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 250 GPa, 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

- **Anvils, diamond, tetrahedral and octahedral**
- **Shock waves (km s^{-1})**
- **Explosions, projectiles**
- **Go to another planet: Jupiter**

(hydrogen is metallic at 100 Gbar)

Earth

Core 3.4 Mbar = 340 GPa, 6000 K
ε-Fe hcp

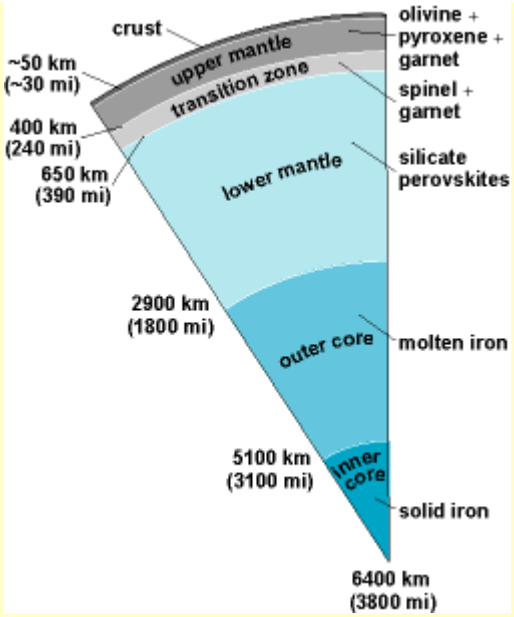
$MgSiO_3$ most abundant silicate mineral within our planet !

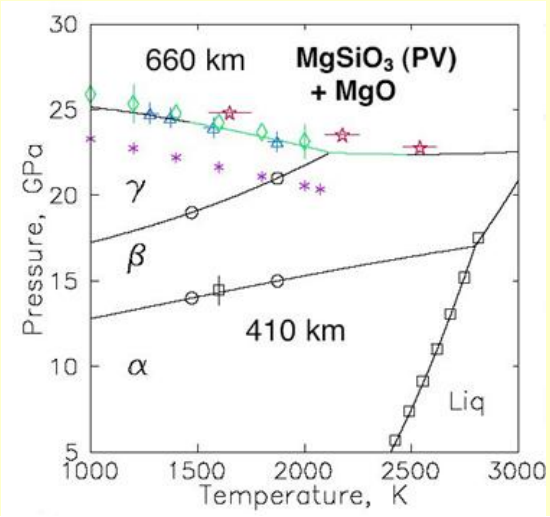
Olivine Mg_2SiO_4 >

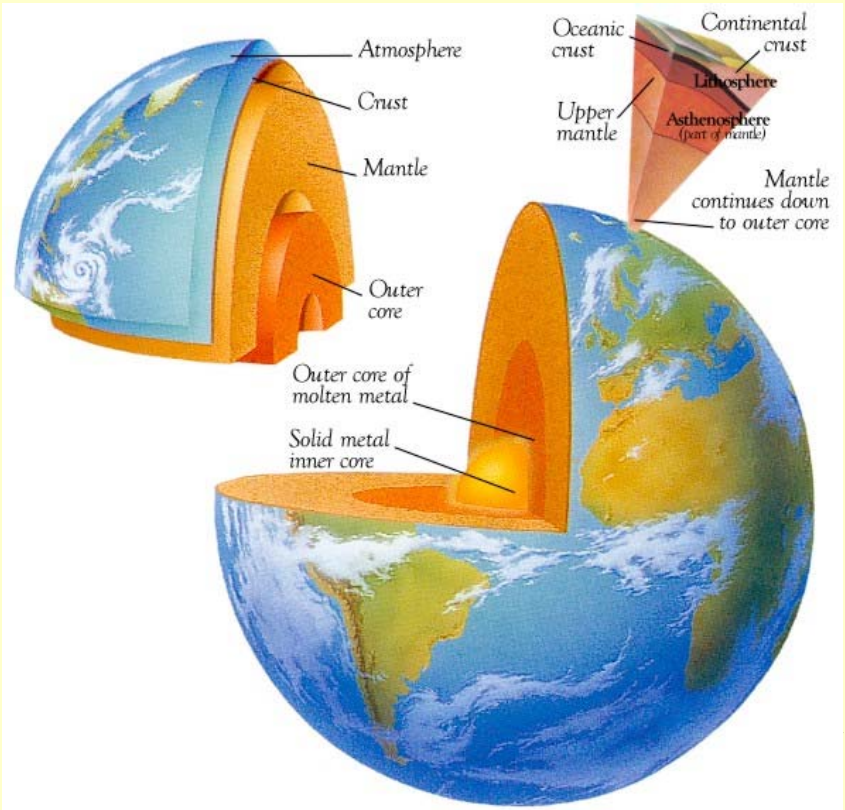
pyroxene (silicate chains) > spinel Mg_2SiO_4

ilmenite > garnet (HT) >

perovskite $MgSiO_3$ Si CN = 6

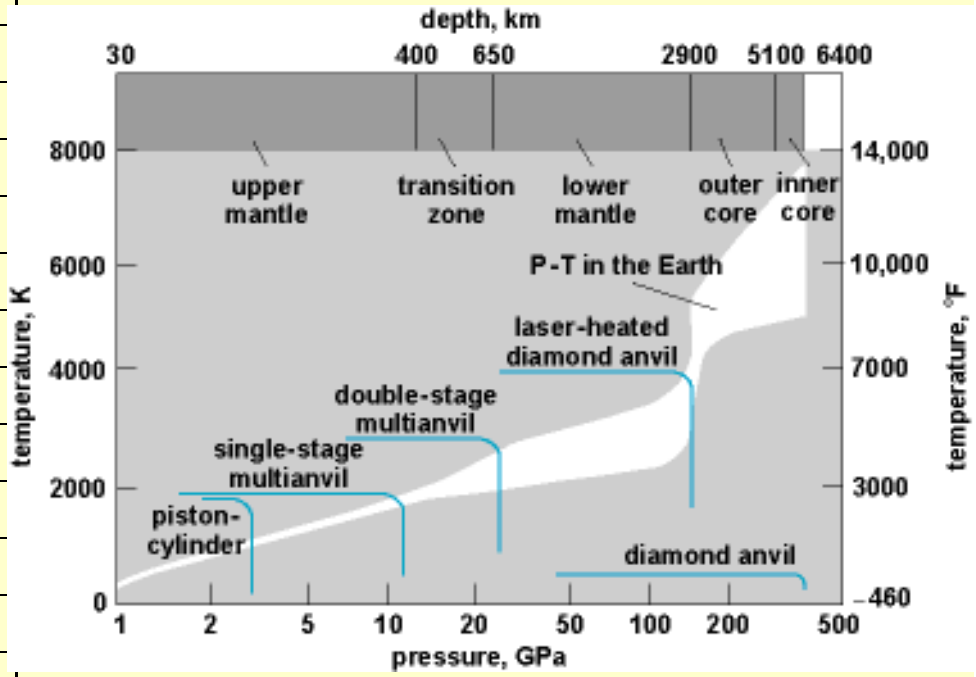






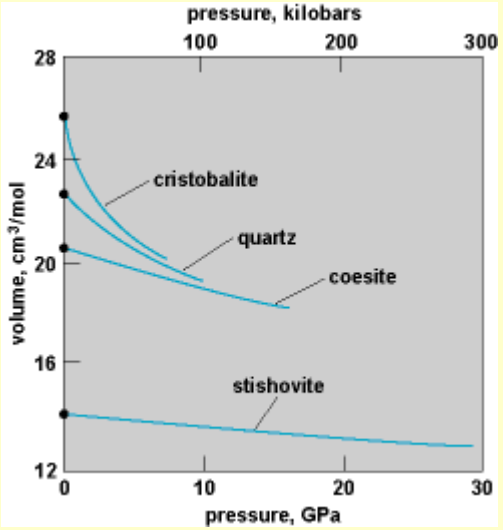
PRESSURE SCALE

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



Dry High-Pressure Methods

Pressure techniques useful for synthesis of unusual structures
TD metastable yet kinetically stable when pressure released
= pressure and temperature quenching
reconstructive transformation hindered at low temperature
insufficient thermal energy for bond-breaking



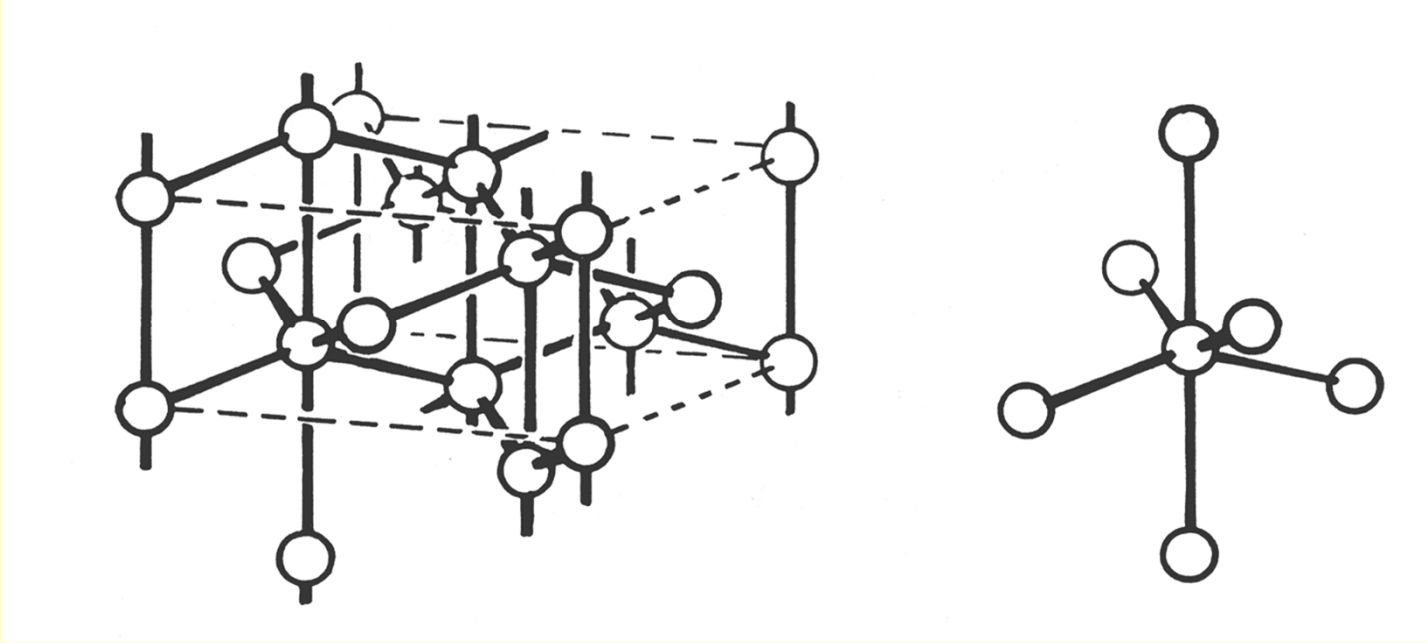
- **high pressure phases**
- **higher density**
- **higher coodination number**
- **higher symmetry**
- **transition to from nonmetal to metal**
- **band mixing**

Pressure/Coordination Number Rule: increasing pressure – higher CN
Pressure/Distance Paradox: increasing pressure – longer bonds

Dry High-Pressure Methods

Gray Sn (diamond type, stable below 13 °C, semiconductor)
Coordination number 4, Sn-Sn bond length 281 pm

