

Dry High-Pressure Methods

Chemistry at the Earth's surface at 100 kPa

Chemistry in the Universe at high 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

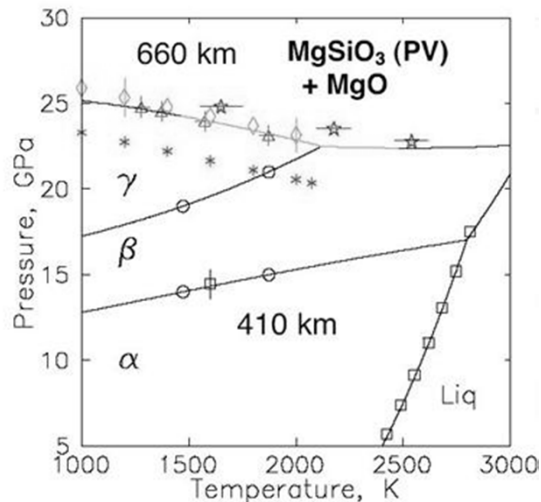
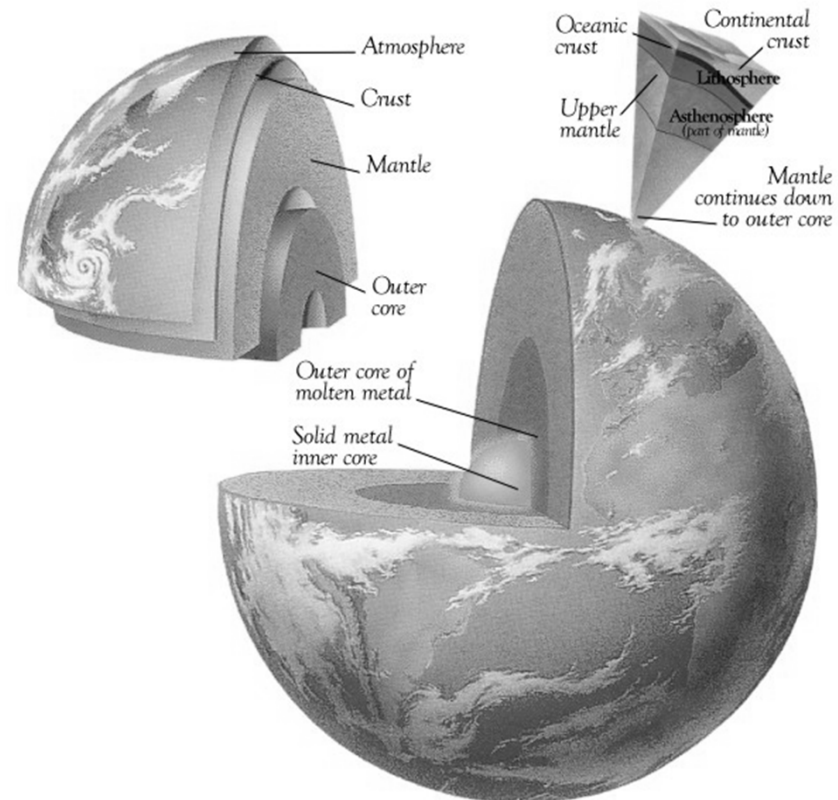
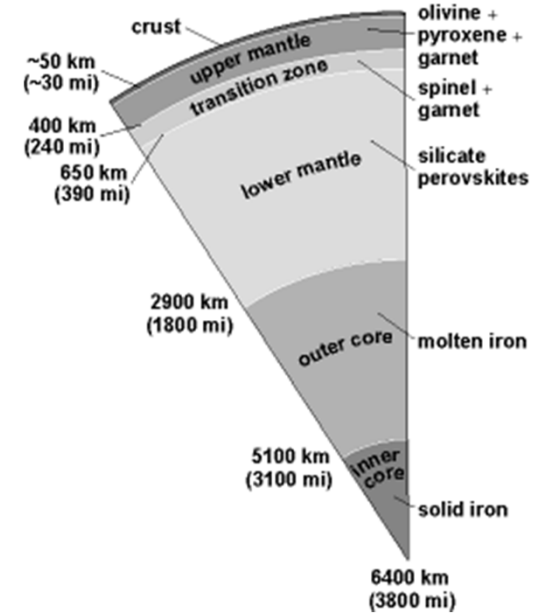
MgSiO₃ most abundant silicate mineral within our planet !

Olivine Mg₂SiO₄ >

pyroxene (silicate chains) > spinel Mg₂SiO₄

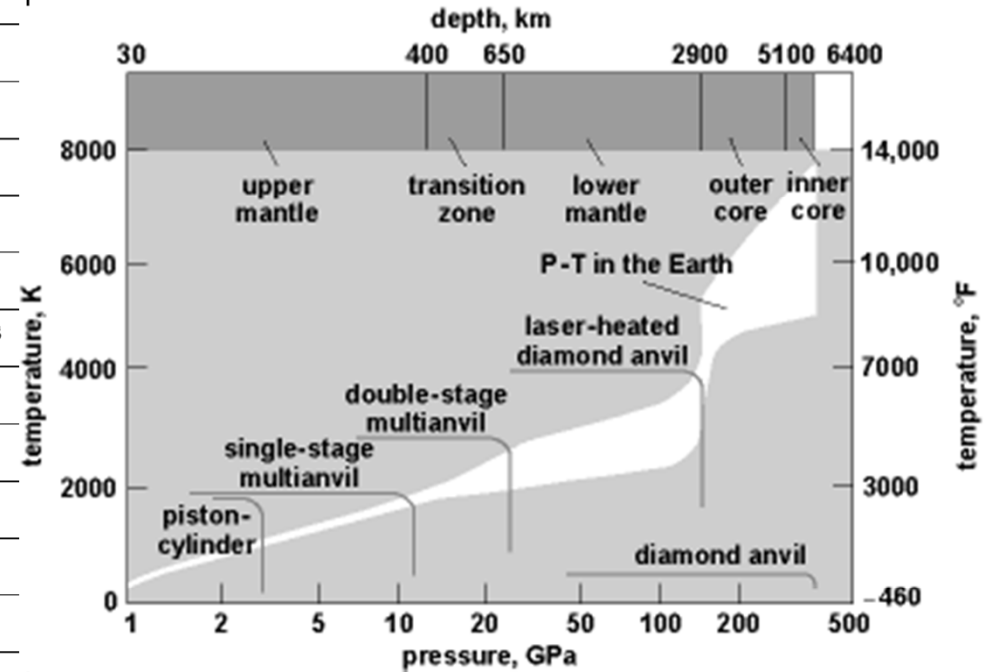
ilmenite > garnet (HT) >

perovskite MgSiO₃ Si CN = 6



PRESSURE SCALE

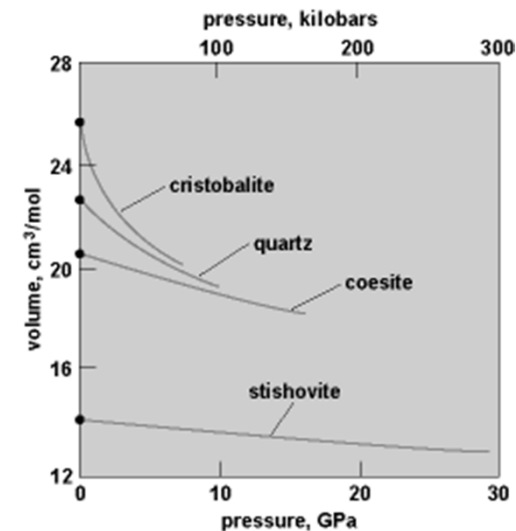
Pressure, bar	System
	1 Mbar = 100 GPa
10^{-12}	high vacuum chamber
1	atmospheric pressure
1.5	kitchen pressure cooker
2.0	car tire
50	a lady in stilleto heels
60	breakdown of human nervous system - divers
73.8	critical pressure of CO ₂
150	autoclave (safety burst disc)
221.2	critical pressure of H ₂ O
10^3	pressure at the bottom of the ocean (11 km)
$2 \cdot 10^3$	LDPE
10^4	Earth crust (30 km)
10^5	synthetic diamond production
$3.4 \cdot 10^6$	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 coordination number**
- **higher symmetry**
- **transition to from nonmetal to metal**
- **band mixing**

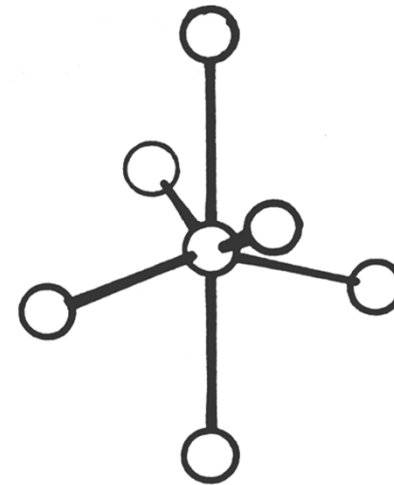
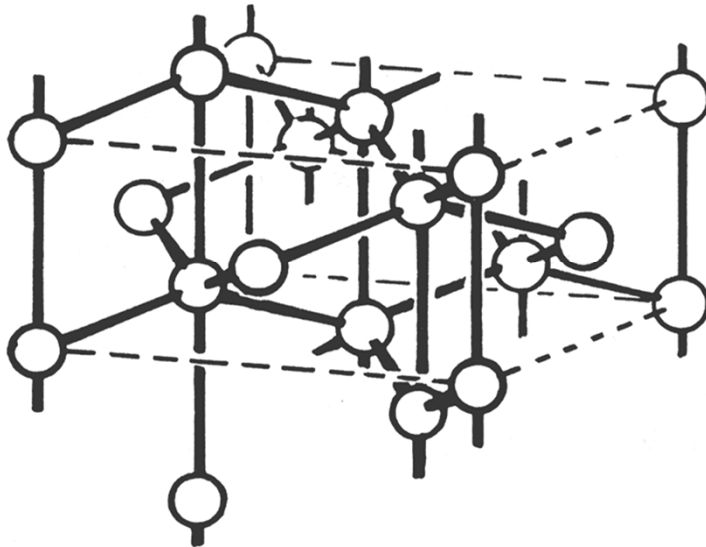


Pressure/Coordination Number Rule: increasing pressure – higher CN
Pressure/Distance Paradox: increasing pressure – longer bonds

