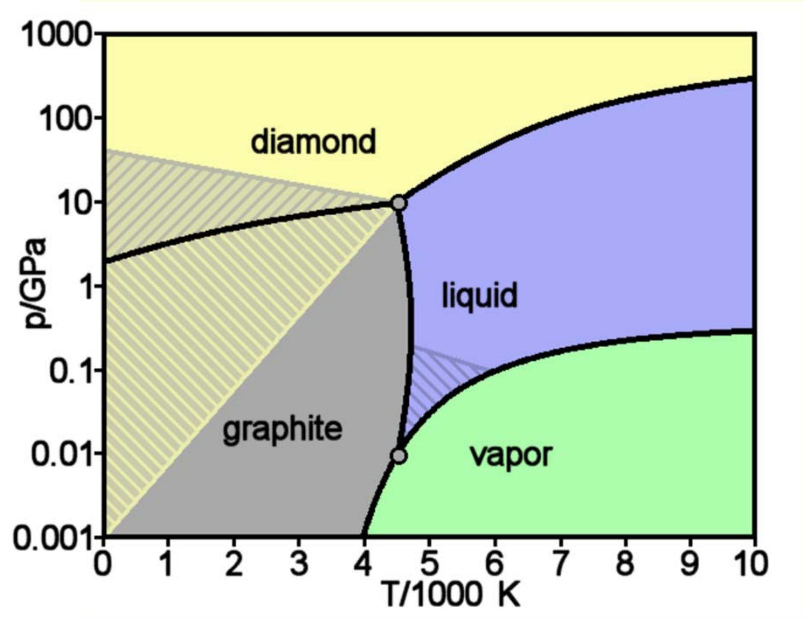






p, T - Diagram of Carbon

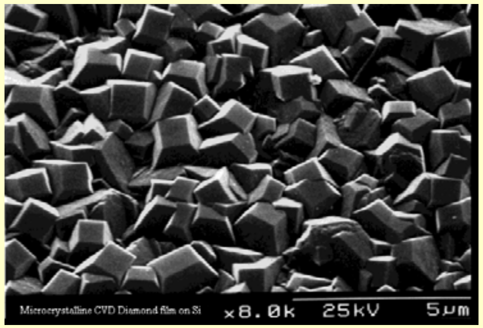




a – shock wave production of diamond
b – high-temperature, high-pressure synthesis of diamond
c – catalytic region for diamond formation
d – CVD diamond
e – transformation of C_{60} into diamond

Diamonds

- Exceptional hardness - the hardest known substance
- Wide spectral range transparency
- Chemical inertness, very resistant to chemical corrosion
- The highest thermal conductivity
- The highest atomic number density
- The highest elastic modulus, very low coefficient of expansion
- Low coefficient of friction, comparable to Teflon
- Biological compatibility
- Good electrical insulator, on doping becomes semiconducting
- Negative electron affinity of H-terminated surface - no energy barrier prevents electrons at the conduction band minimum to exit into the vacuum - photocathodes and cold-cathode emitters



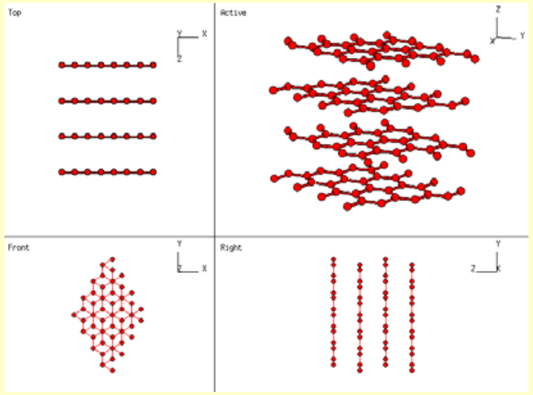
High Pressure High Temperature (HPHT) Synthesis of Diamonds