White Sn (metallic)
Coordination number 6, Sn-Sn bond lengths 302 and 318 pm

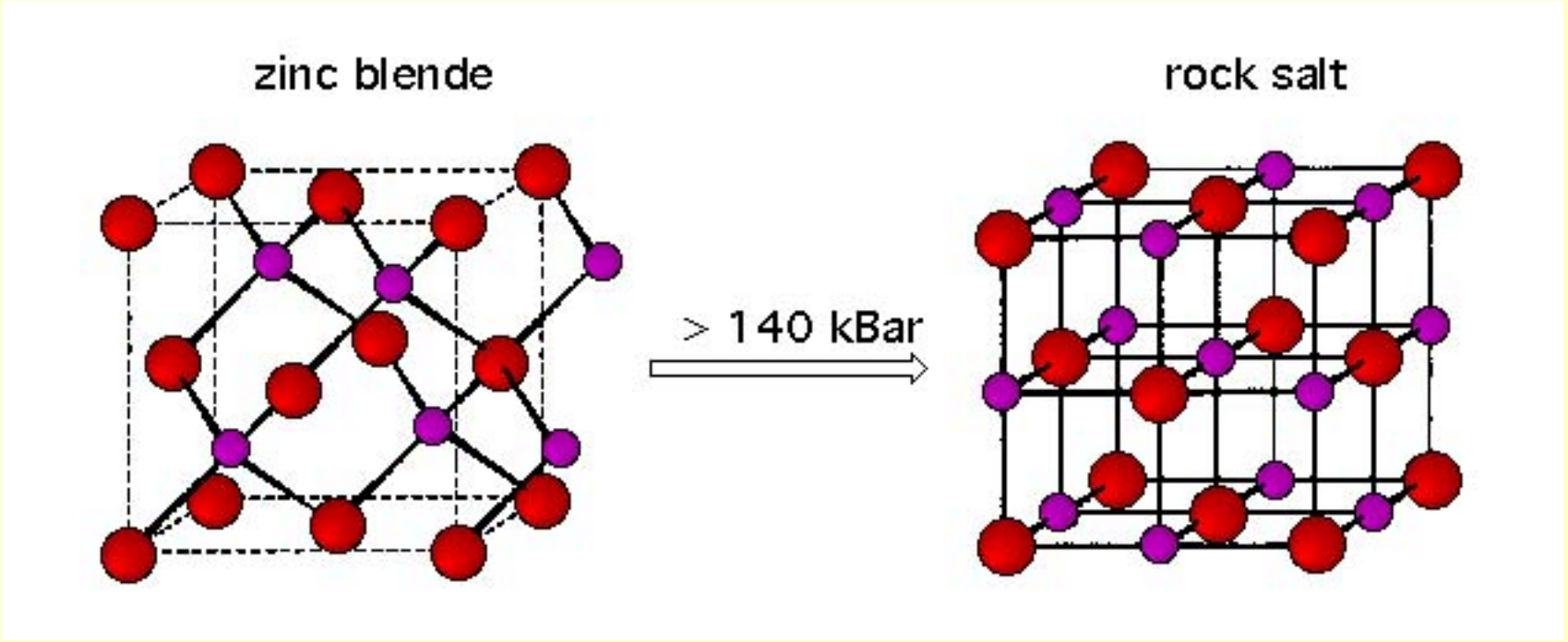


Dry High-Pressure Methods

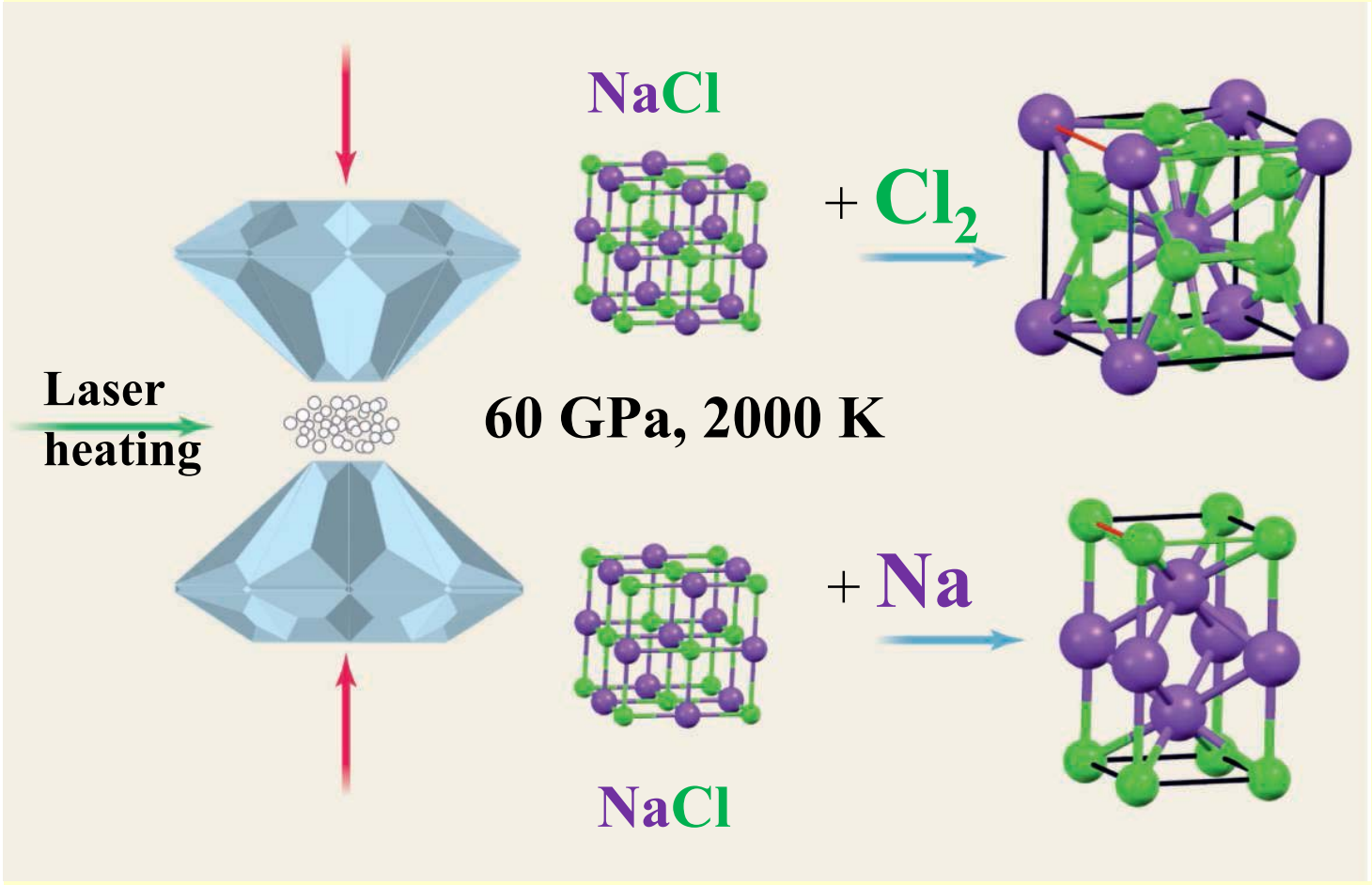
Examples of high pressure polymorphism for some simple solids

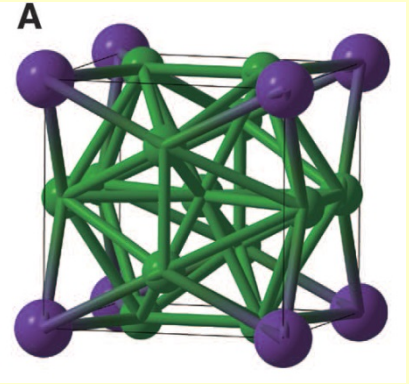
Solid	Normal structure and coordination number	Typical transformation conditions P(kbar)	Typical transformation conditions T(^{o}C)	High pressure structure and coordination number
C	Graphite 3	130	3000	Diamond 4
CdS	Wurtzite 4:4	30	20	Rock salt 6:6
KCl	Rock salt 6:6	20	20	CsCl 8:8
SiO_2	Quartz 4:2	120	1200	Rutile 6:3
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

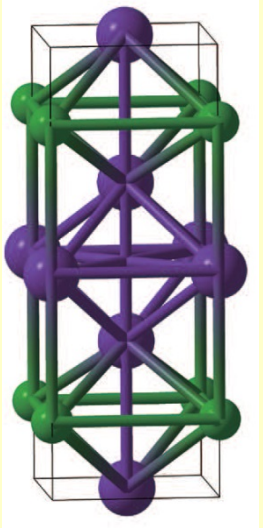
High-Pressure Phase Transformations



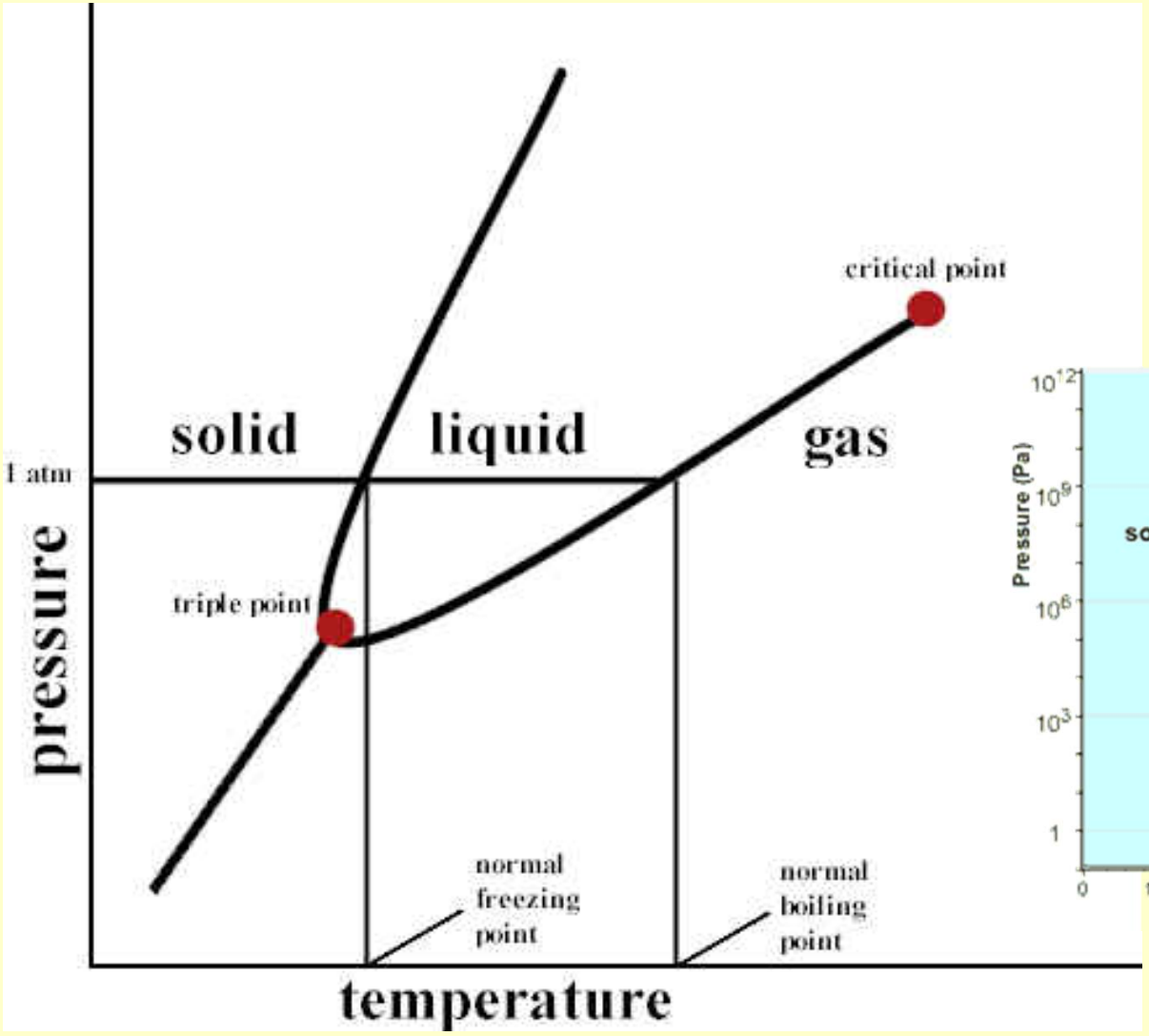
Unusual Stoichiometries under High-Pressure