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



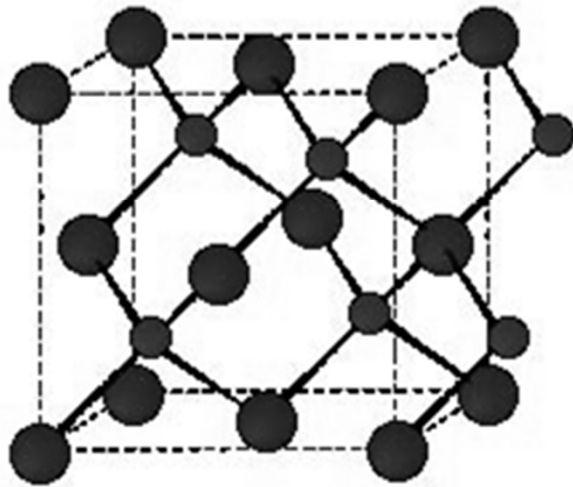
Dry High-Pressure Methods

Examples of high pressure polymorphism for some simple solids

Solid	Normal structure and coordination number	Typical transformation conditions P(kbar)	Typical transformation conditions T(°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
SiO₂	Quartz 4:2	120	1200	Rutile 6:3
Li₂MoO₄	Phenacite 4:4:3	10	400	Spinel 6:4:4
NaAlO₂	Wurtzite 4:4:4	40	400	Rock salt 6:6:6

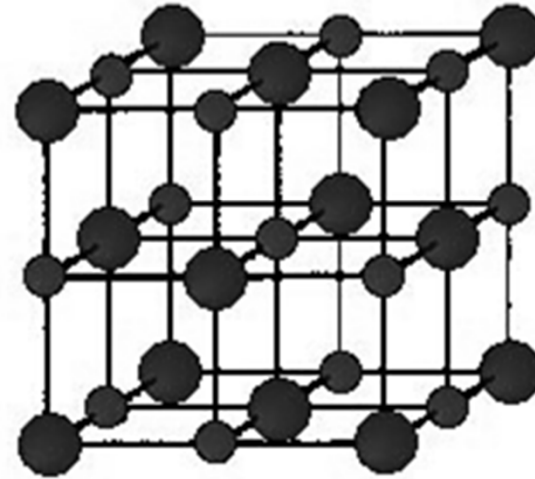
High-Pressure Phase Transformations

zinc blende

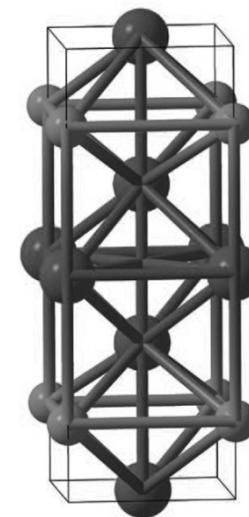
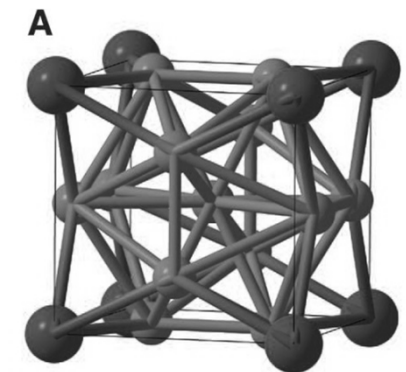
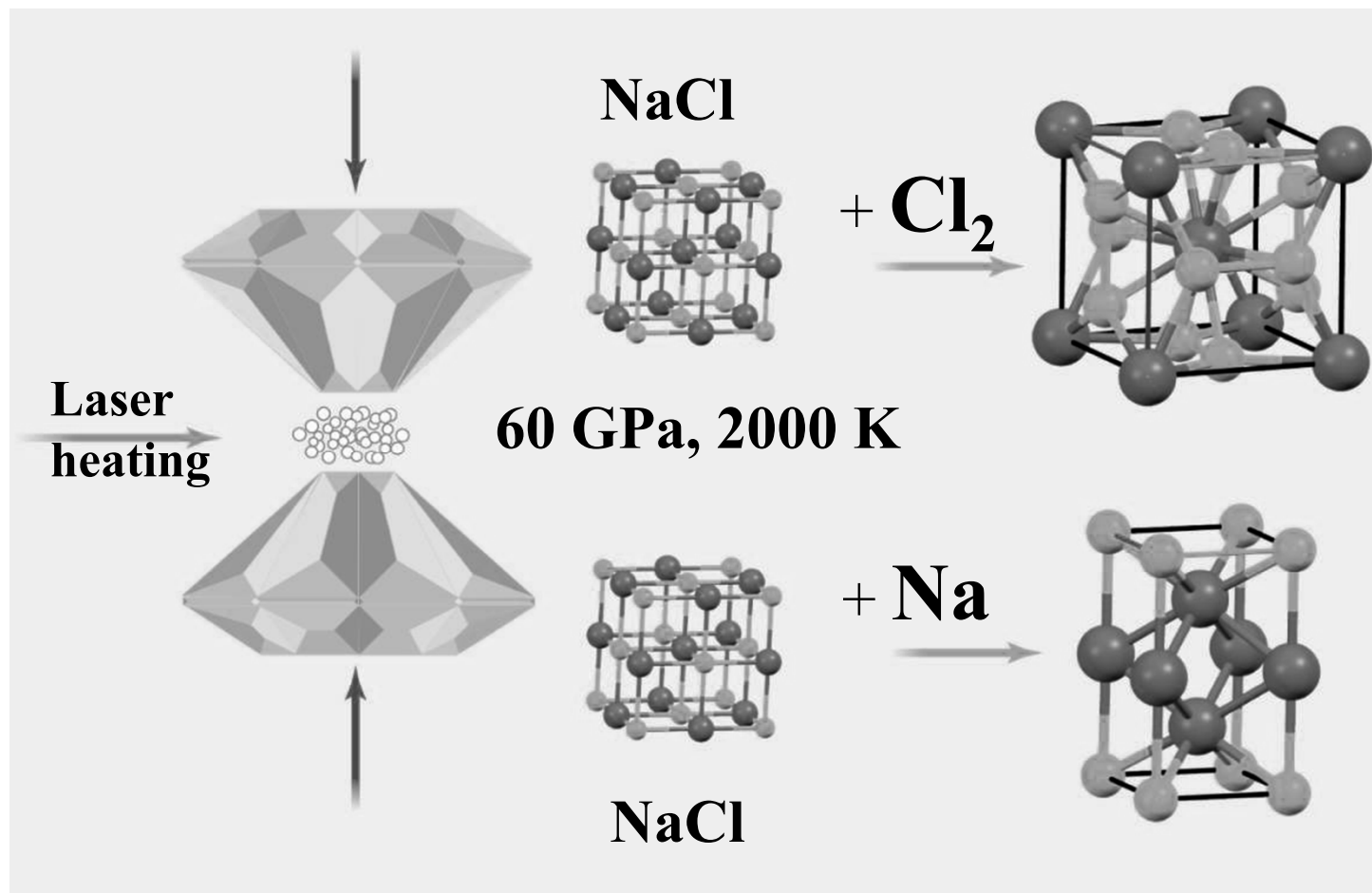


> 140 kBar
→

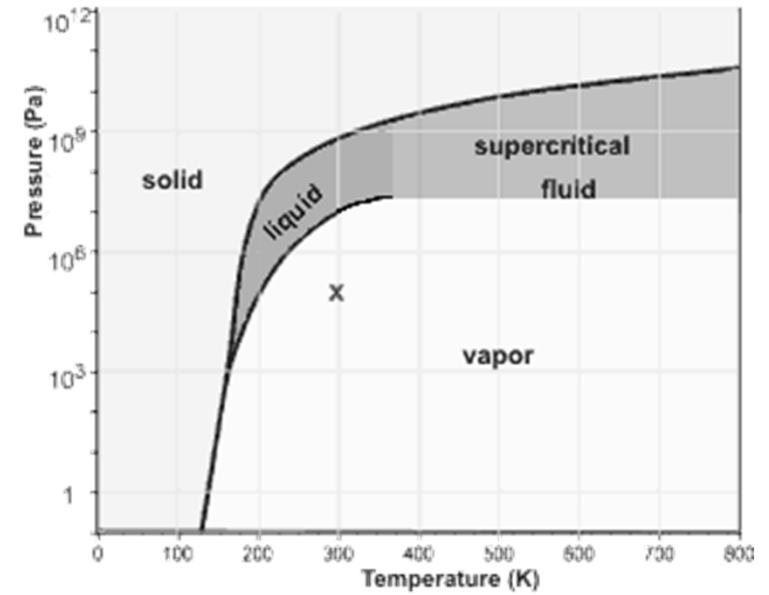
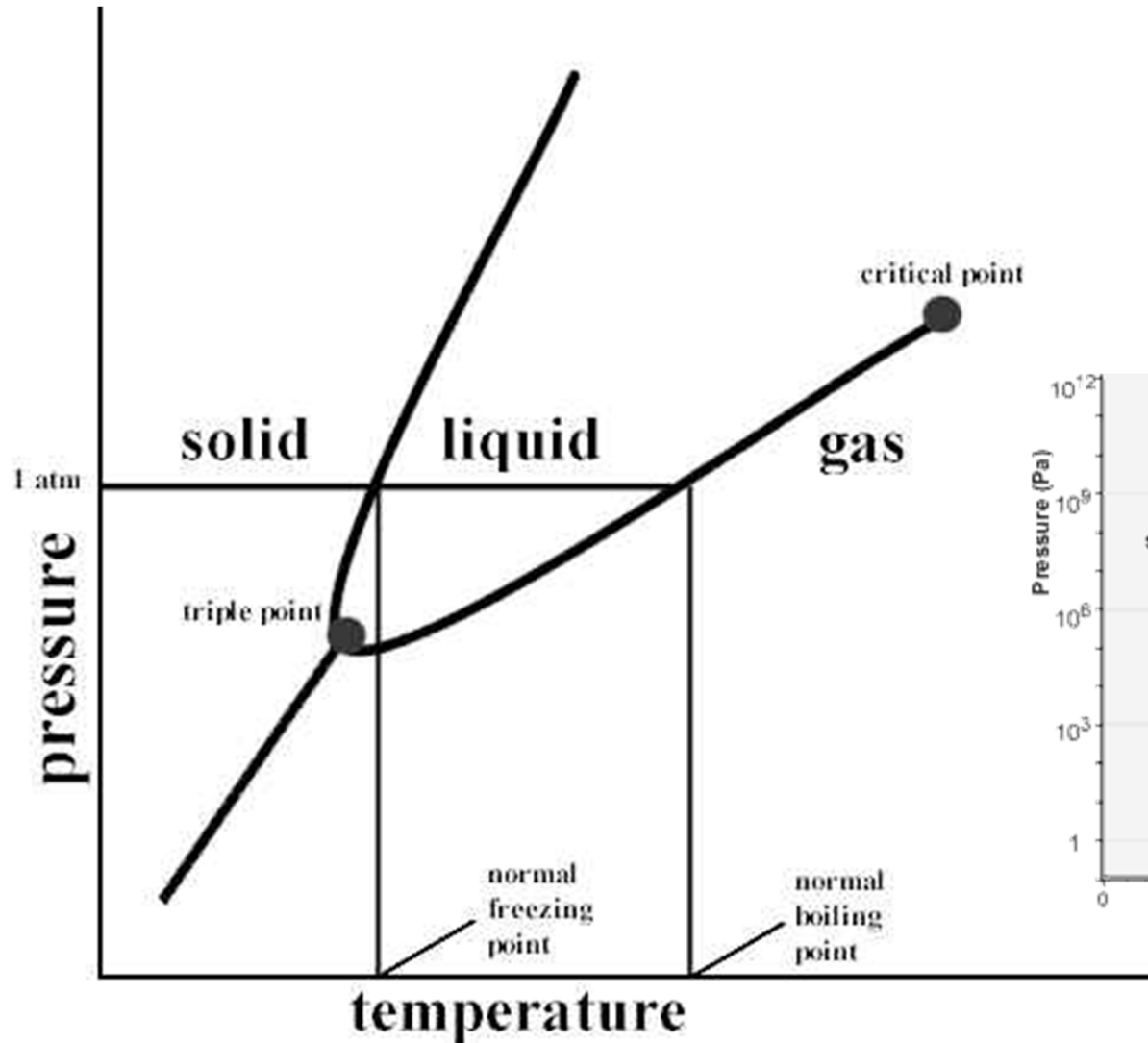
rock salt