Difficult to transform graphite into diamond

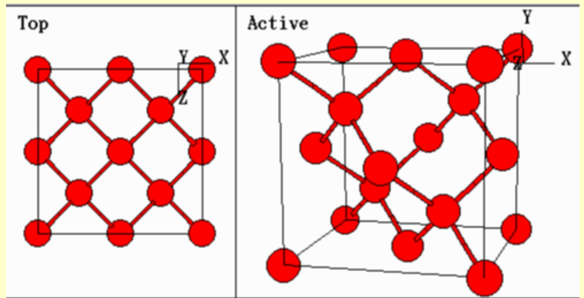
The activation energy required for a sp^2 3-coordinate to a sp^3 4-coordinate structural transformation is very high, so requires extreme conditions

Industrial diamonds (GE, 1954)
made from graphite at 3000 ^{o}C and 13 GPa

$\Delta G° = +\ 2.9$ kJ
$\Delta\ H°_r = +\ 1.86$ kJ/mol
$\Delta S° = -3.36$ J/K

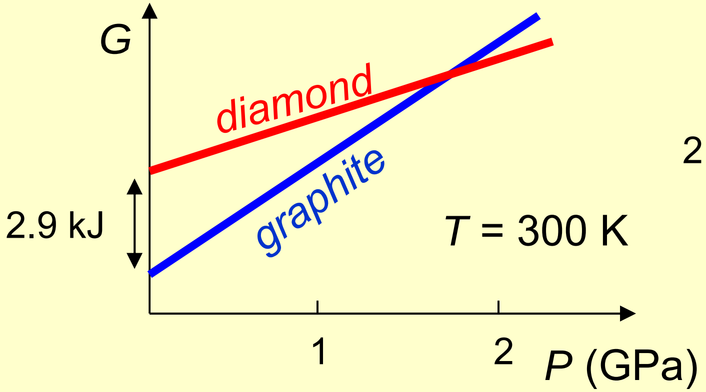


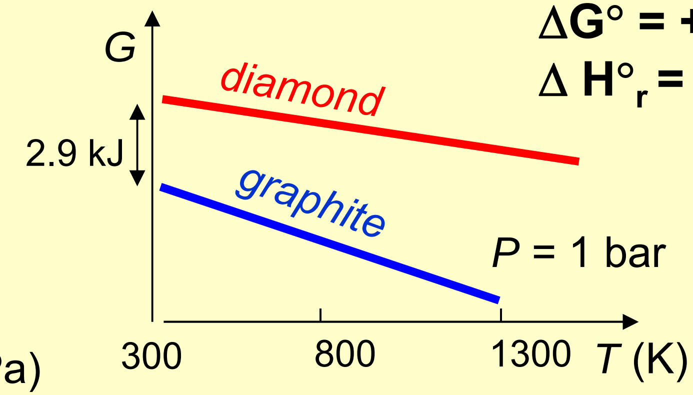
Graphite → Diamond



H. Tracy Hall
(1919 – 2008)

HPHT Synthesis of Diamonds





$\Delta G° = + 2.9$ kJ
$\Delta H°_r = 1.86$ kJ/mol

The molar volume
$V_g = 5.31\ 10^{-6}\ m^3$
$V_d = 3.42\ 10^{-6}\ m^3$

integrate

$$\left(\frac{\partial G}{\partial P}\right)_{T,N} = V \quad \Rightarrow \quad \begin{aligned} G_g &= V_g P = 5.31 \times 10^{-6} P \\ G_d &= V_d P = 2900 + 3.42 \times 10^{-6} P \end{aligned}$$