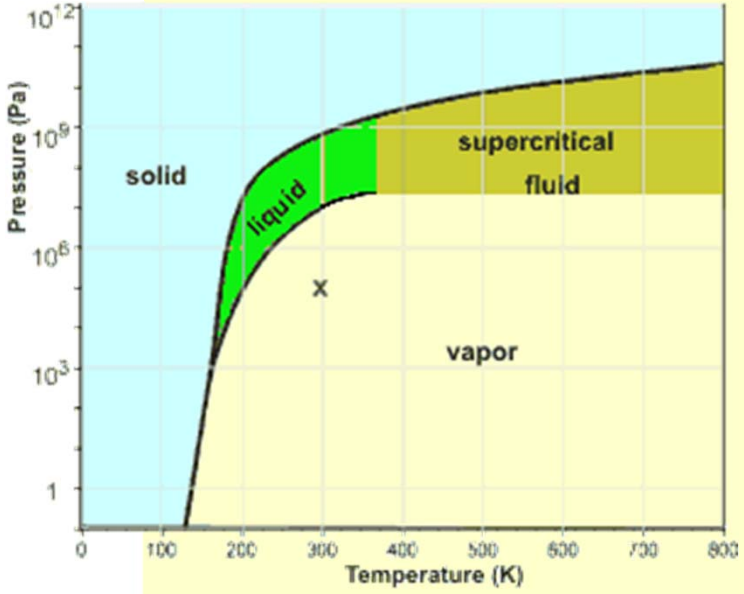


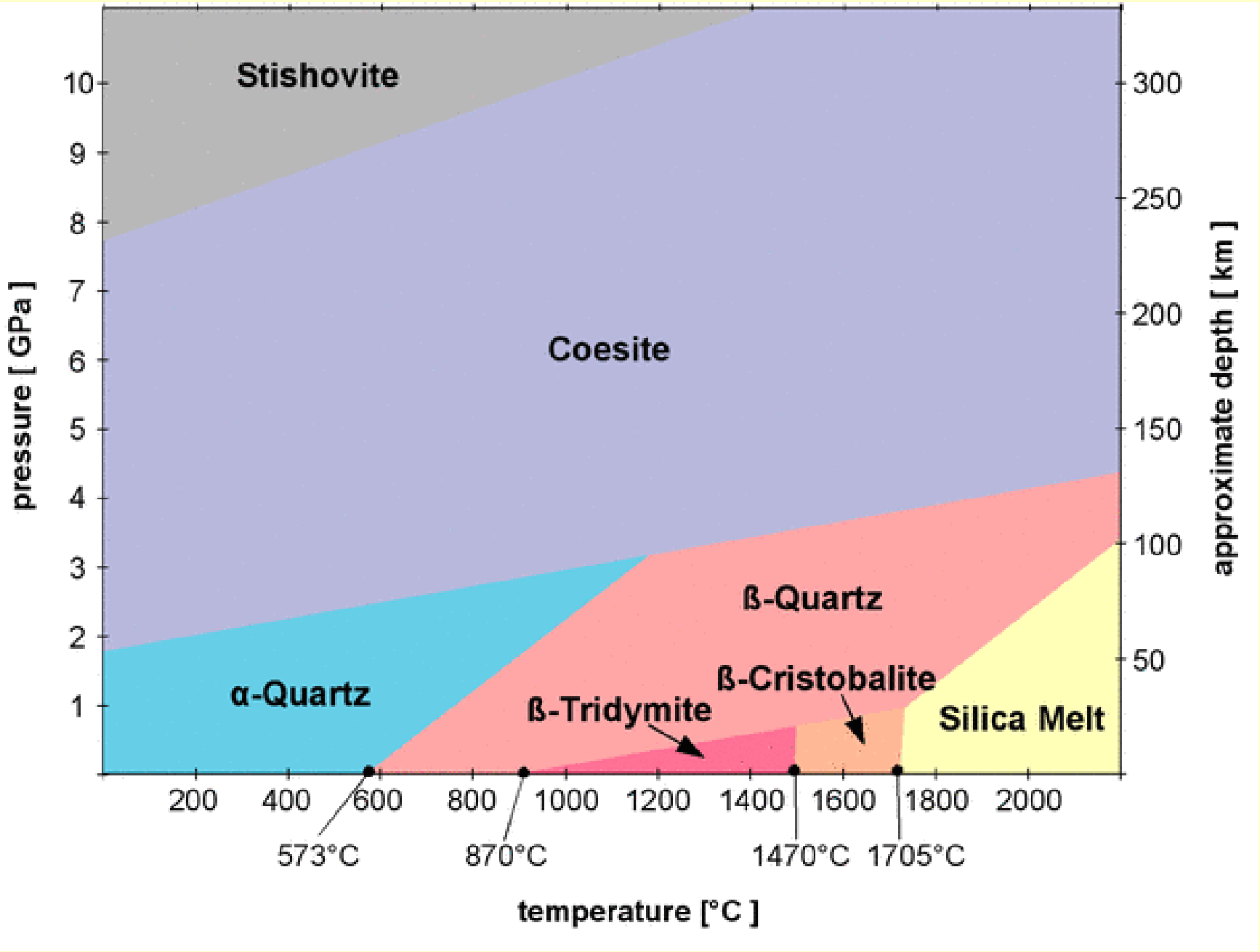


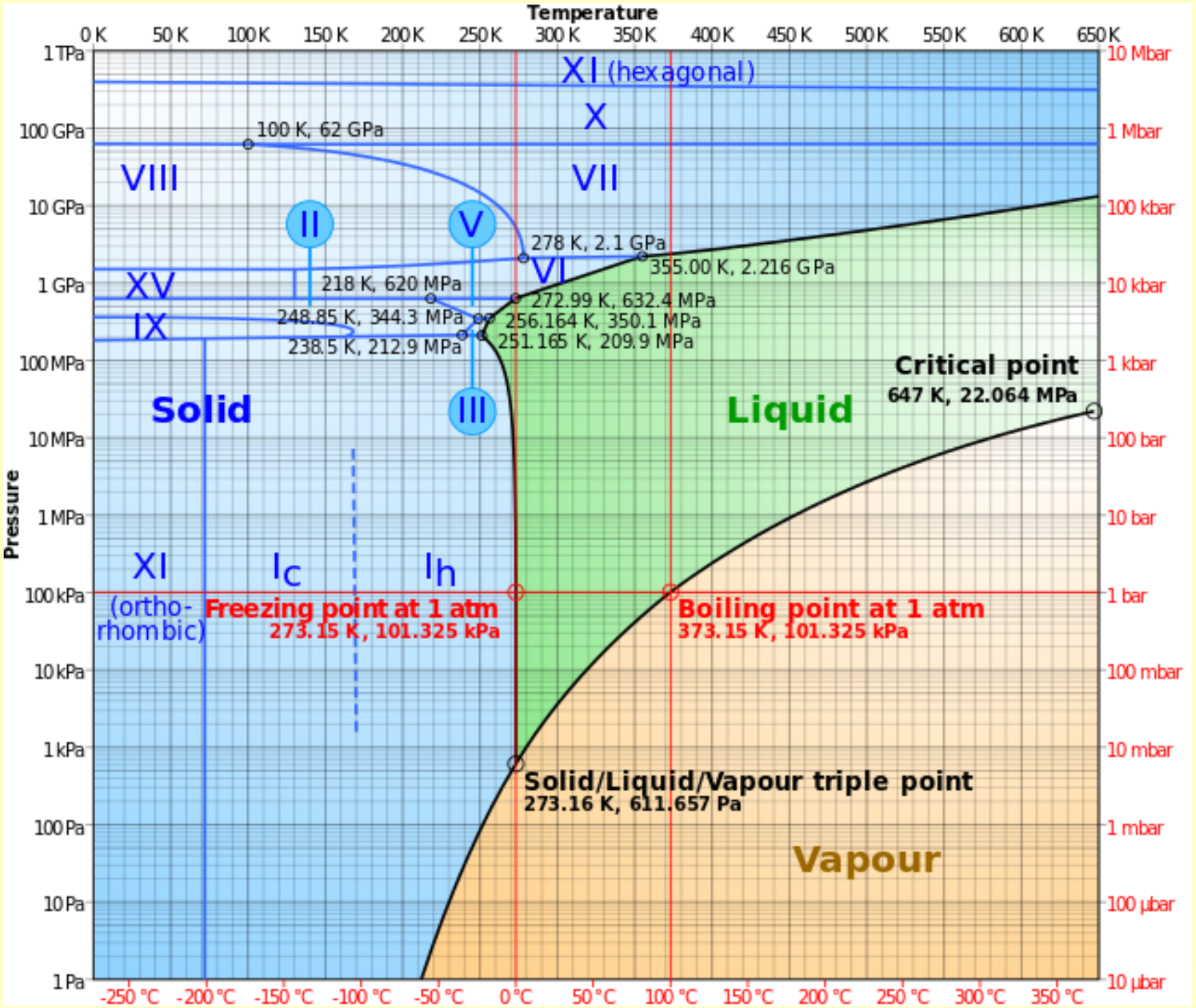


p-T Phase Diagrams






Stishovite
Coesite
ß-Quartz
α-Quartz
ß-Tridymite
ß-Cristobalite
Silica Melt
pressure [GPa]
approximate depth [km]
temperature [°C]
10
9
8
7
6
5
4
3
2
1
300
250
200
150
100
50
200
400
600
800
1000
1200
1400
1600
1800
2000
573°C
870°C
1470°C
1705°C


Temperature
0 K
50 K
100 K
150 K
200 K
250 K
300 K
350 K
400 K
450 K
500 K
550 K
600 K
650 K
Pressure
1 TPa
100 GPa
10 GPa
1 GPa
100 MPa
10 MPa
1 MPa
100 kPa
10 kPa
1 kPa
100 Pa
10 Pa
1 Pa
10 Mbar
1 Mbar
100 kbar
10 kbar
1 kbar
100 bar
10 bar
1 bar
100 mbar
10 mbar
1 mbar
100 µbar
10 µbar
-250 °C
-200 °C
-150 °C
-100 °C
-50 °C
0 °C
50 °C
100 °C
150 °C
200 °C
250 °C
300 °C
350 °C
XI (hexagonal)
X
VIII
VII
II
V
VI
XV
IX
III
100 K, 62 GPa
278 K, 2.1 GPa
355.00 K, 2.216 GPa
218 K, 620 MPa
272.99 K, 632.4 MPa
248.85 K, 344.3 MPa
256.164 K, 350.1 MPa
238.5 K, 212.9 MPa
251.165 K, 209.9 MPa
Solid
Liquid
Critical point
647 K, 22.064 MPa
XI
(ortho-
rhombic)
Ic
Ih
Freezing point at 1 atm
273.15 K, 101.325 kPa
Boiling point at 1 atm
373.15 K, 101.325 kPa
Solid/Liquid/Vapour triple point
273.16 K, 611.657 Pa
Vapour

Water

17 phases of ice

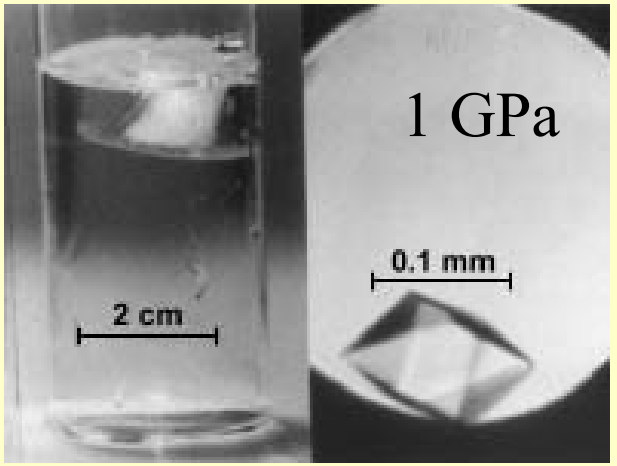
Ice-VII m.p. 100 °C

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

$MgSiO_3$ most abundant silicate mineral within our planet !

pyroxene (silicate chains)

ilmenite > garnet > perovskite Si CN = 6

Condensed gases

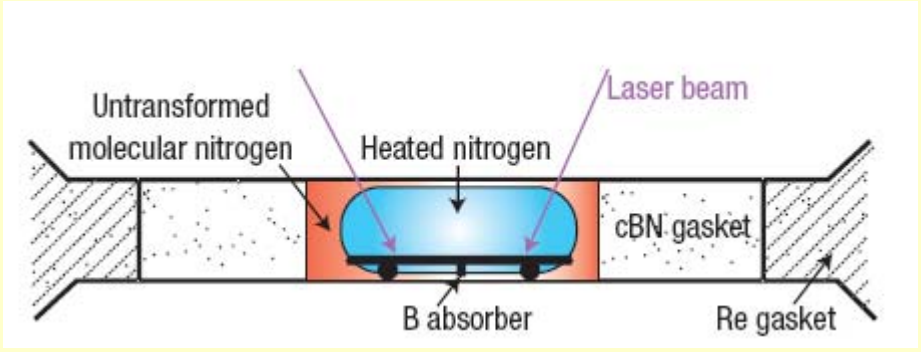
H_2 metallic conductivity in dense fluid hydrogen

$H_2^+ H_2^-$

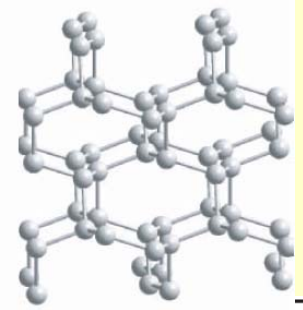
$NO_2 + N_2O$ $NO^+ NO_3^-$ calcite

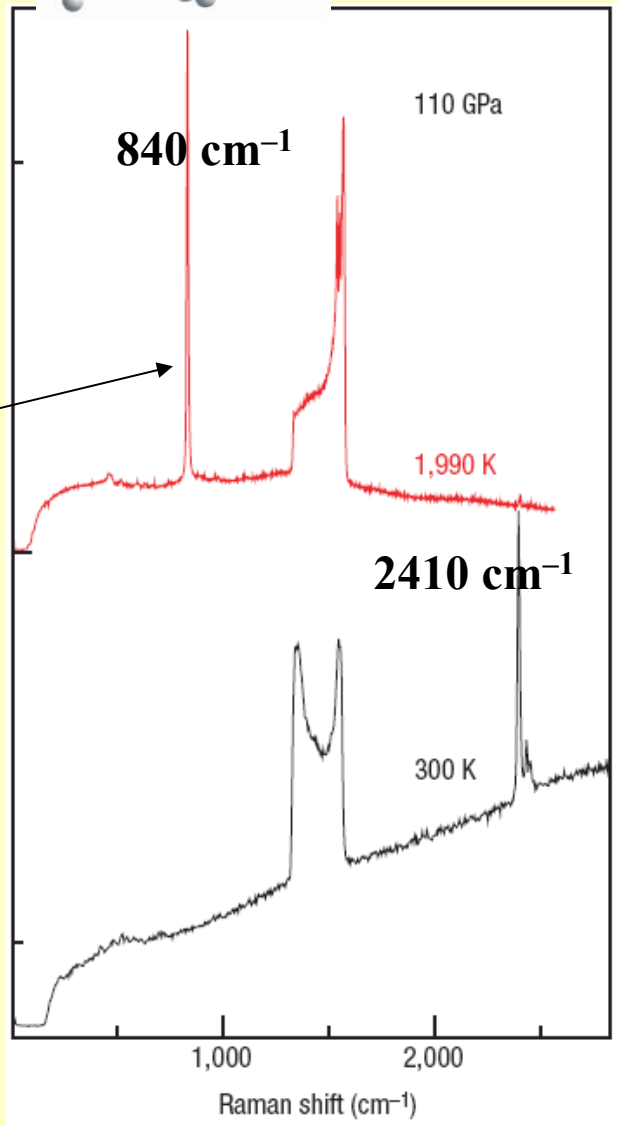
N_2 semiconducting oligomers $(-N-)_x$ at 100-240 GPa