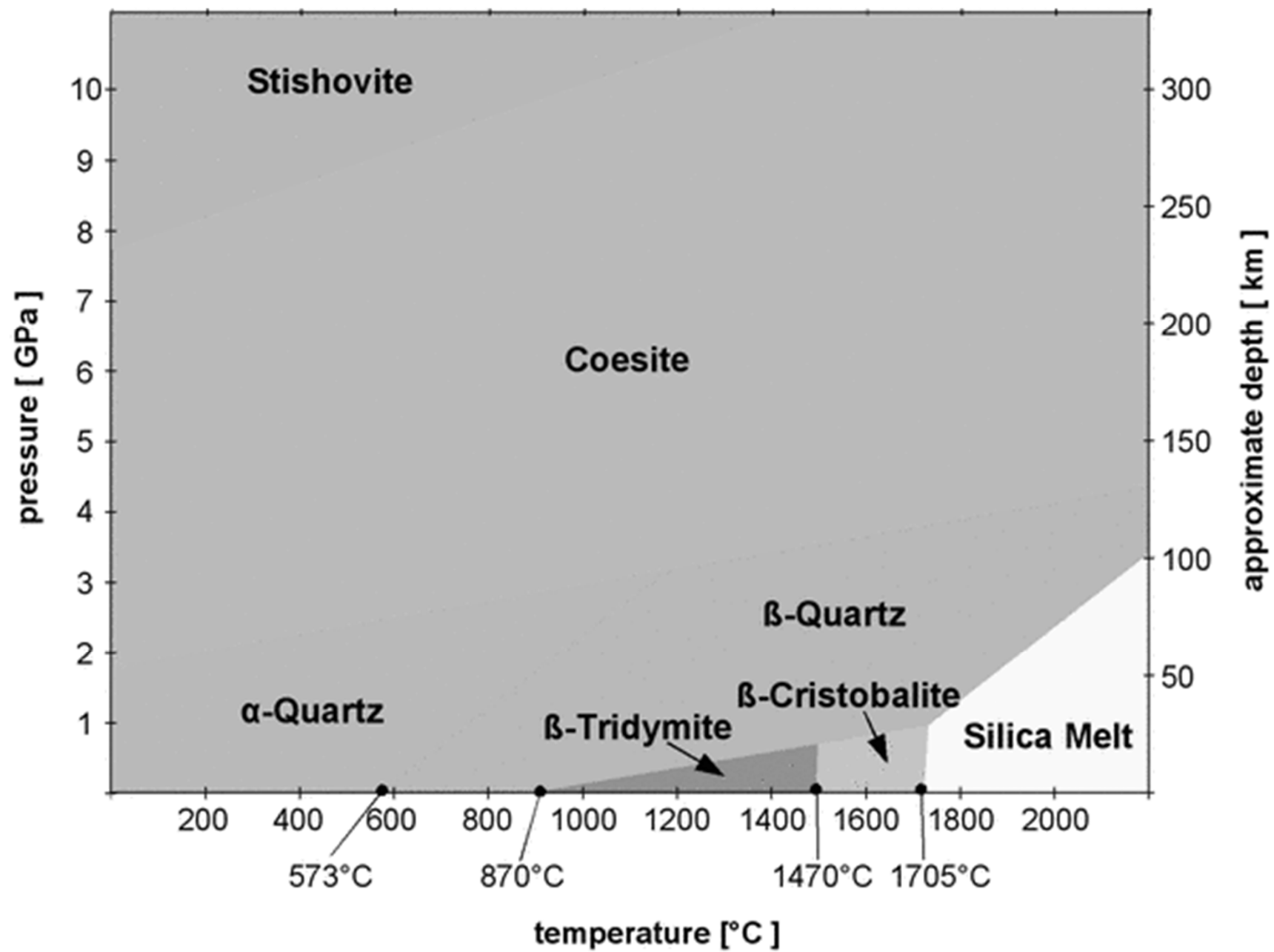


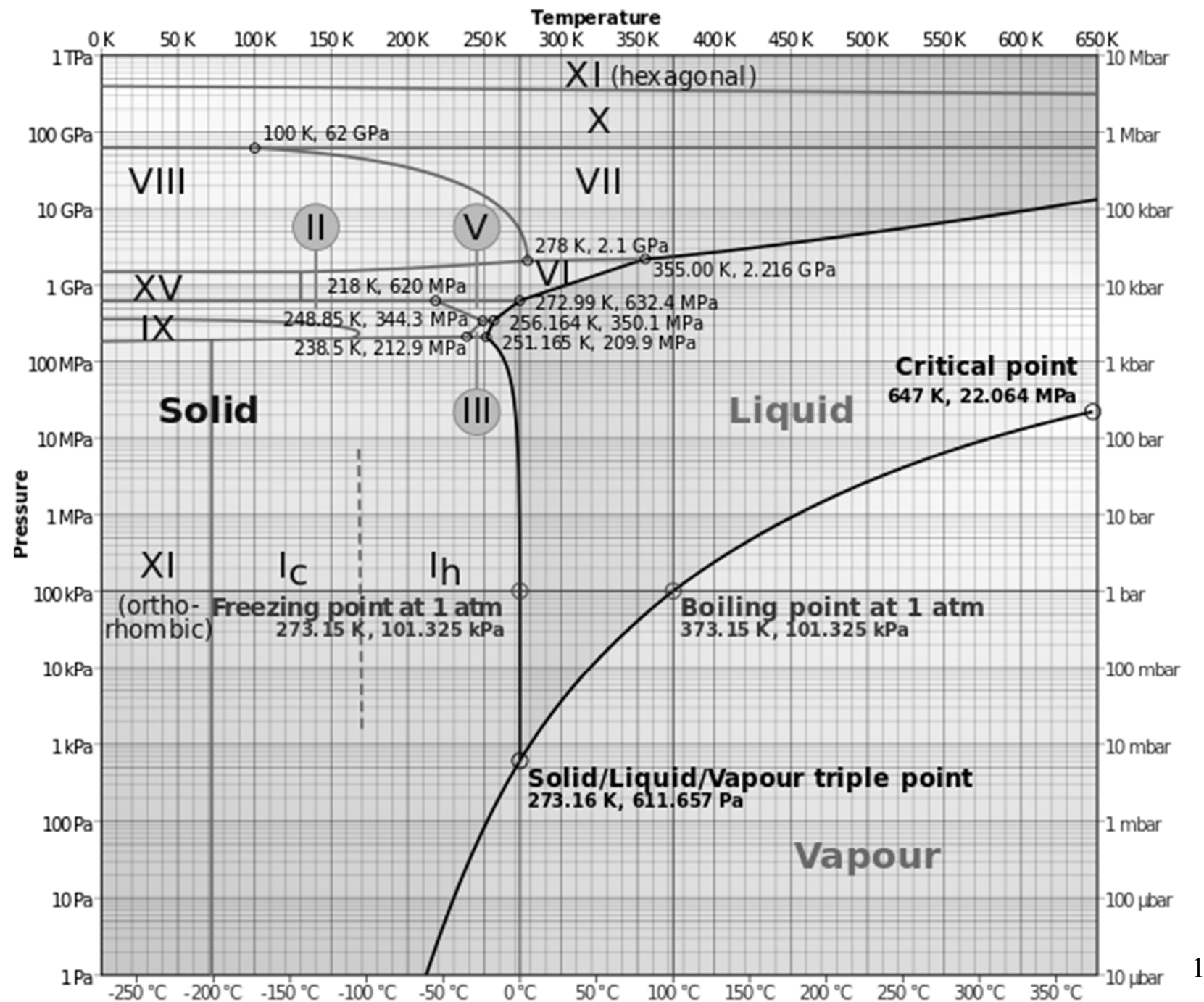
Unusual Stoichiometries under High-Pressure



p-T Phase Diagrams







Water

17 phases of ice

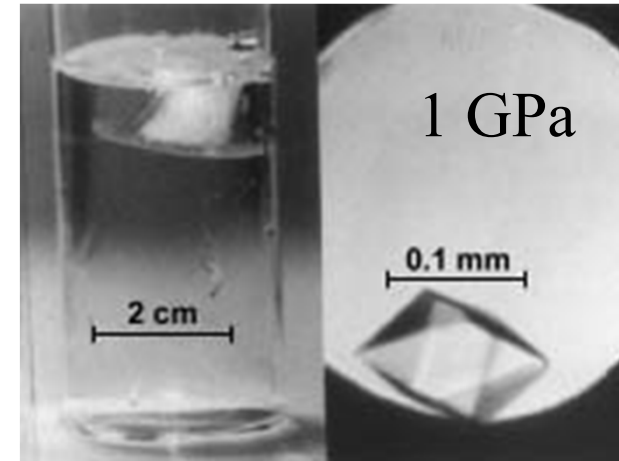
Ice-VII m.p. 100 °C

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

MgSiO₃ most abundant silicate mineral within our planet !