$P_{gd} = 1.534\ 10^9$ Pa

$S°_g = 5.74$ J/K
$S°_d = 2.38$ J/K
$\Delta S° = -3.36$ J/K

$\Delta G° = \Delta H° - T\,\Delta S°$

Higher T makes g more stable than d

$$\log \text{rate} = \text{constant} - \frac{\Delta V^{\ddagger} P}{RT}$$

$\Delta V^{\pm} > 0$

Higher pressure slows down the reaction

Higher temperature speeds up the reaction

Synthesis of Diamonds

Ways of getting round the difficulty

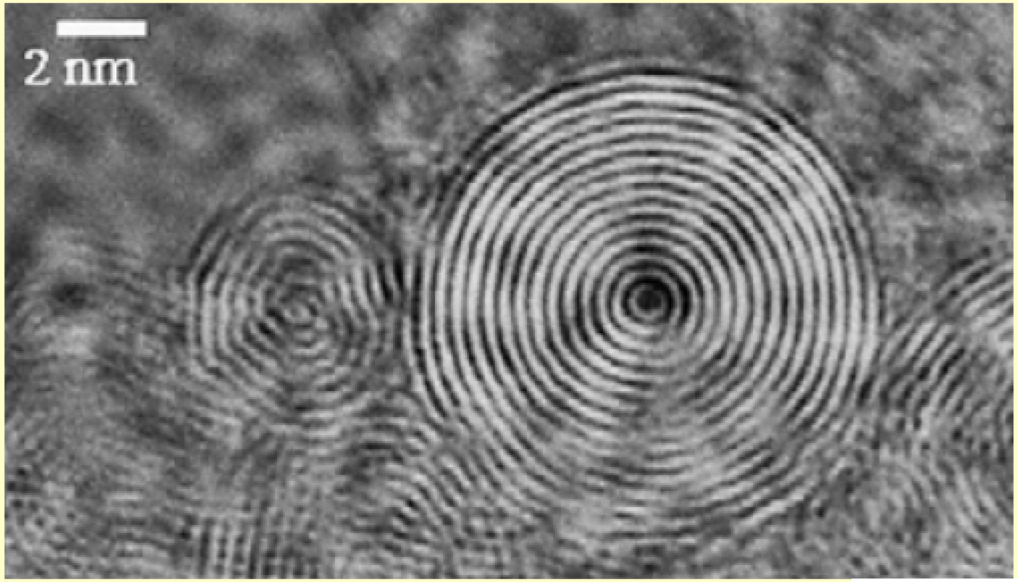
♦ Catalyst: transition metals (graphite is dissolved in molten metal: Fe, Ni, Co, 6 GPa, 1000 °C), alloys (Nb-Cu), $CaCO_3$, hydroxides, sulfates, P (7.7 GPa, 2200 °C, 10 min)

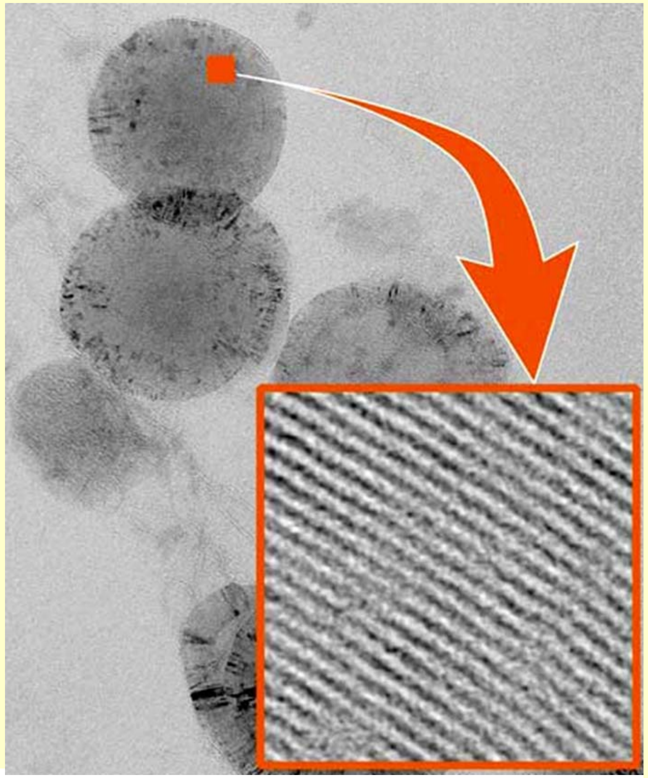
♦ Squeezing (uniaxial not hydrostatic pressure), no heating, buckyball carbons are already intermediate between sp^{2-3}
C_{60}, diamond anvil, 25 GPa instantaneous transformation to bulk crystalline diamond, highly efficient process, fast kinetics