cubic diamond 110 GPa, 2000 K

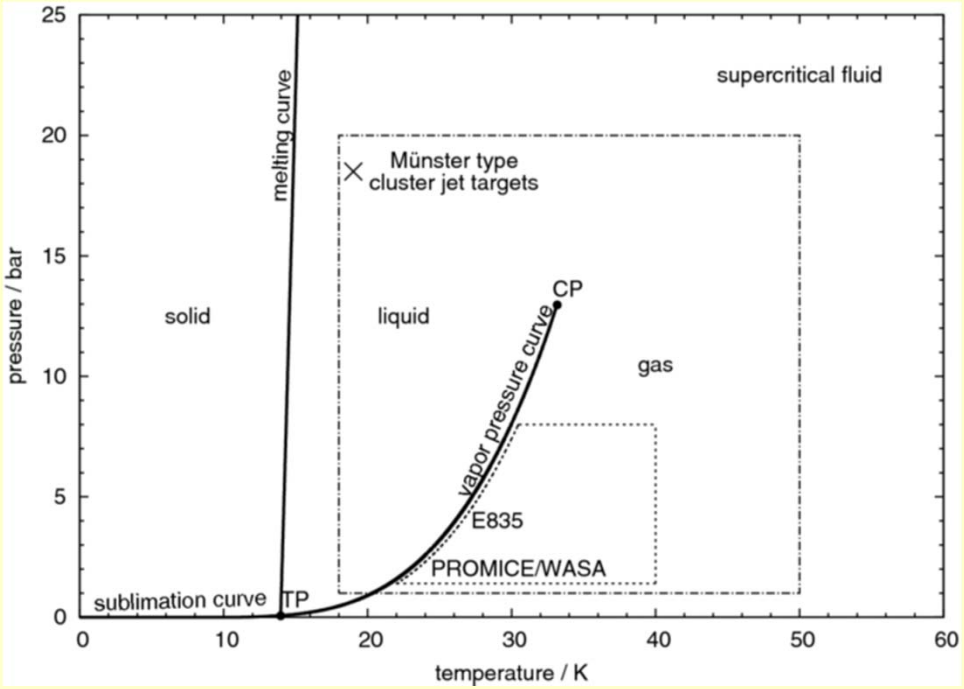


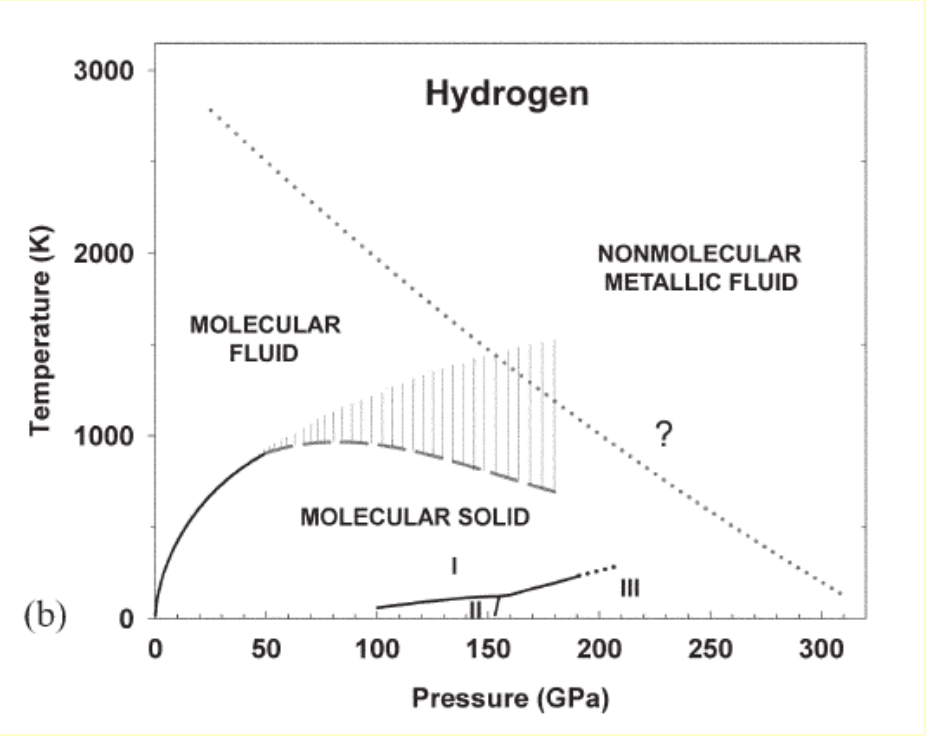
Heating: 1-μm B plate (absorber of laser radiation rests on c-BN pieces that thermally insulate the plate from the bottom anvil. The sample squeezed between the anvils is surrounded by the c-BN/epoxy gasket followed by the metallic (Re) supporting ring.

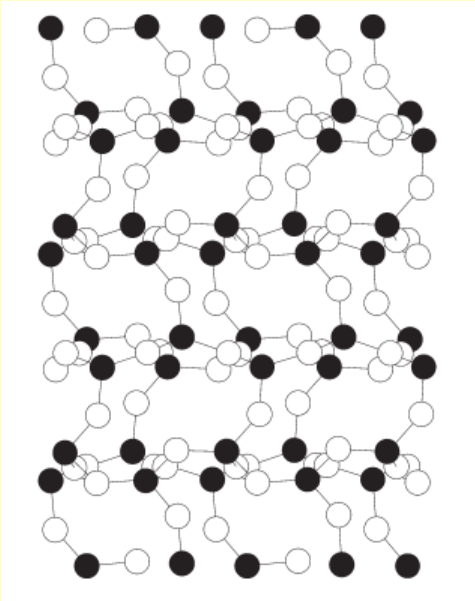




Phase Diagram of Hydrogen







Phase Diagram of CO_2

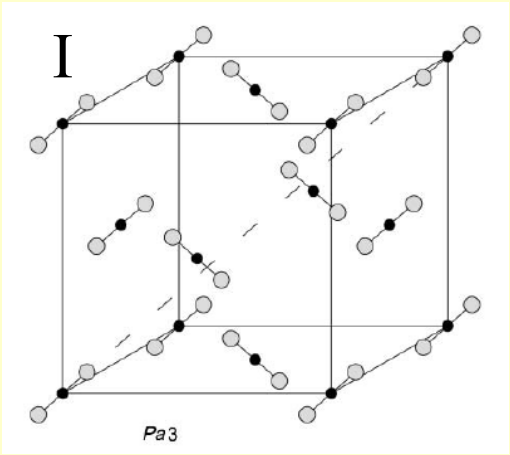
CO_2-V
Quartz
superhard

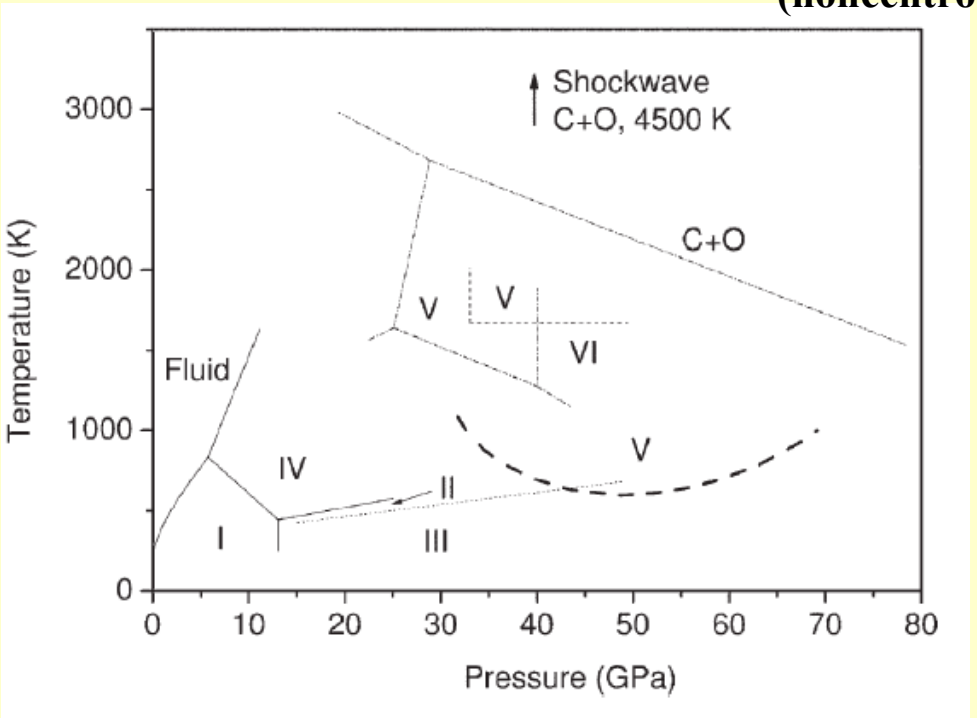
CO_2 heating at 10-20 GPa

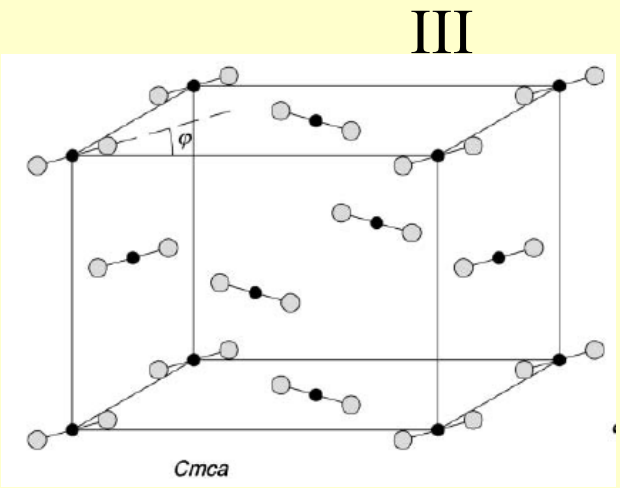
sp^3 bonded CO_4

cristobalite, tridymite

40 GPa quartz
(noncentrosymmetric)







Reaction Equlibrium and Pressure

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

$$A \rightleftarrows C$$

$$K = \frac{C}{A}$$

$$\Delta G^0 = -RT \ln K$$

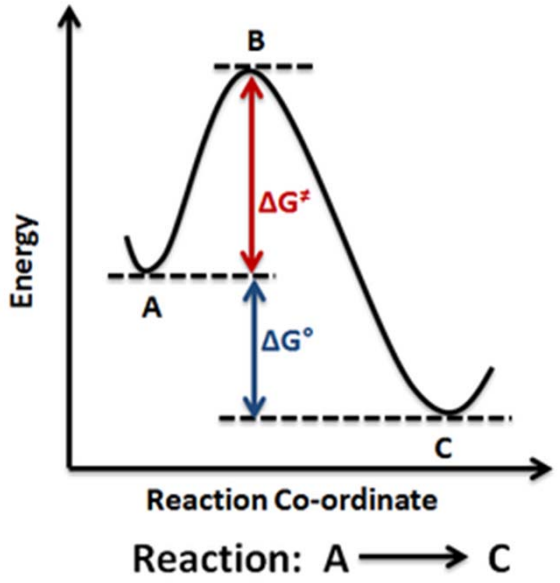
$$\left(\frac{\partial RT \ln K}{\partial P}\right)_T = -\Delta V^0$$

Associative type = negative ΔV^0

K increases with increasing pressure

Dissociative type = positive ΔV^0

K decreases with increasing pressure

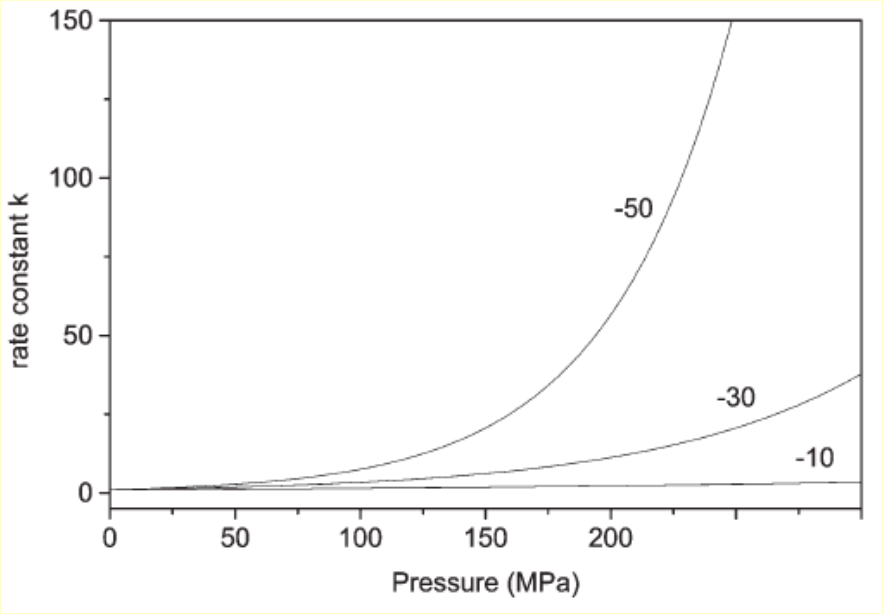


$$\left(\frac{\partial \ln k}{\partial T}\right)_P = -\frac{E_a}{RT}$$

Reaction Kinetics

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

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



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

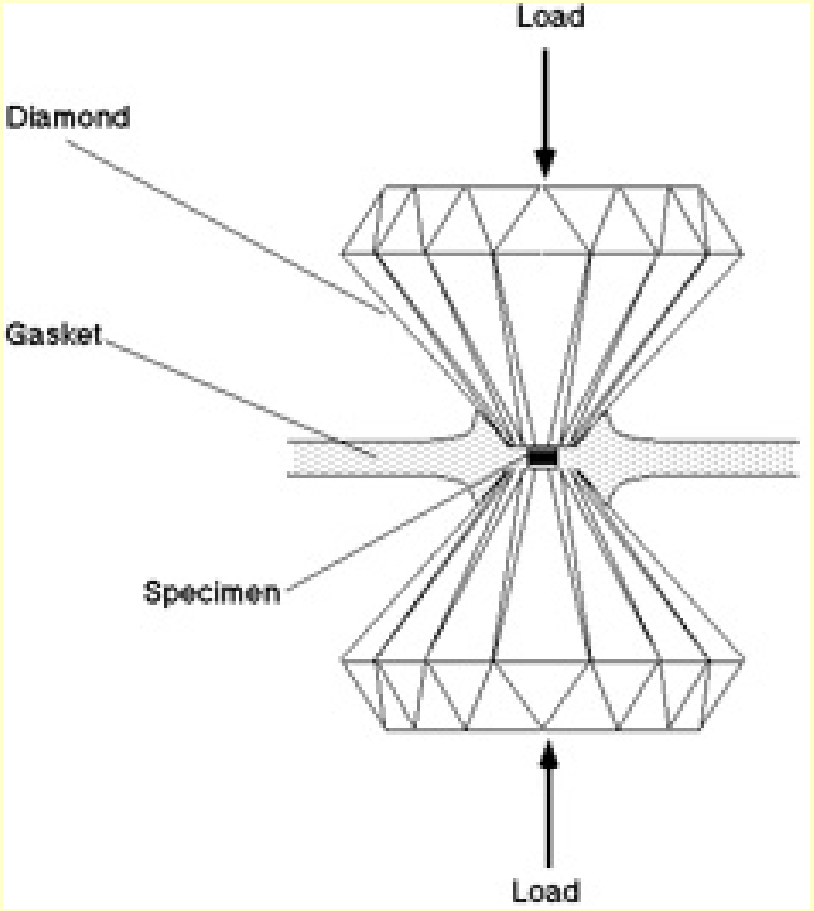
Associative type = the rate determining step involves the formation of a covalent bond