pyroxene (silicate chains)

ilmenite > garnet > perovskite Si CN = 6

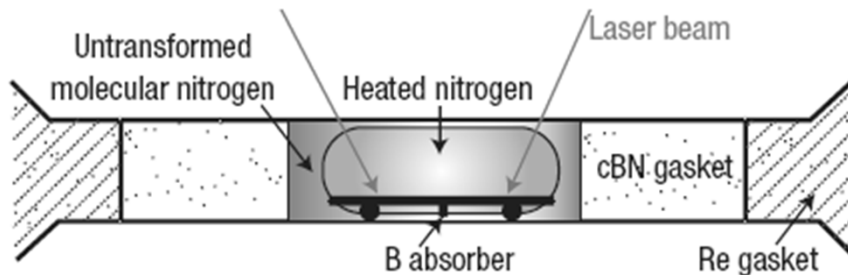
Condensed gases

H_2 metallic conductivity in dense fluid hydrogen

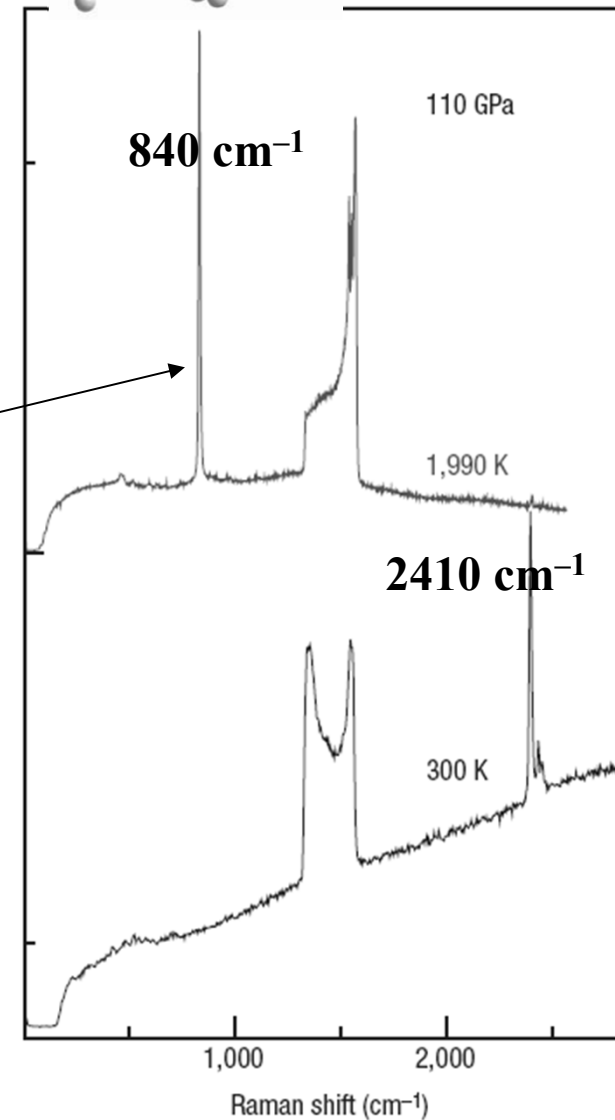
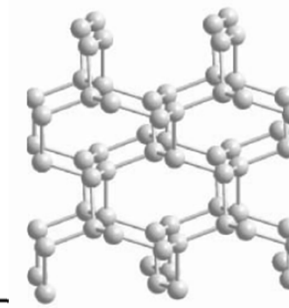
$\text{H}_2^+ \text{H}_2^-$

$\text{NO}_2 + \text{N}_2\text{O}$ $\text{NO}^+ \text{NO}_3^-$ calcite

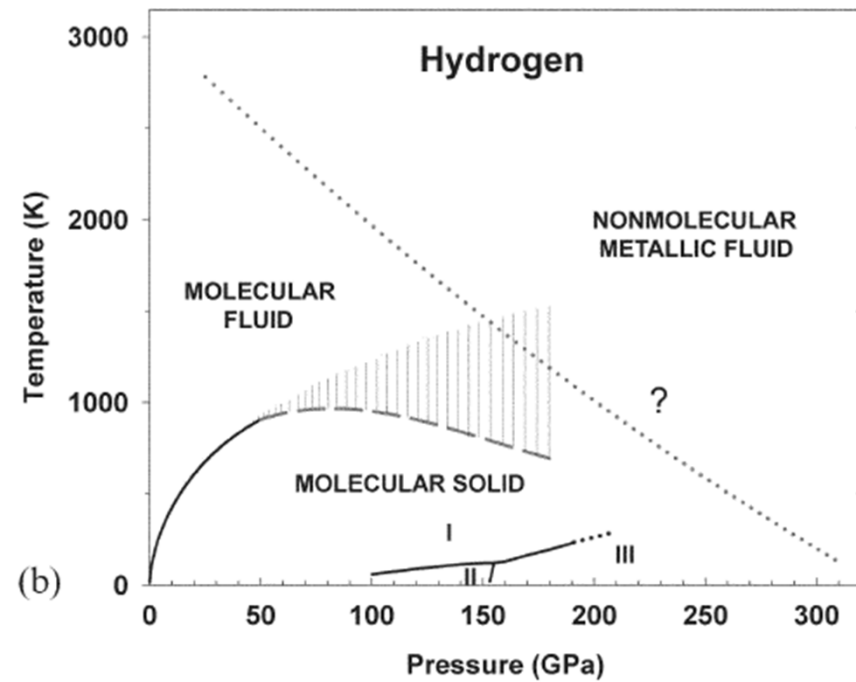
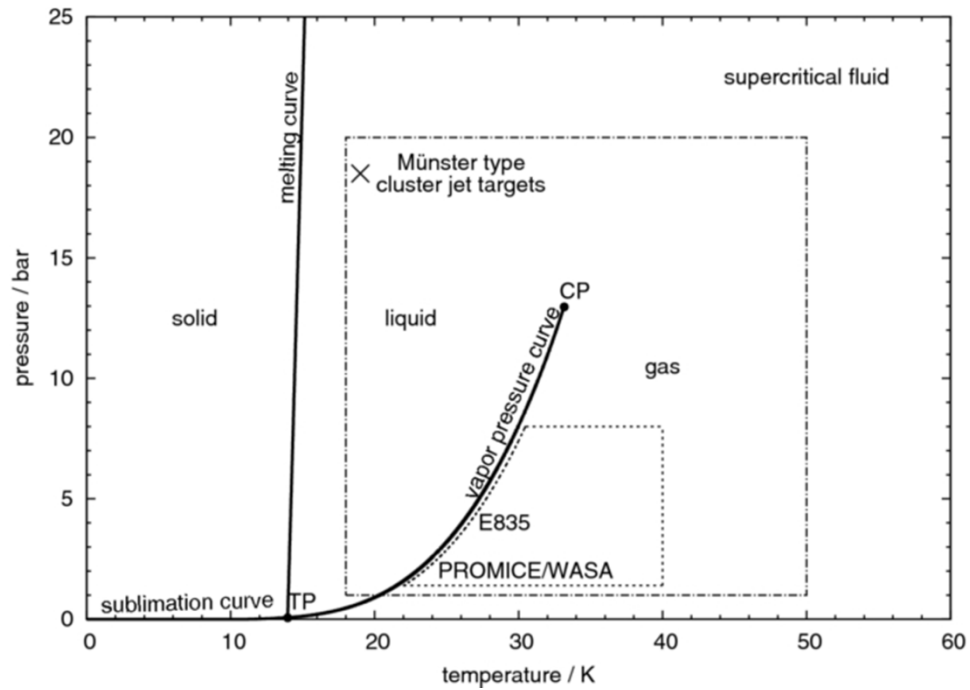
N_2 semiconducting oligomers $(-\text{N}-)_x$ at 100-240 GPa
cubic diamond 110 GPa, 2000 K

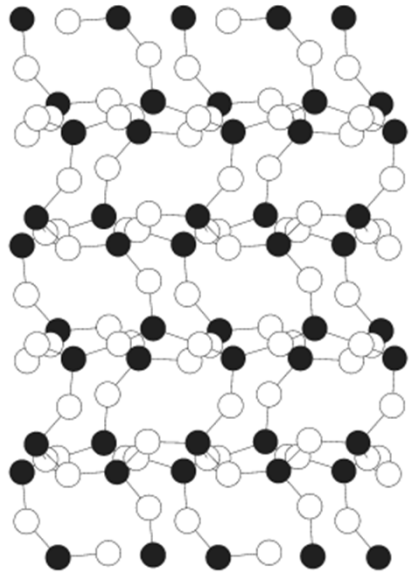


Heating: 1- μm B plate (absorber of laser radiation rests on c-BN pieces that thermally insulate the plate from the bottom anvil. The sample squeezed between the anvils is surrounded by the c-BN/epoxy gasket followed by the metallic (Re) supporting ring.