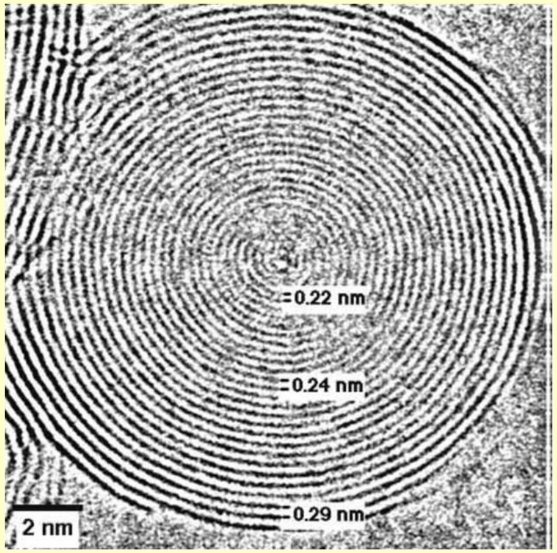
♦ Carbon onions, electron irradiation of graphite, concentric spherical graphite layers, spacing decreases from 3.4 Å to 2.2 Å in the onion center, 100 GPa, 200 keV beam, in several hours, pressureless conversion to diamond

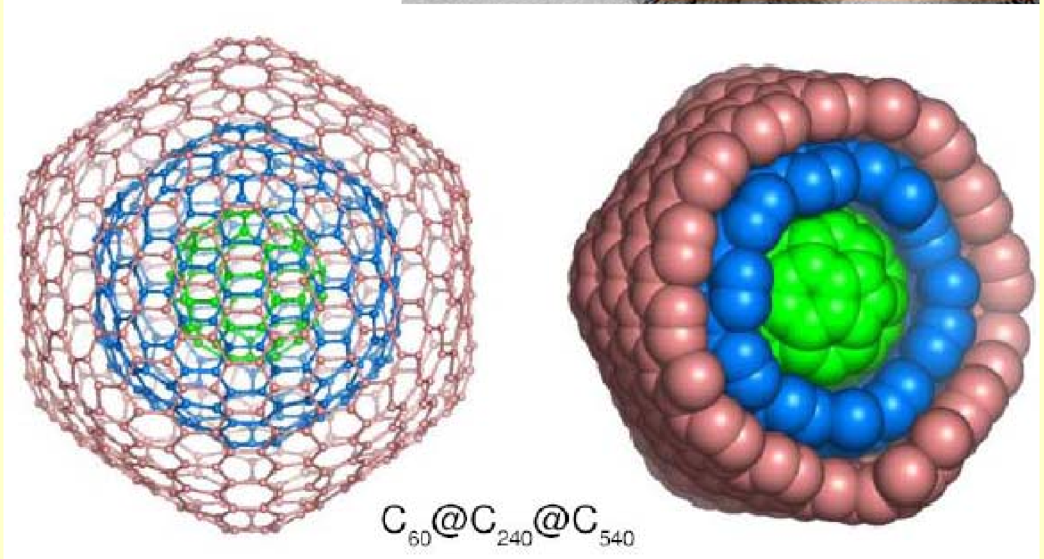
♦ Using CH_4/H_2 microwave discharges to create reactive atomic carbon whose valencies are more-or-less free to form sp^3 diamond, atomic hydrogen saturates the dangling bonds, dissolves soot faster than diamond, a route for making diamond films, 50 mm