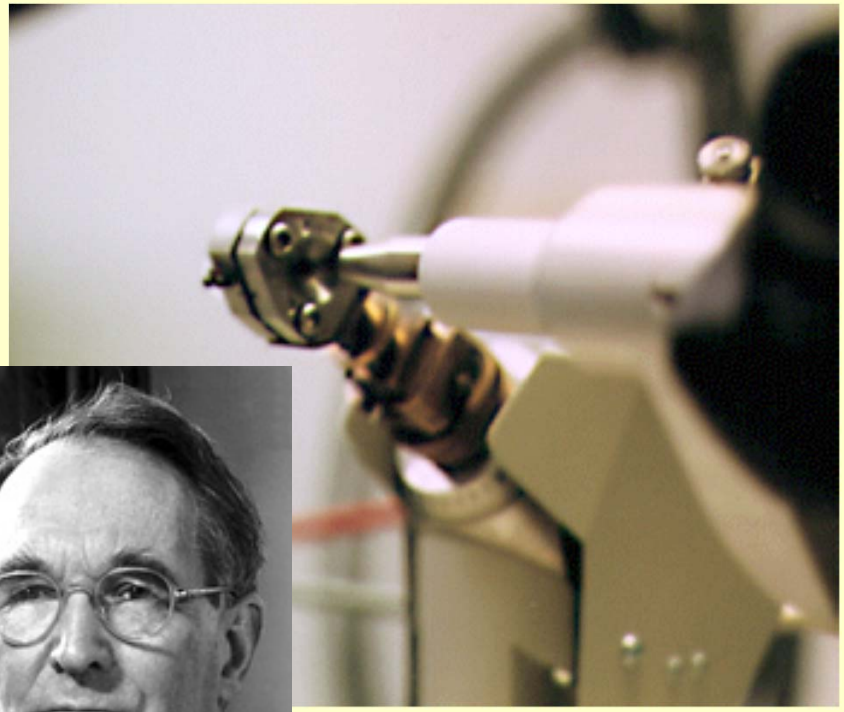
negative $\Delta V^{\neq}$ → reaction rate increases with increasing pressure

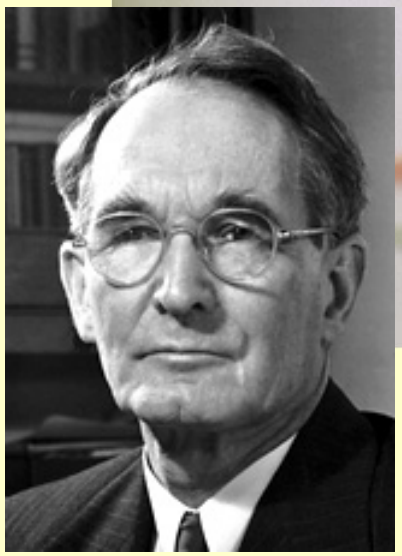
Dissociative type = the breaking of a covalent bond

positive $\Delta V^{\neq}$ → reaction rate decreases with increasing pressure

Diamond Anvil Cell







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

Diamond Anvil Cell

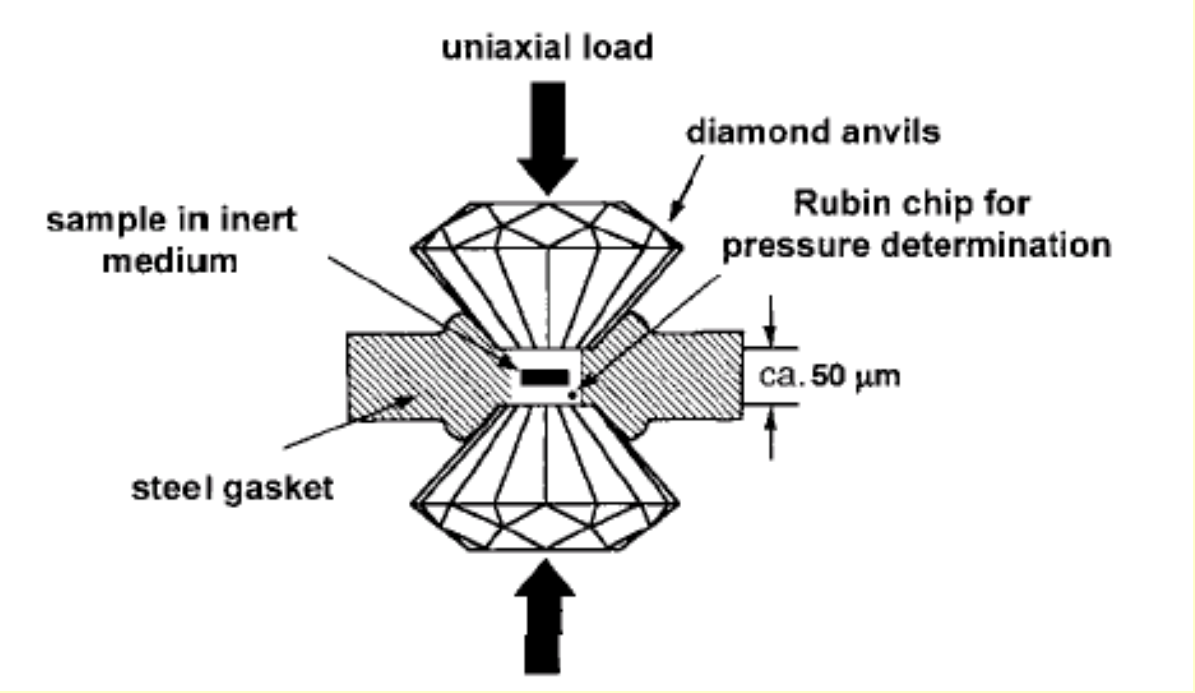
Diamond anvil cell

p = F/A

p = 40 GPa

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

A_{culet} = 100-200 µm



laser heating T > 2500 °C

Re, steel gasket

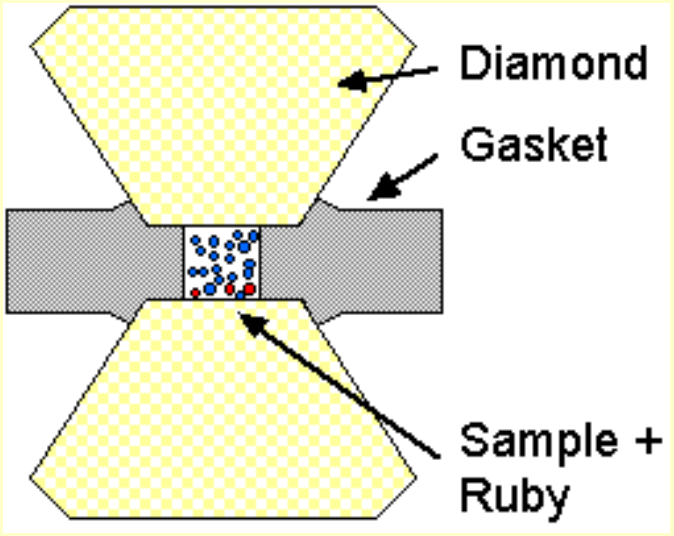
Diamond transparent

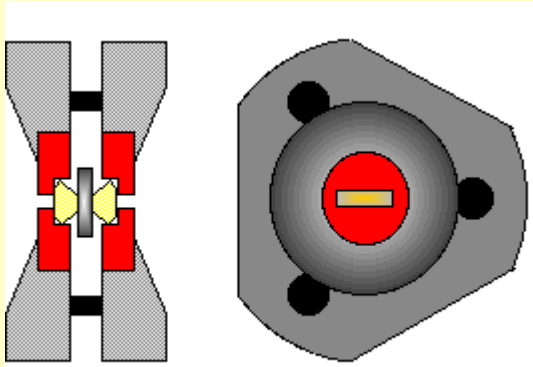
to radiation from IR to X-ray

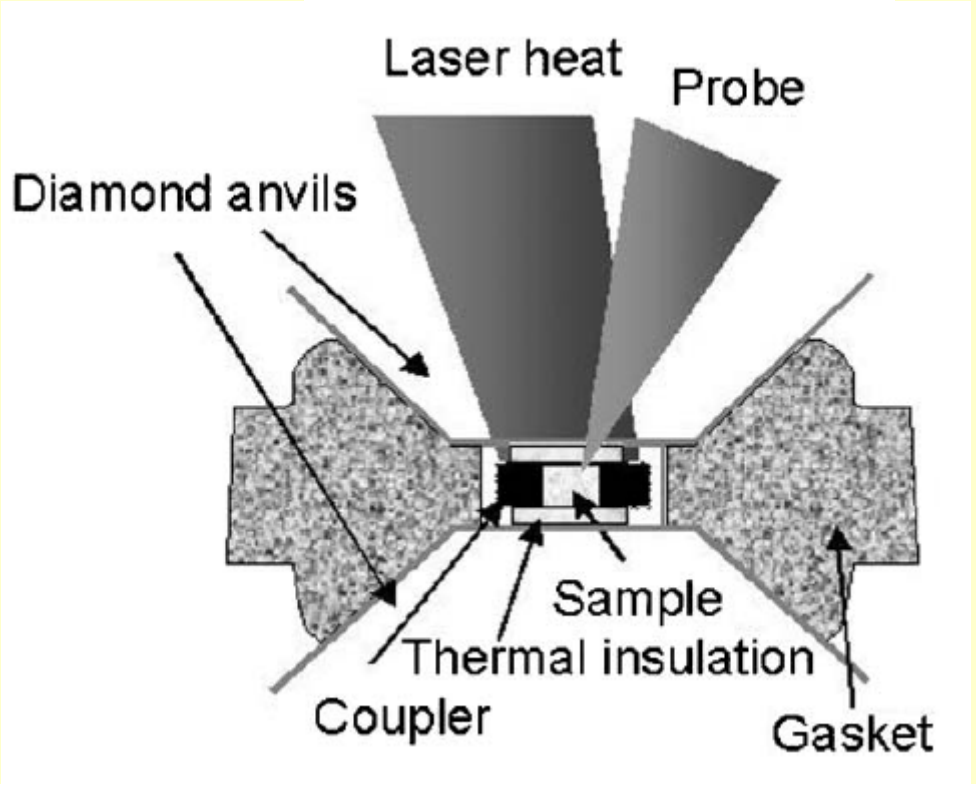
pressure transmitting medium:

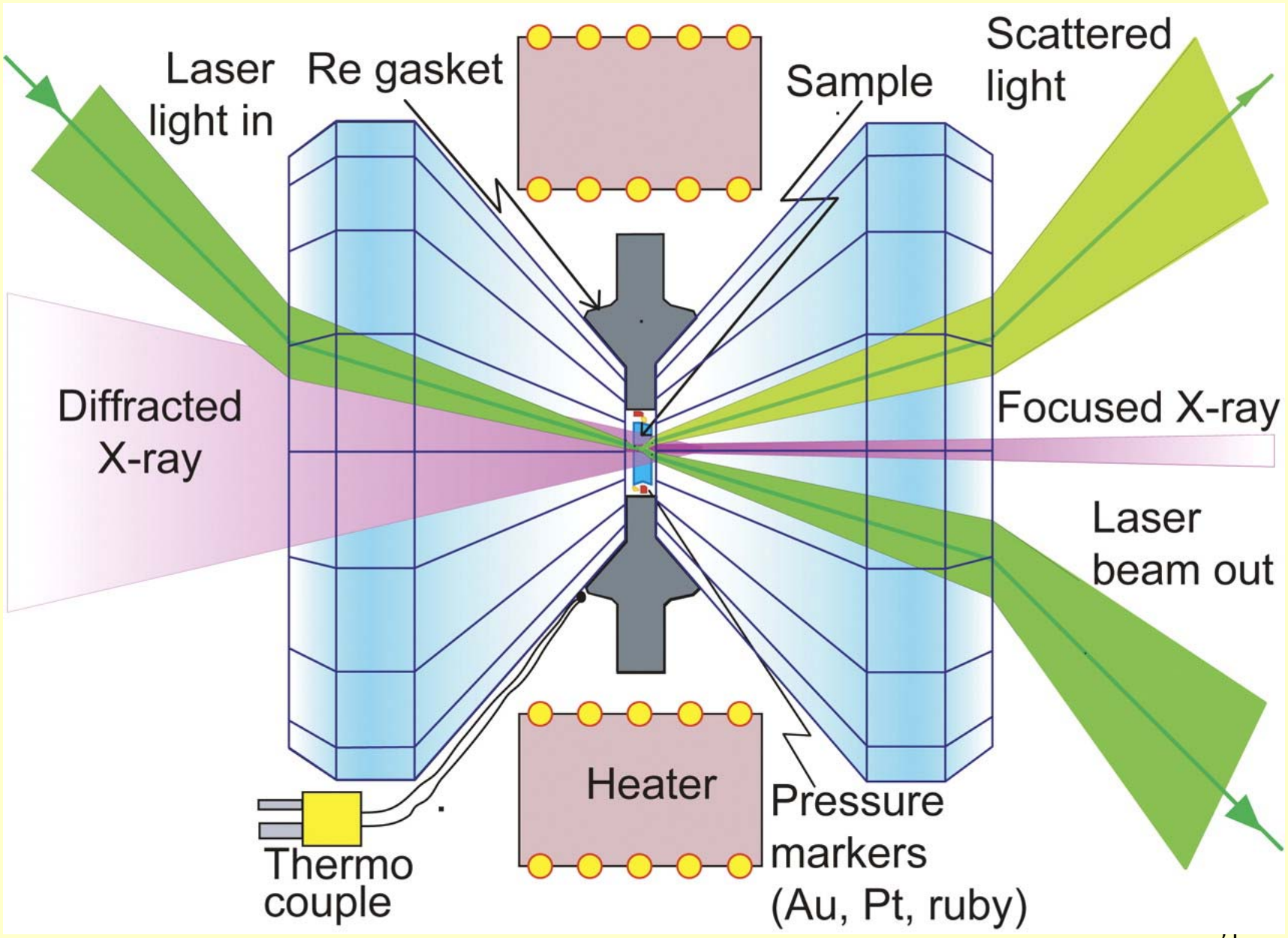
solid Ar, N_2, O_2,

Diamond Anvil Cell







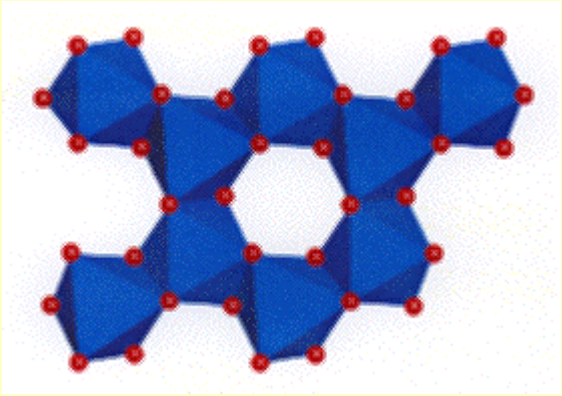

Laser
light in
Re gasket
Sample
Scattered
light
Diffracted
X-ray
Focused X-ray
Laser
beam out
Heater
Thermo
couple
Pressure
markers
(Au, Pt, ruby)

Dry High-Pressure Methods

Calibrating a high pressure diamond anvil

- **Ruby - fluorescence transition**
- **Bi, Tl, Ba pressure induced phase transition**

Ruby = Cr doped corundum

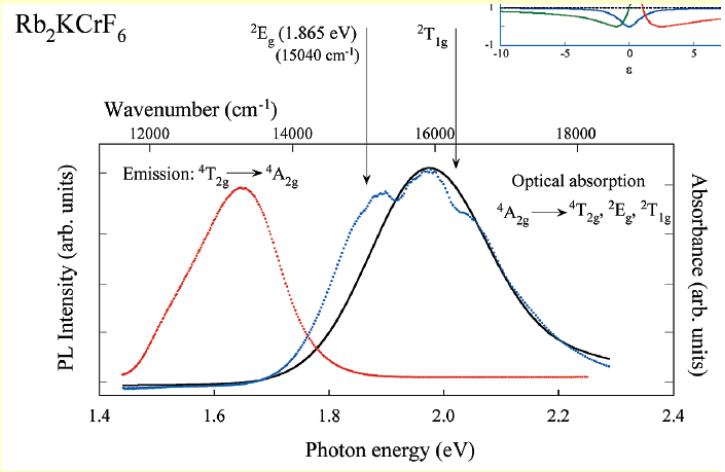


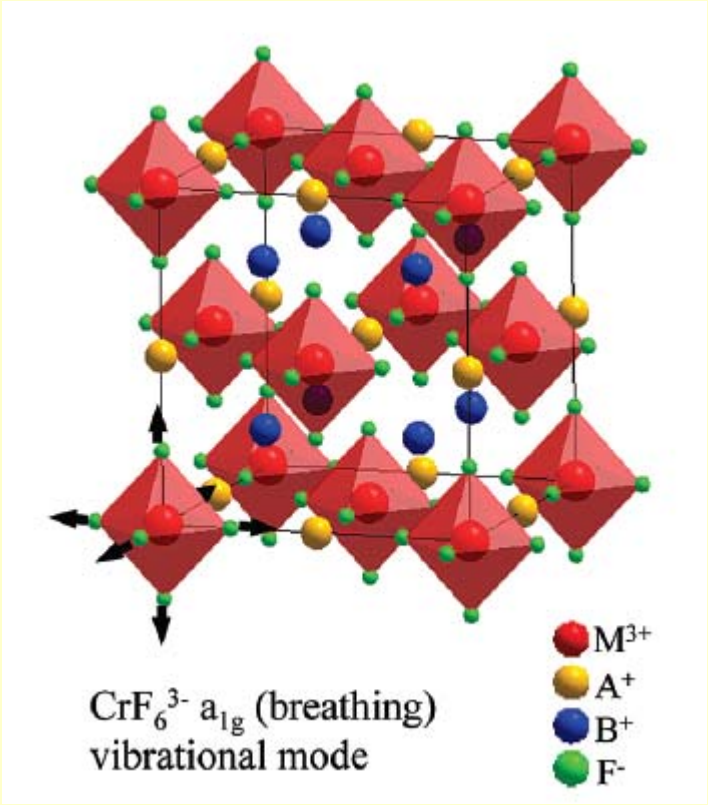
High pressure synthesis

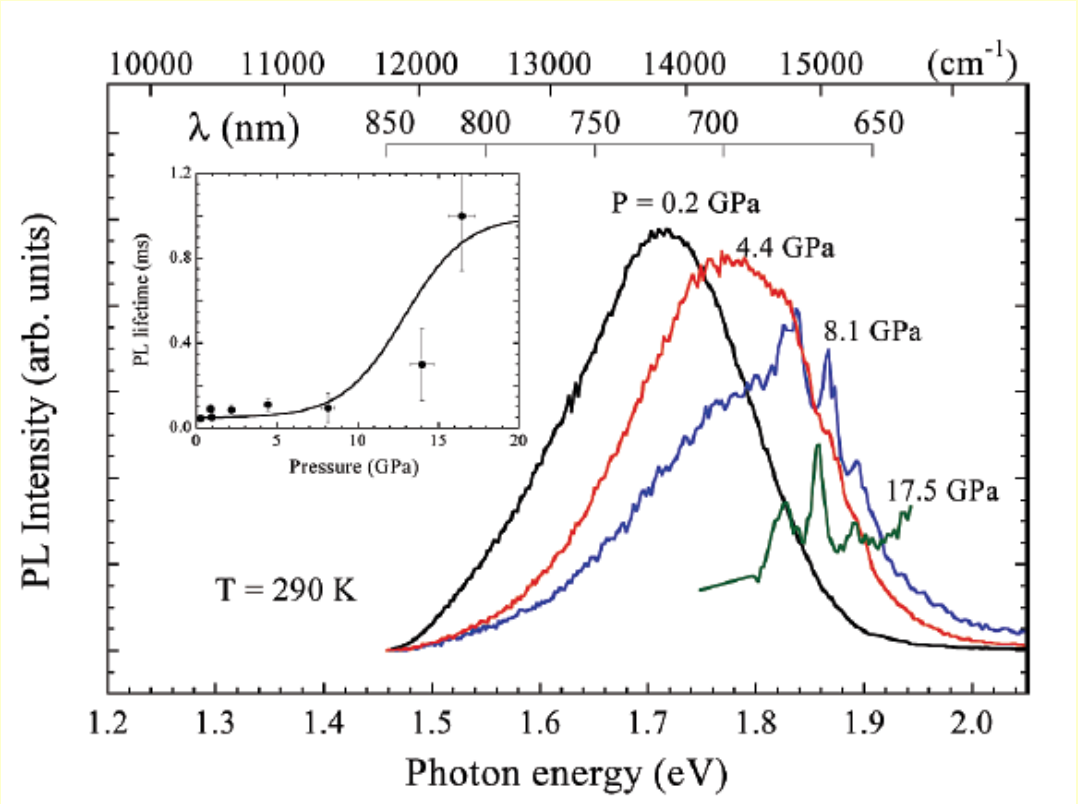
$SnO_2 + Pb_2SnO_4 \longrightarrow 2\ PbSnO_3$ **perovskite** **7 GPa, 400 °C**

At ambient pressure only SnO_2 and PbO products

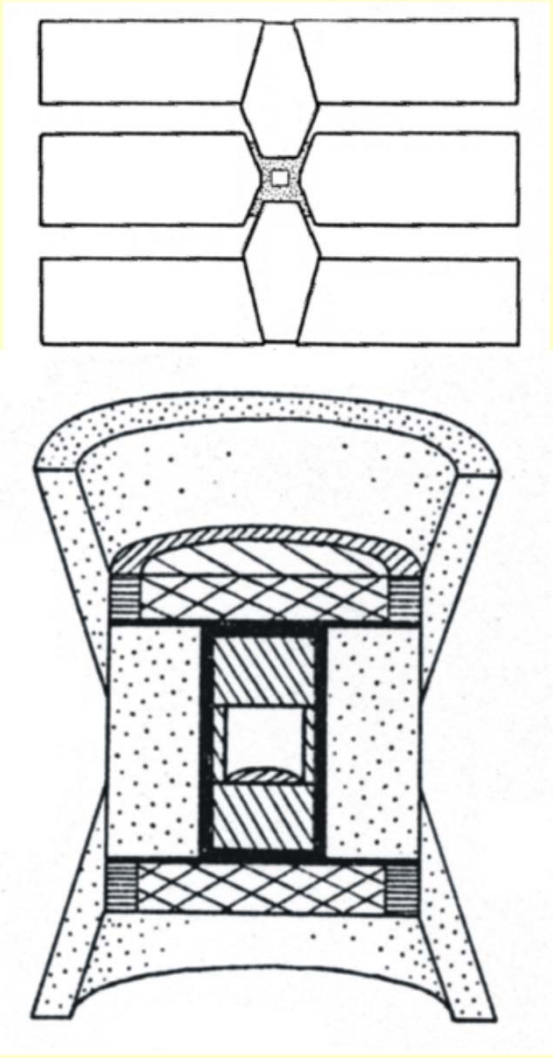
Rb_2KCrF_6

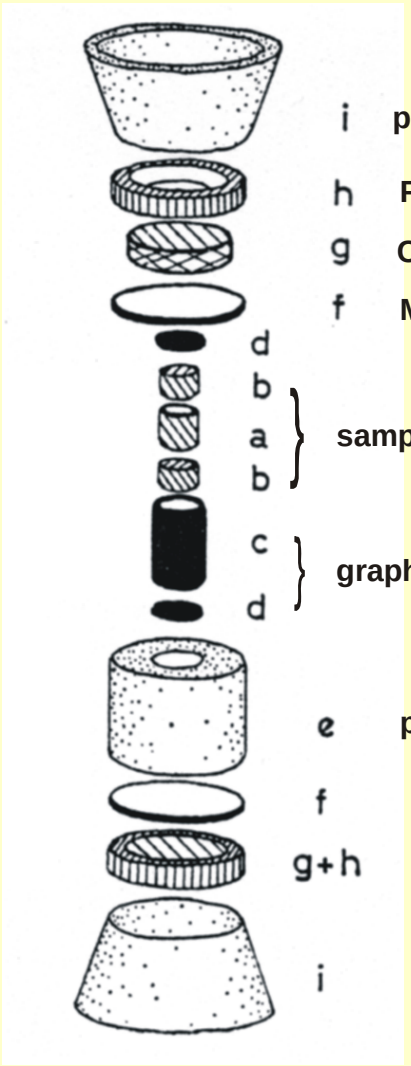

Rb2KCrF6
2Eg (1.865 eV)
(15040 cm-1)
2T1g
Wavenumber (cm-1)
12000
14000
16000
18000
Emission: 4T2g → 4A2g
Optical absorption
4A2g → 4T2g, 2Eg, 2T1g
PL Intensity (arb. units)
Absorbance (arb. units)
1.4
1.6
1.8
2.0
2.2
2.4
Photon energy (eV)


M3+
A+
B+
F-
CrF6 3- a1g (breathing)
vibrational mode


10000
11000
12000
13000
14000
15000
(cm-1)
λ (nm)
850
800
750
700
650
PL Intensity (arb. units)
PL lifetime (ms)
Pressure (GPa)
P = 0.2 GPa
4.4 GPa
8.1 GPa
17.5 GPa
T = 290 K
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
Photon energy (eV)

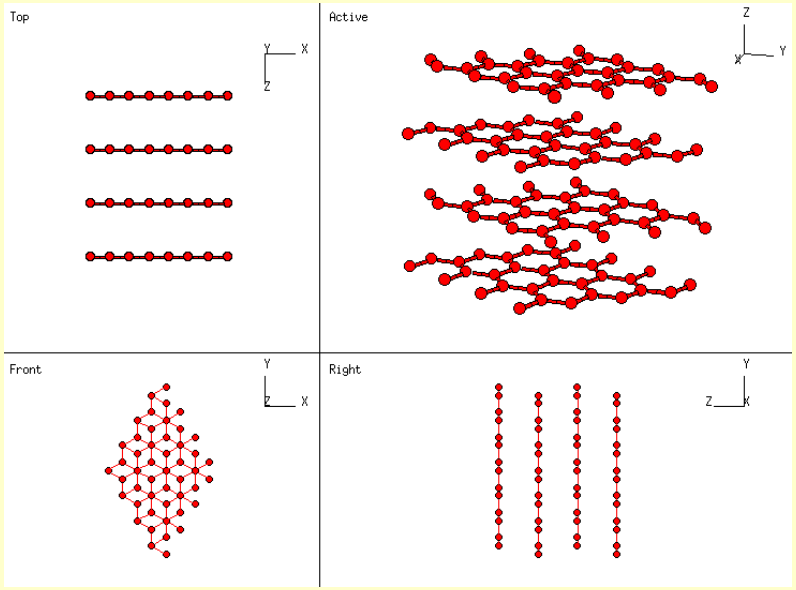
High Pressure Two-Die Belt-Type Apparatus