Phase Diagram of Hydrogen

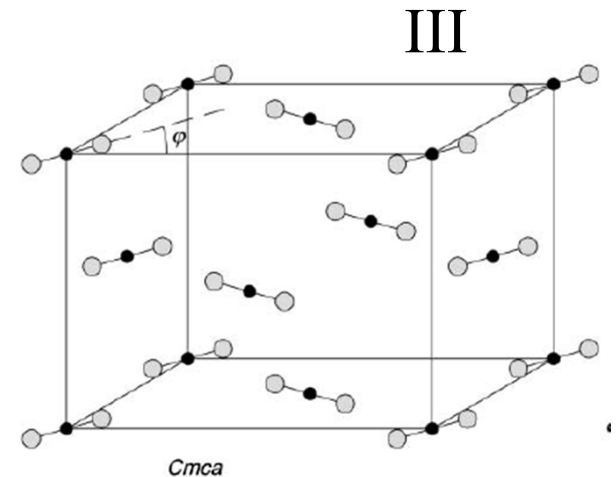
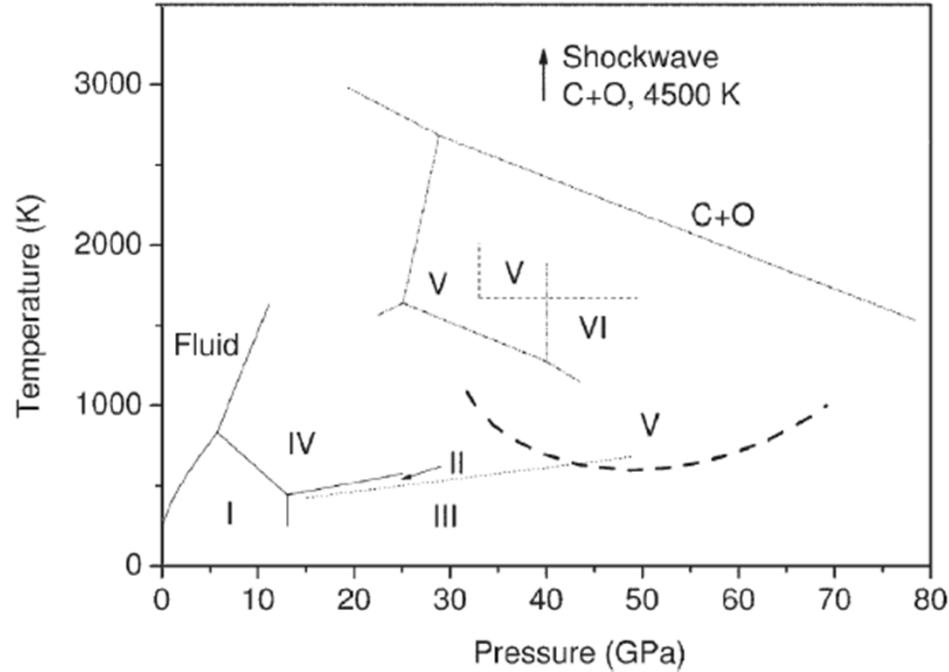
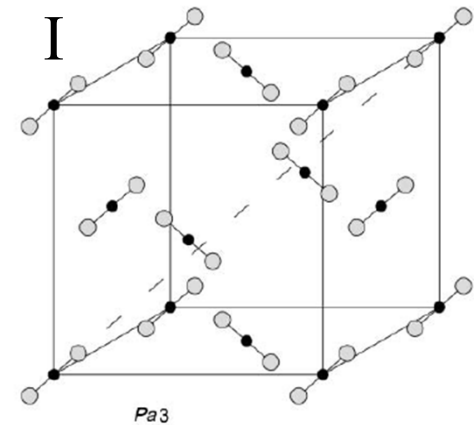




Phase Diagram of CO₂

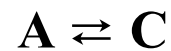
CO₂-V
Quartz
superhard

CO₂ heating at 10-20 GPa
sp³ bonded CO₄
cristobalite, tridymite
40 GPa quartz
(noncentrosymmetric)



Reaction Equilibrium and Pressure

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



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

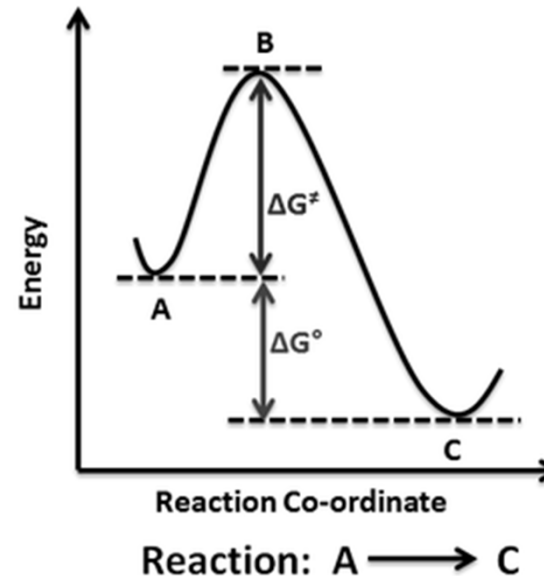
$$\Delta G^0 = -RT \ln K \quad \longrightarrow \quad \left(\frac{\partial RT \ln K}{\partial P} \right)_T = -\Delta V^0$$

Associative type = negative ΔV^0

K increases with increasing pressure

Dissociative type = positive ΔV^0

K decreases with increasing pressure

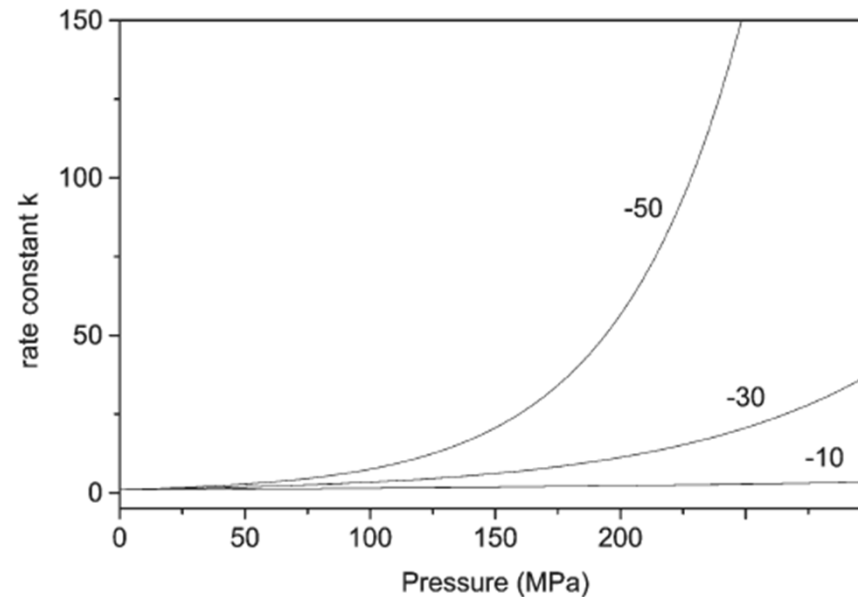


$$\left(\frac{\partial \ln k}{\partial T}\right)_P = -\frac{E_a}{RT}$$

Reaction Kinetics

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

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



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

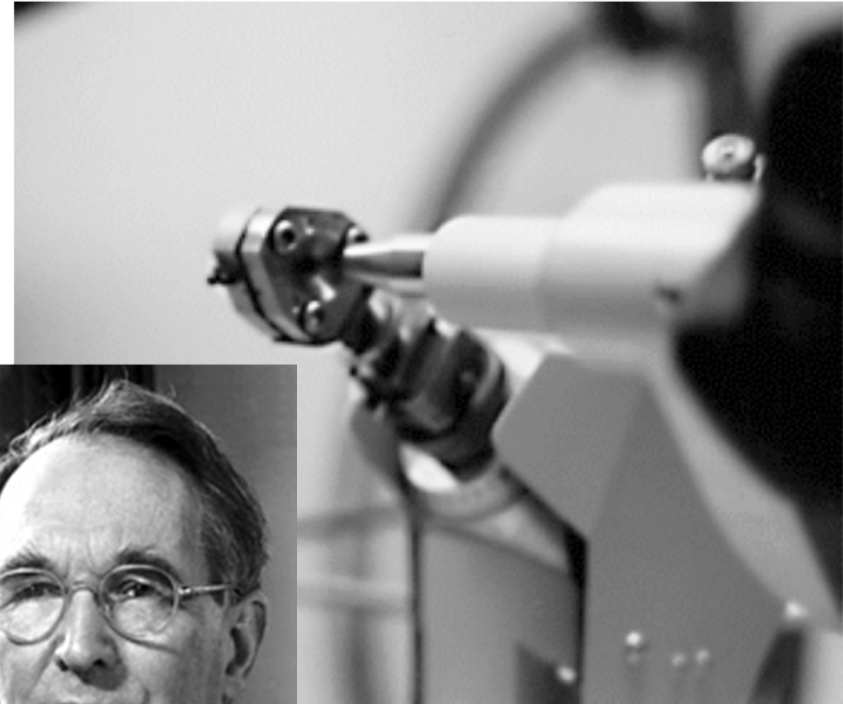
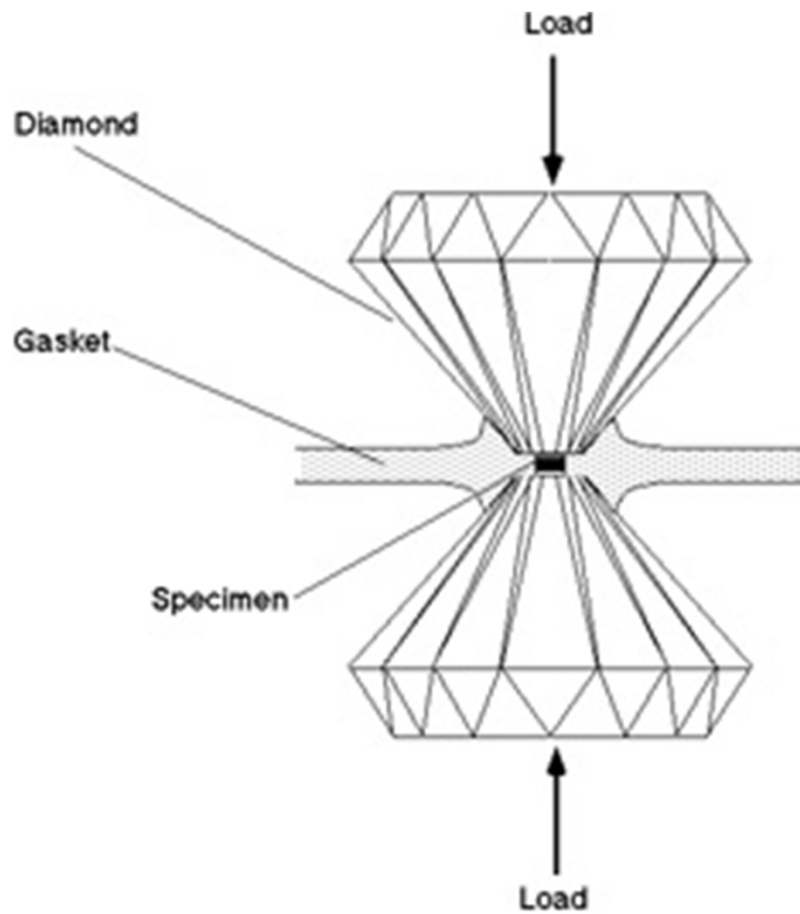
Associative type = the rate determining step involves the formation of a covalent bond

negative $\Delta V^\ddagger \rightarrow$ reaction rate increases with increasing pressure

Dissociative type = the breaking of a covalent bond

positive $\Delta V^\ddagger \rightarrow$ reaction rate decreases with increasing pressure