Carbon Onions

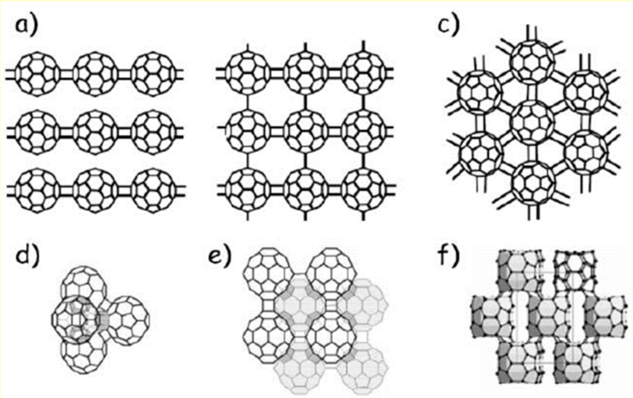


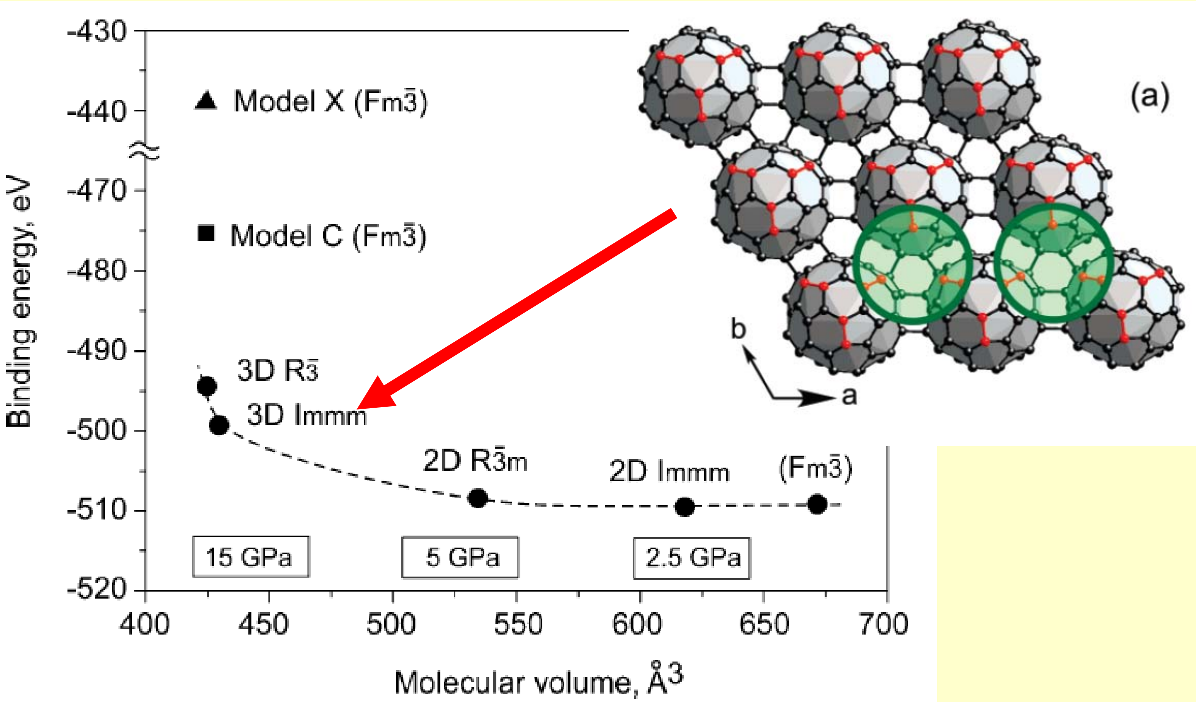


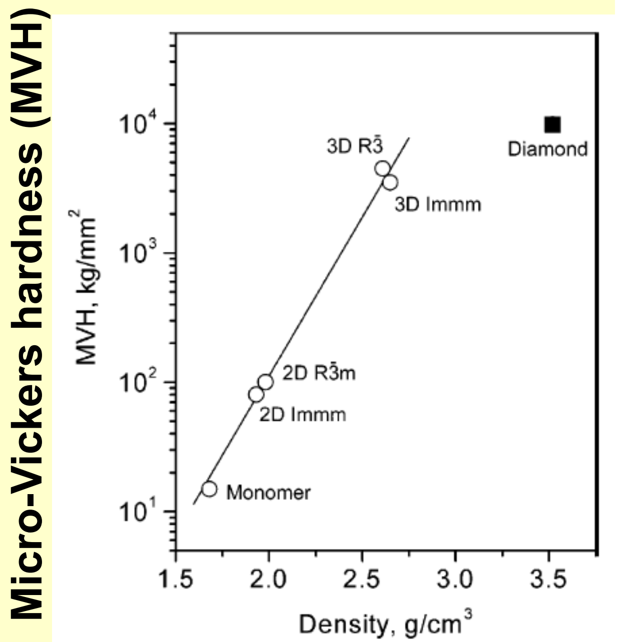




Topochemical 3D Polymerization of C_{60} under High P and T

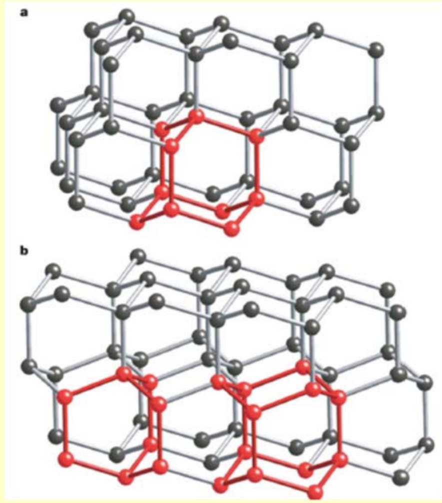






C_{60} phase	no. of covalently bonded neighbors	MVH, kg/mm^2	d_{calcd} g/cm^3	d_{obs} g/cm^3
monomer	0	15	1.684	1.68
2D *Immm*	4	80	1.936	1.93
2D $R\bar{3}m$	6	100	2.004	1.98
3D *Immm*	8	3,500	2.78	2.65
3D $R\bar{3}$	12	4,500	2.81	2.61
Diamond[a]		10,000	3.52	
c-BN[a]		5,000		

Lonsdaleite - Hexagonal Diamond



Discovered in the Canyon Diablo meteorite
(AZ, 50 ky, 30 t)
Found also in some rocks

May be stronger and stiffer than diamond

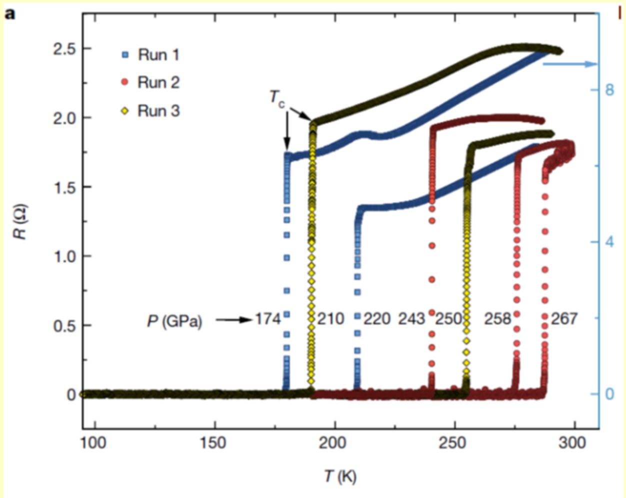
Synthesized in the laboratory at static pressure of 130 kbar and temperature over 1000 °C from well-crystallized graphite in which the *c* axes of the crystallites are parallel to each other and to the direction of compression

The crystal structure is hexagonal with a = 2.52 Å and c = 4.12 Å. density is 3.51 g/cm^3, same as cubic diamond

Prepared also from crystalline graphite by a method involving intense shock compression and strong thermal quenching

Pressure and Electrical Conductivity

- Electrical conductivity of semiconductors increases with T
- The change of conductivity with T is one way of measuring the band gap
- Conductivity also increases with p, because atoms are pushed closer together
- All elements eventually adopt metallic structures at high p
- The interior of Jupiter is thought to contain metallic hydrogen!
- Room-temperature superconductivity in a carbonaceous sulfur hydride - $(H_2S)(CH_4)H_2$ - achieved at 287 K and 270 GPa



Pressure and Electrical Conductivity

Sodium - BCC structure at ambient conditions, FCC at 65 GPa, further transformations
Prediction: will transform under pressure into insulating states, owing to pairing of alkali atoms

Pressure-induced transformation of Na into an optically transparent phase at 200 GPa

Core electrons overlap, p–d hybridizations of valence electrons and their repulsion by core electrons into the lattice interstices, ionic cores and localized interstitial electron pairs, in analogy to electrides

Hexagonal
Na1 octahedral
Na2 triangular prismatic