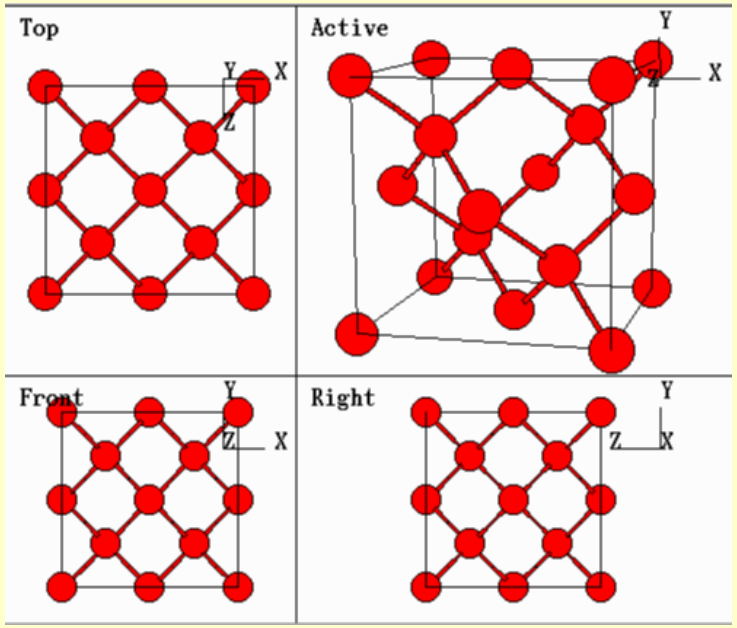




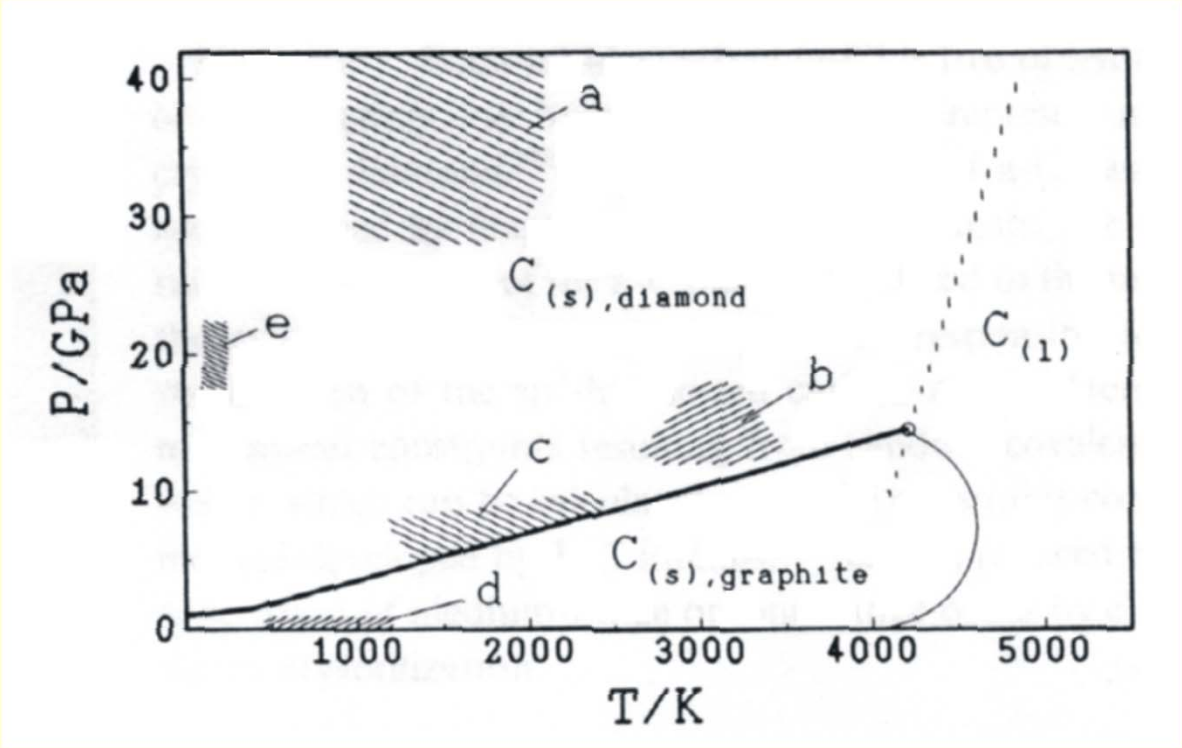
Synthesis of Diamonds

The hardest known substance, the highest thermal conductivity
Difficult to transform graphite into diamond
Industrial diamonds (GE) made from graphite around 3000 ^{o}C and 13 GPa





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

Synthesis of Diamonds

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

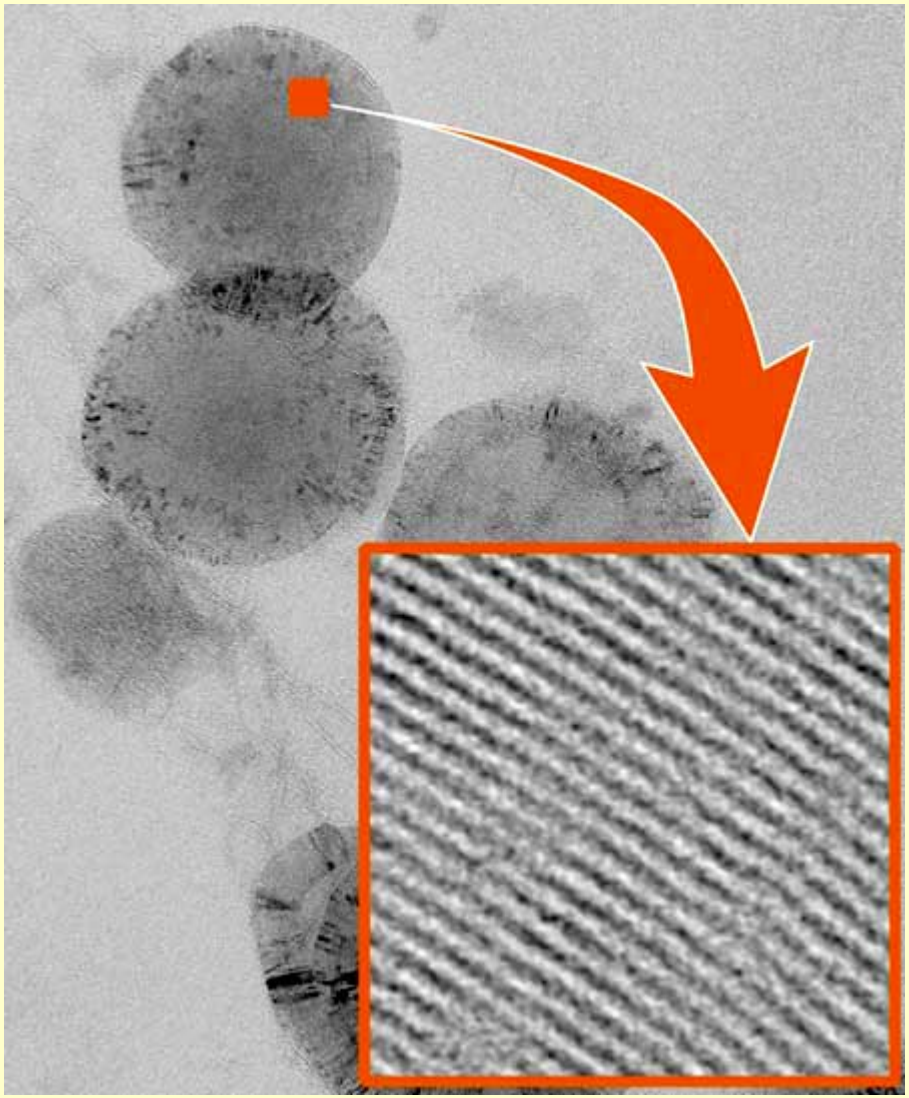
Ways of getting round the difficulty

♦ 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)

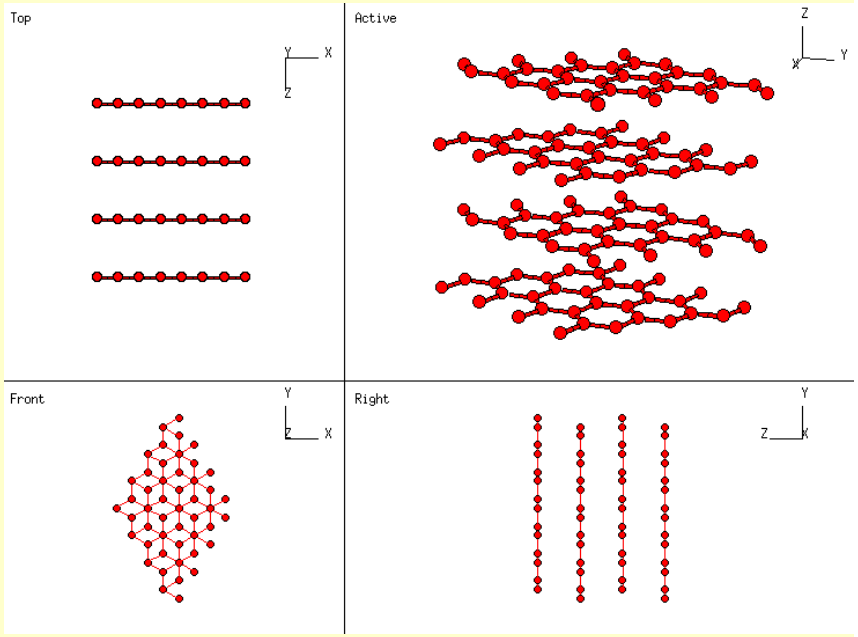
♦ Squeezing (uniaxial not hydrostatic pressure), no heating, buckyball carbons are already intermediate between sp^{2-3}
C_{60}, diamond anvil, 25 GPa instantaneous transformation to bulk crystalline diamond, highly efficient process, fast kinetics

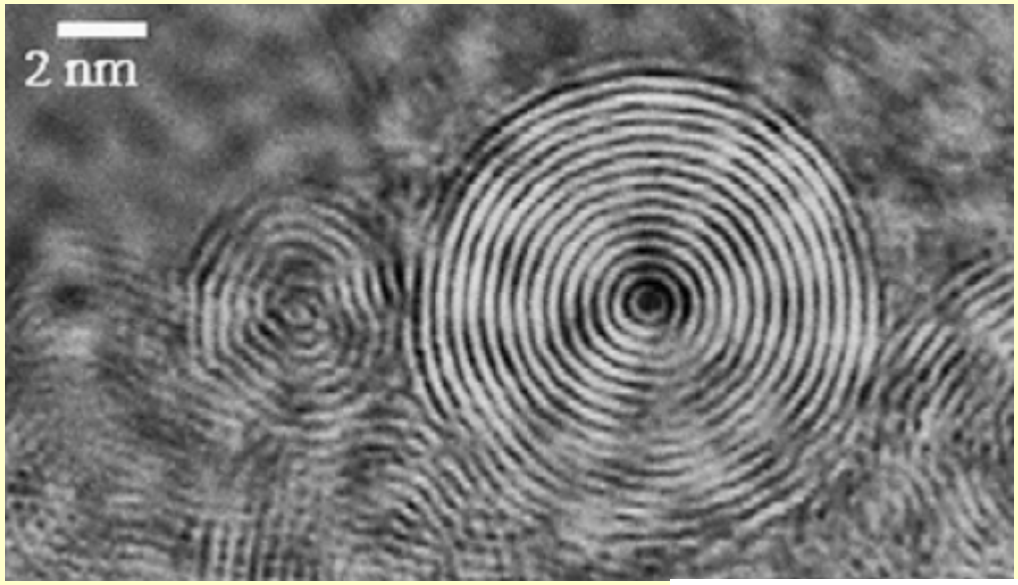
♦ Carbon onions, electron irradiation of graphite, concentric spherical graphite layers, spacing decreases from 3.4 Å to 2.2 Å in the onion center, 100 GPa, 200 keV beam, in several hours, pressureless conversion to diamond