Diamond Anvil Cell



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

Diamond Anvil Cell

Diamond anvil cell

$$p = F/A$$

$$p = 40 \text{ GPa}$$

$$A_{\text{table}} / A_{\text{culet}} = 10 : 1$$

$$A_{\text{culet}} = 100\text{-}200 \mu\text{m}$$

laser heating $T > 2500 \text{ }^\circ\text{C}$

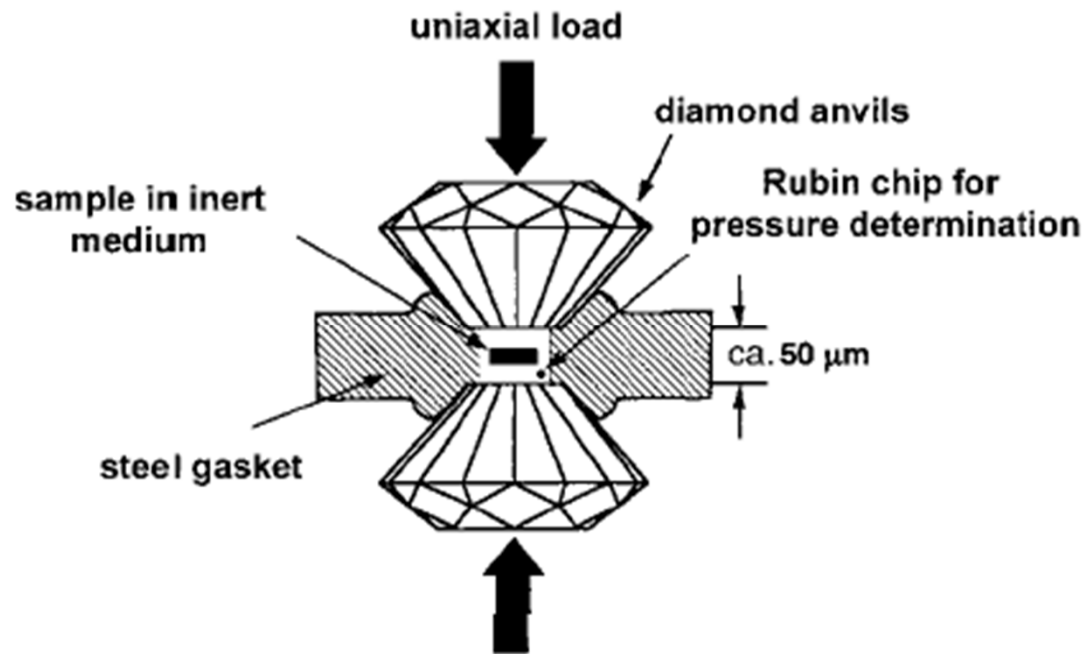
Re, steel gasket

Diamond transparent

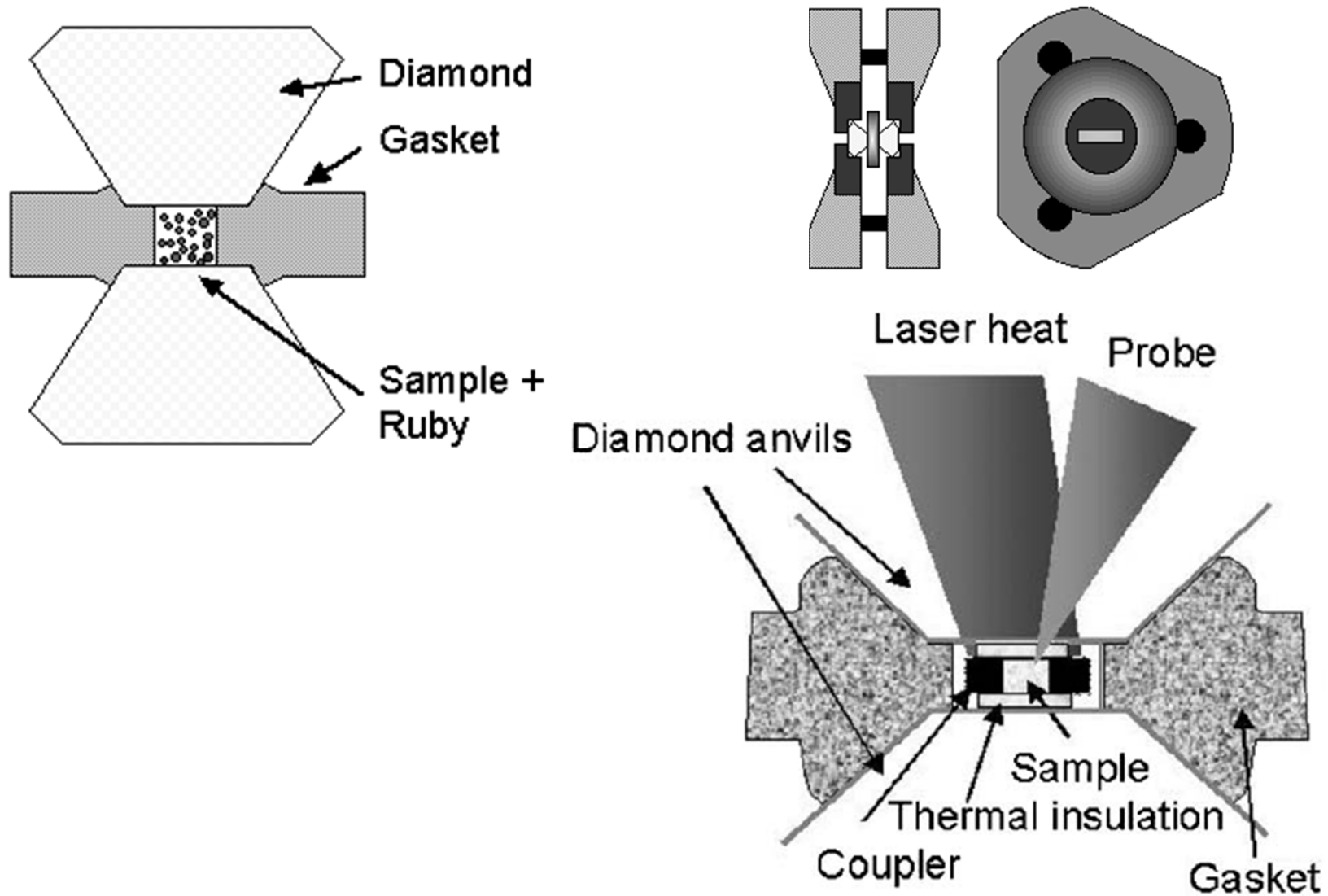
to radiation from IR to X-ray

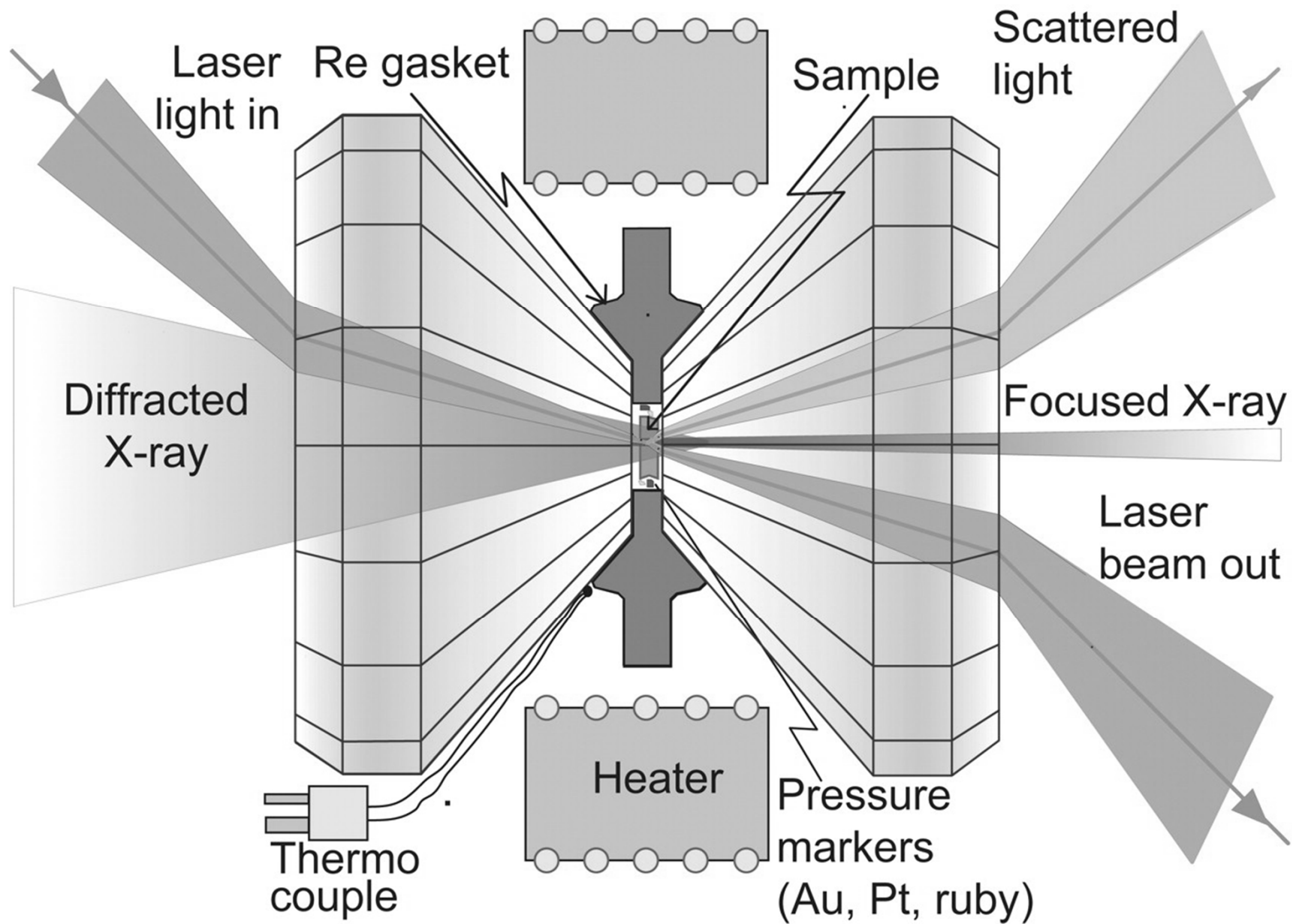
pressure transmitting medium:

solid Ar, N₂, O₂,



Diamond Anvil Cell



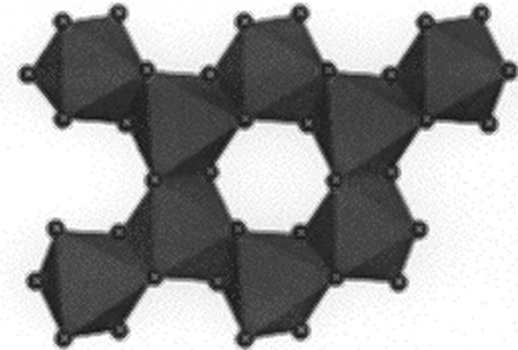


Dry High-Pressure Methods

Calibrating a high pressure diamond anvil

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

Ruby = Cr doped corundum

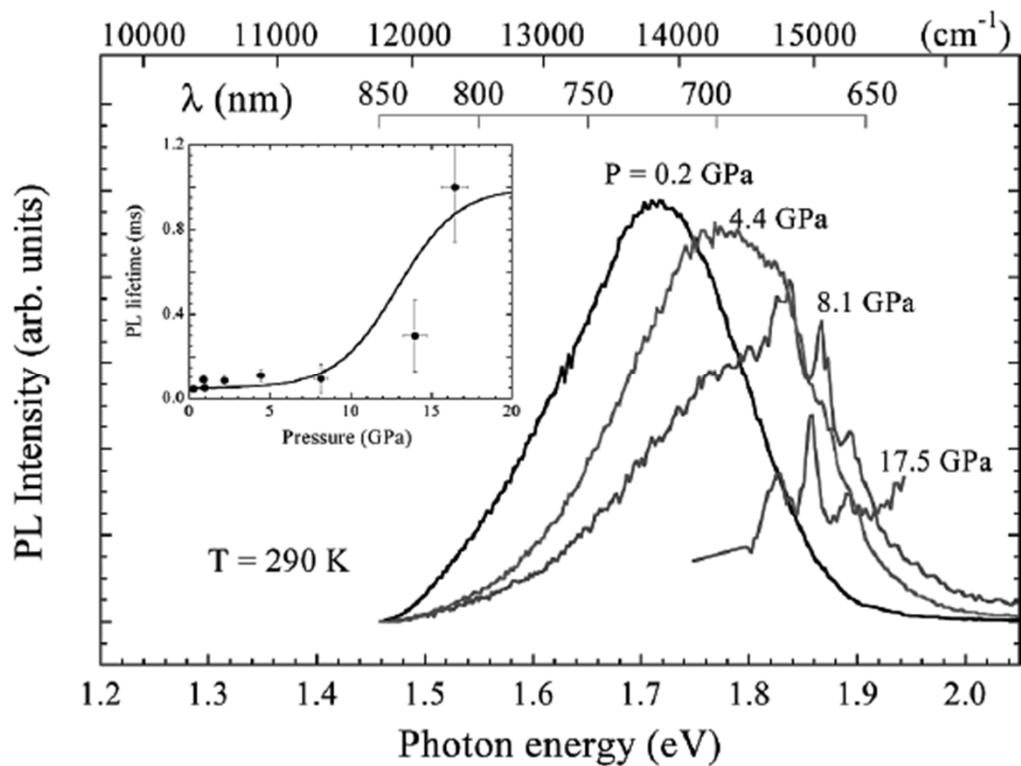
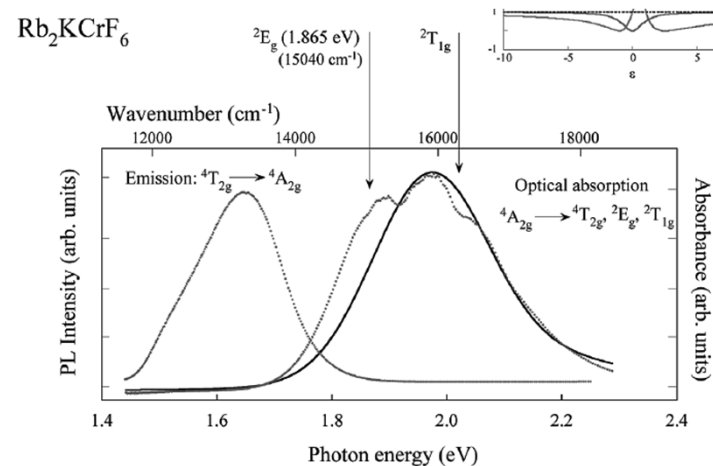
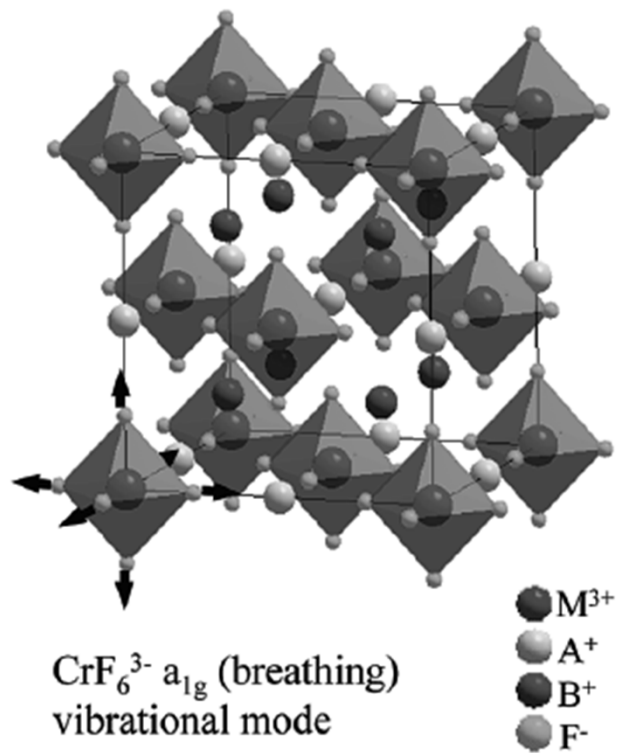