♦ 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 μm

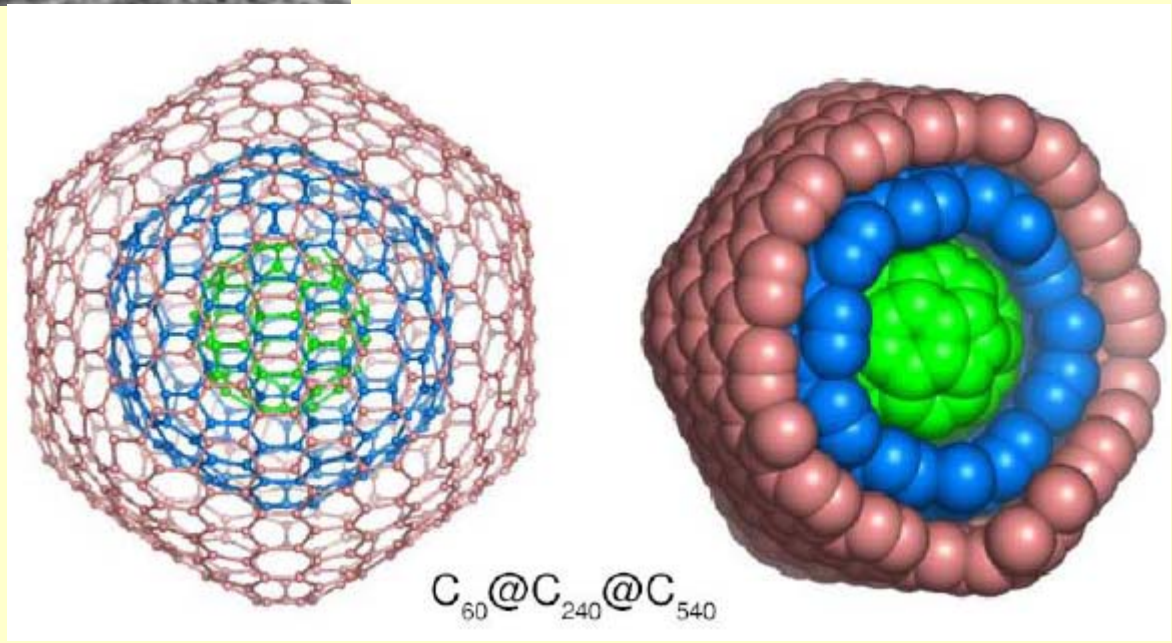


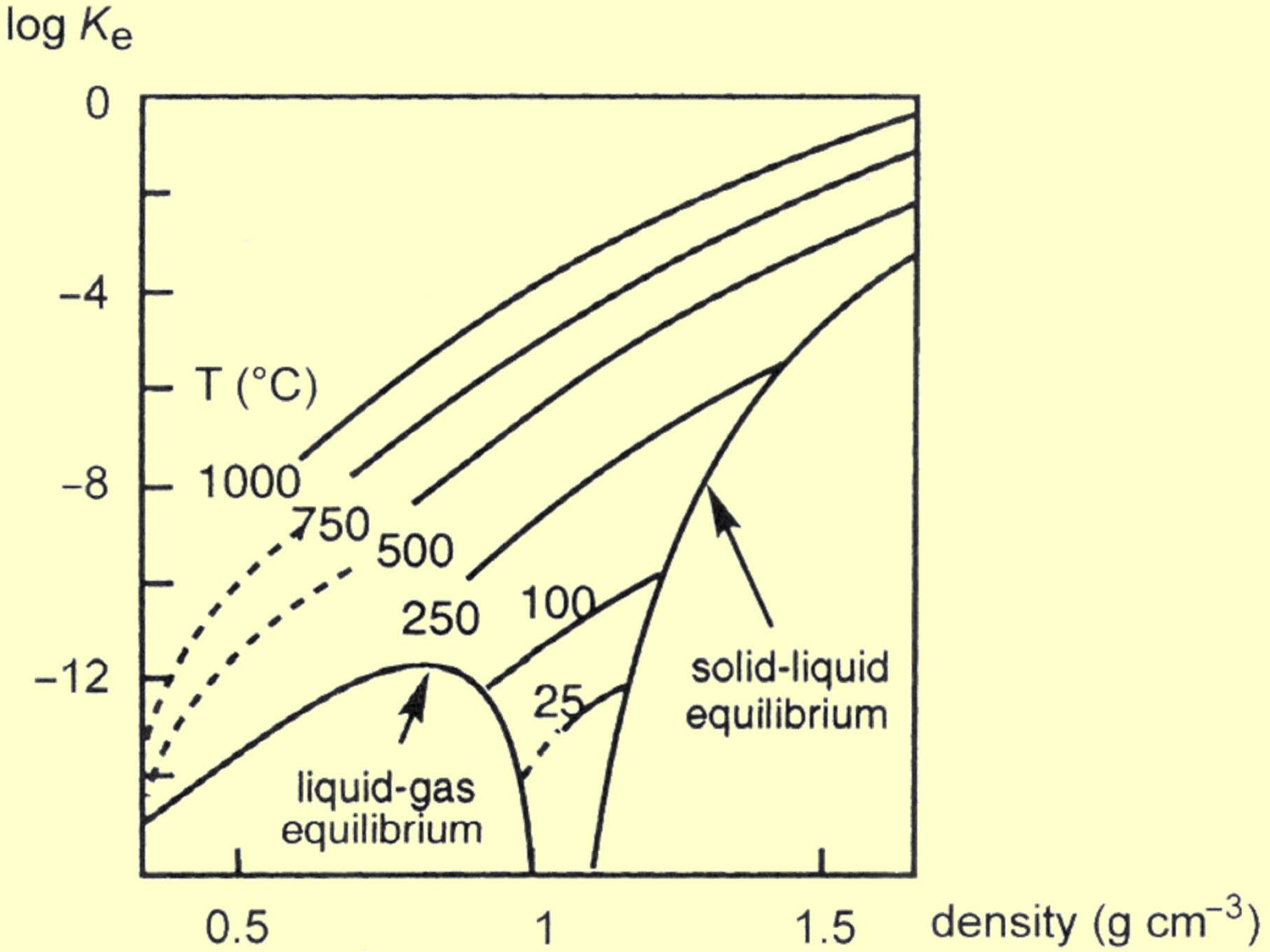
Graphite





Carbon onions




log K_e
0
−4
−8
−12
T (°C)
1000
750
500
250
100
25
liquid-gas
equilibrium
solid-liquid
equilibrium
0.5
1
1.5
density (g cm^{-3})

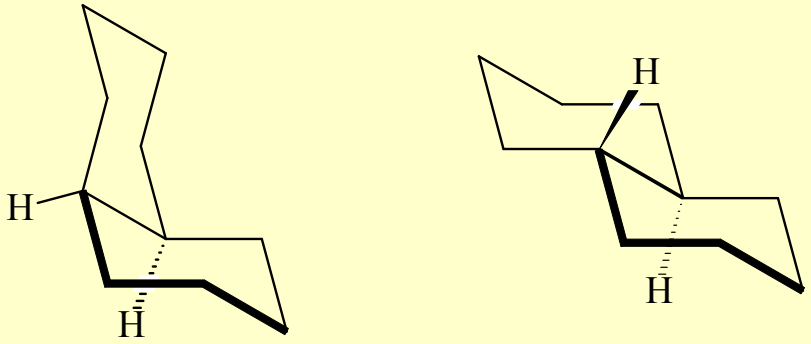
Organic molecule theory of diamond cleavage

The jeweler's chisel if placed correctly on a diamond, with a well oriented blow, always cause cleavage along {111} greater than 90% of the time, imagine the cost of a mistake with a large crystal

The number of bonds broken per unit area (that is, surface energies) for different planes does not explain the observations of preferential {111} cleavage!!!

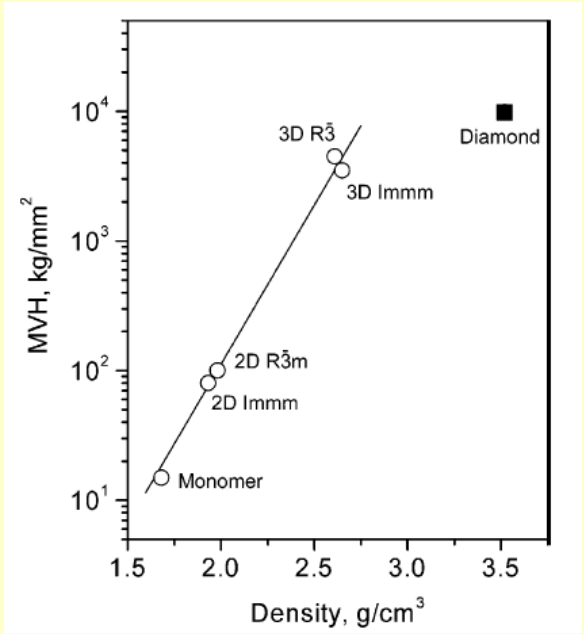
Diamond viewed in terms of layers of polycondensed cyclohexane rings with axial bonds between layers and equatorial bonds within layers
Unfavorable axial-axial C-C bond interactions at 2.51 Å versus equatorial-equatorial at 2.96 Å

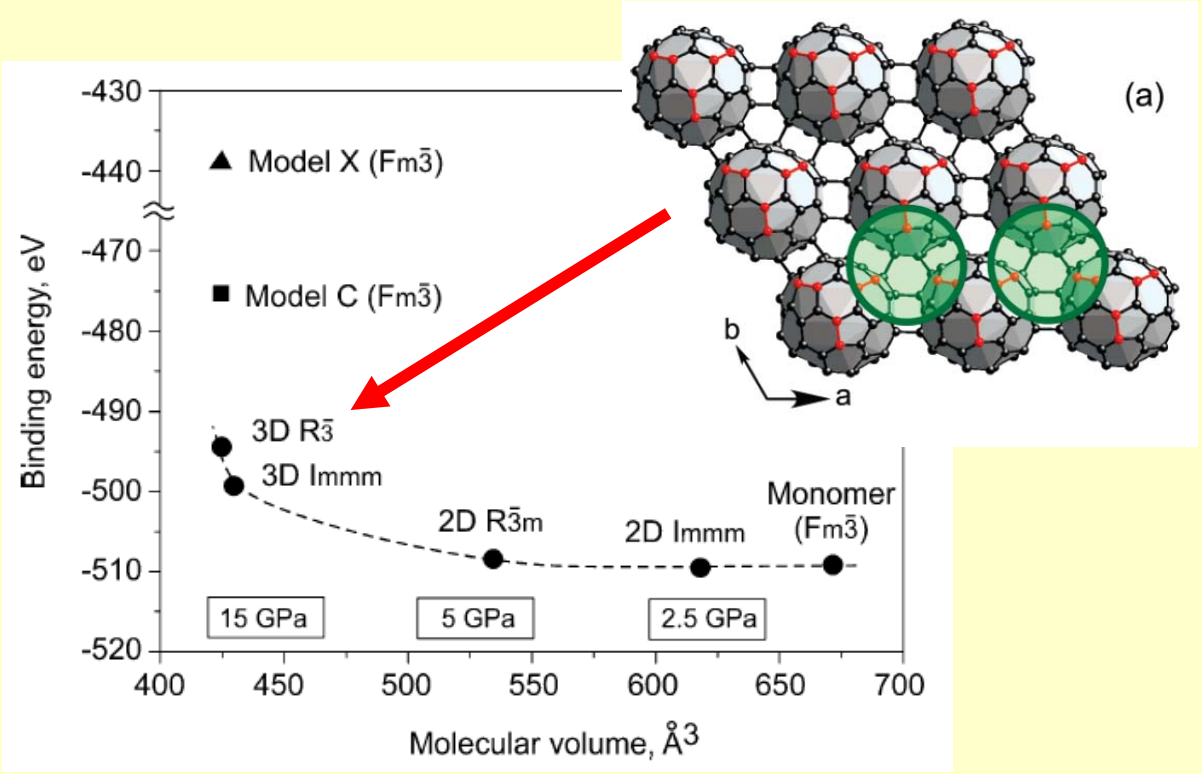
Model compounds like cis-decalin versus trans-decaline comprised of two fused cyclohexane rings
trans-decalin is 11-12 kJmol^{-1} more stable because cis-strain cannot be relieved by bond rotation as in cyclohexane itself,
cis can only isomerize to trans by bond cleavage followed by recombination, hence origin of the high activation energy for the cis-to-trans isomerization of decalin.



A breaking molecule theory: axial-axial unfavorable interactions cause the mechanical energy of the jeweler's chisel to be funneled into preferential breakage of an axial C-C bond
This then induces a kind of domino effect whereby the adjacent axial C-C bonds break and C-C bonds throughout the entire {111} plane are severed

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

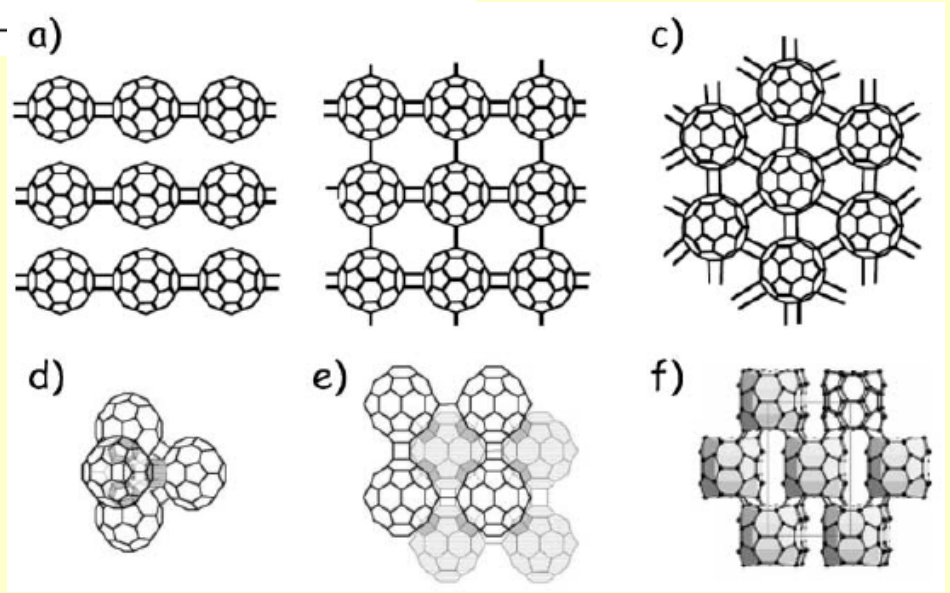




Micro-Vickers hardness (MVH)

Polymerization of C_{60}

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		



- **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!**