High pressure synthesis

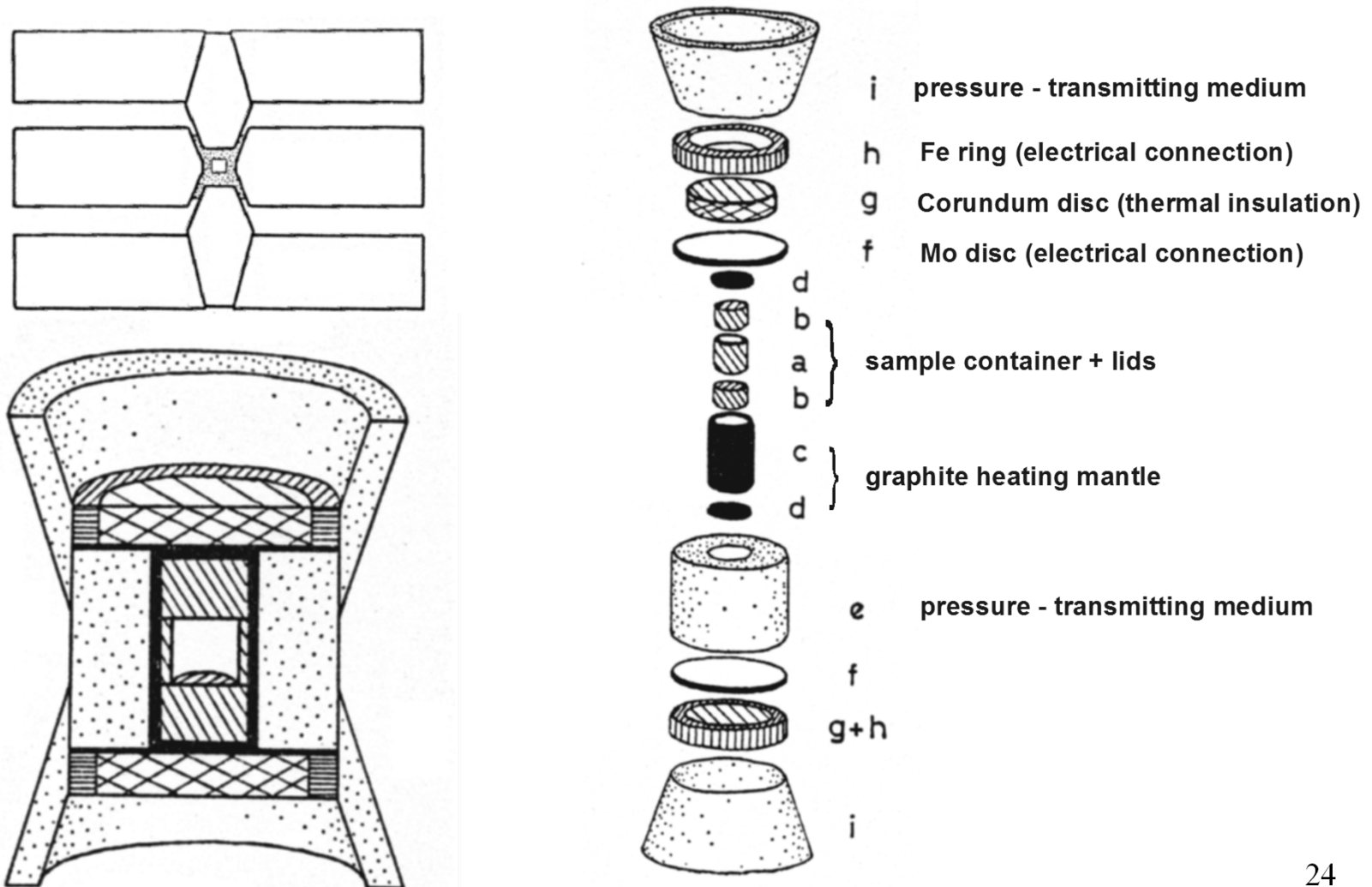


At ambient pressure only SnO_2 and PbO products

Rb₂KCrF₆



High Pressure Two-Die Belt-Type Apparatus



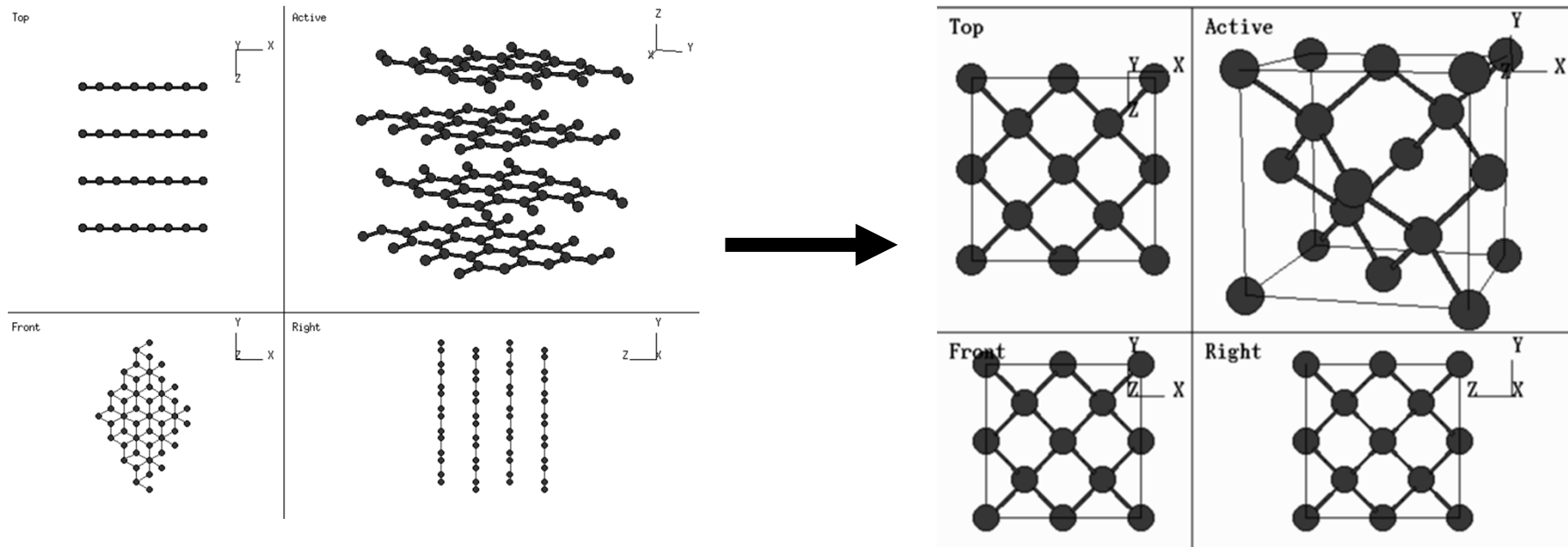
Synthesis of Diamonds



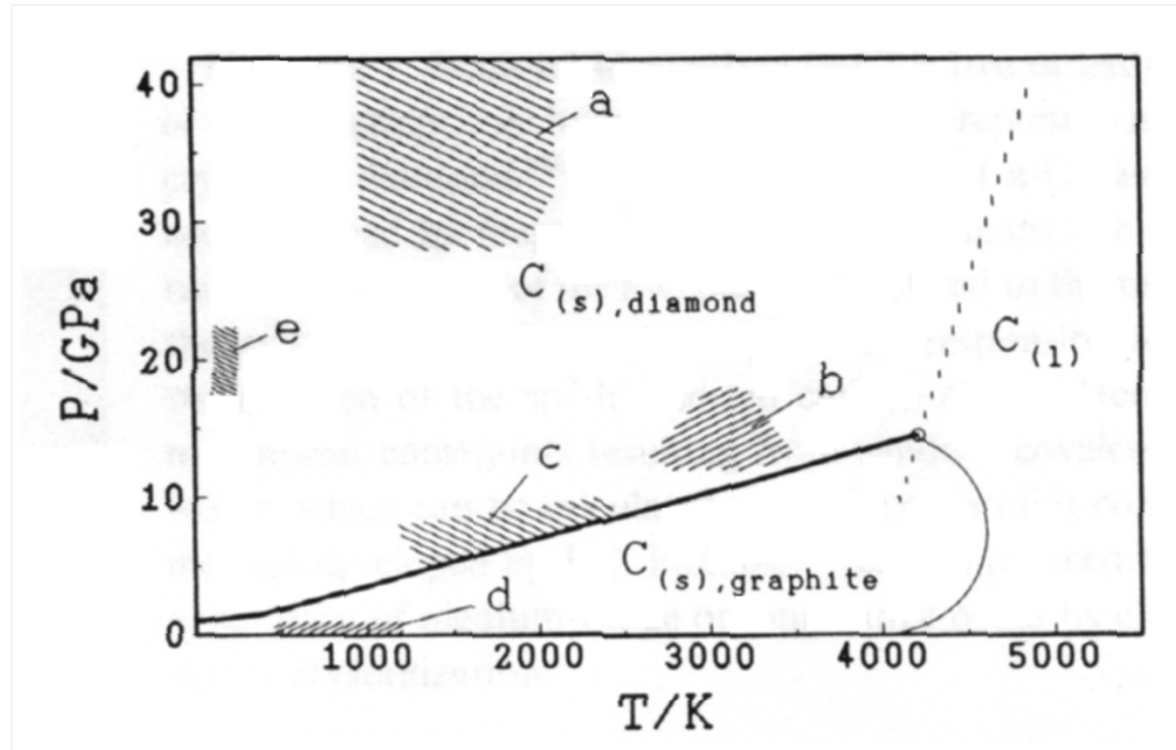
The hardest known substance, the highest thermal conductivity

Difficult to transform graphite into diamond

Industrial diamonds (GE) made from graphite around 3000 °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

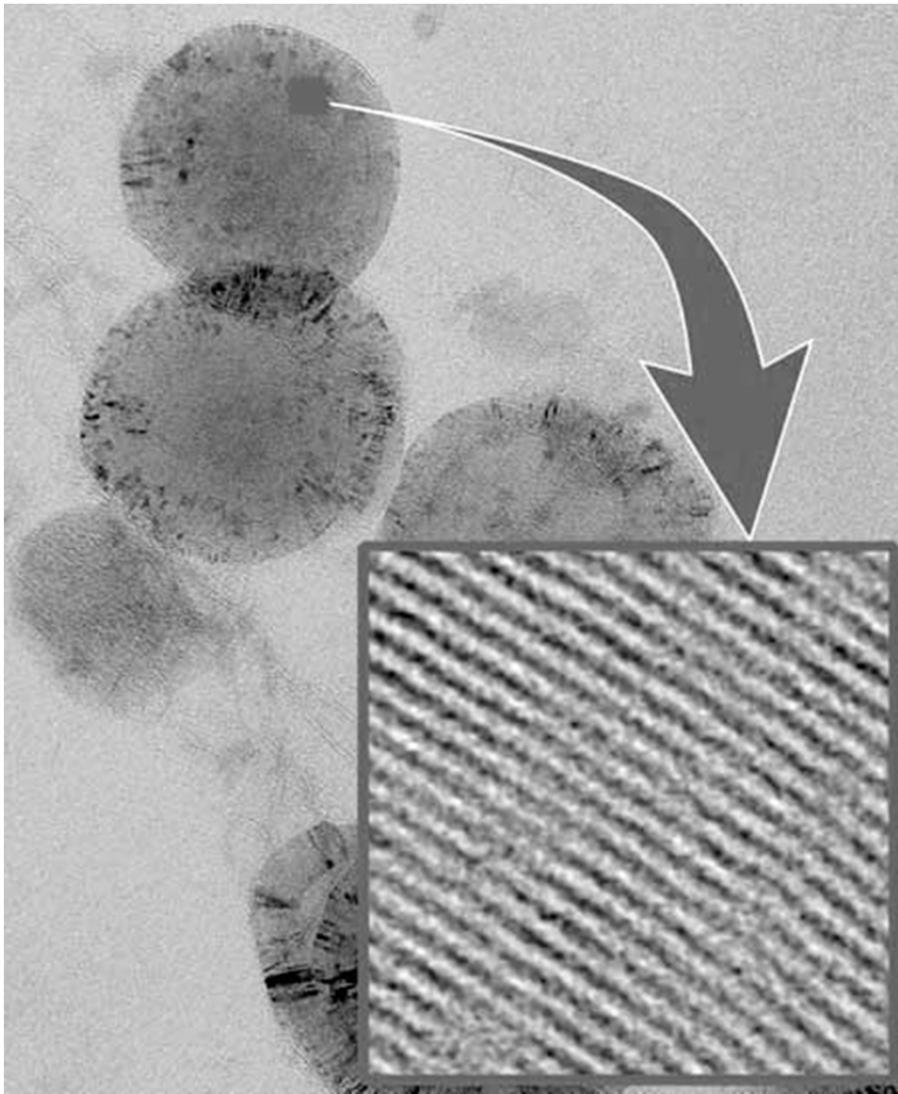
◆ Catalyst: transition metals (graphite is dissolved in molten metal: Fe, Ni, Co, 6 GPa, 1000 °C), alloys (Nb-Cu), $CaCO_3$, hydroxides, sulfates, P (7.7 GPa, 2200 °C, 10 min)

◆ Squeezing (uniaxial not hydrostatic pressure), no heating, buckyball carbons are already intermediate between sp^{2-3}

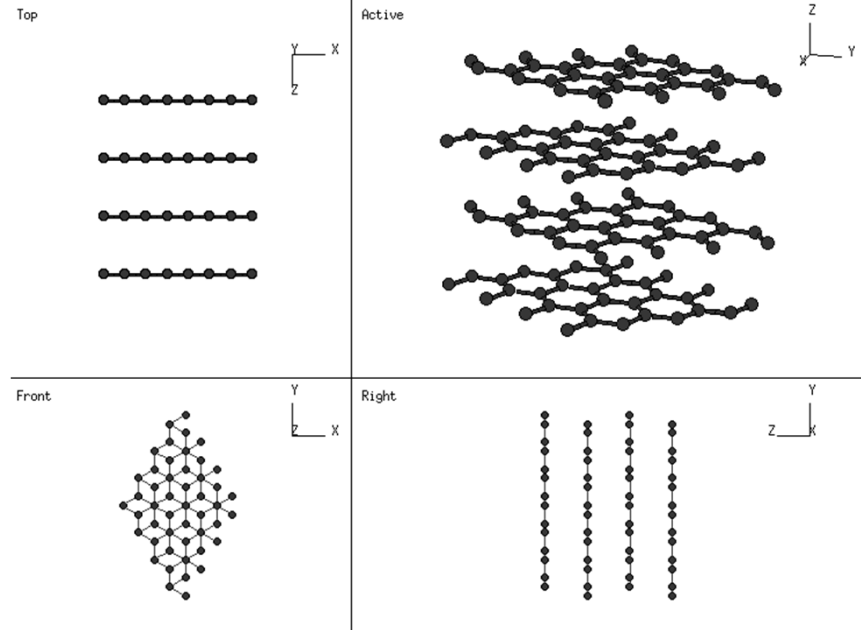
C_{60} , diamond anvil, 25 GPa instantaneous transformation to bulk crystalline diamond, highly efficient process, fast kinetics

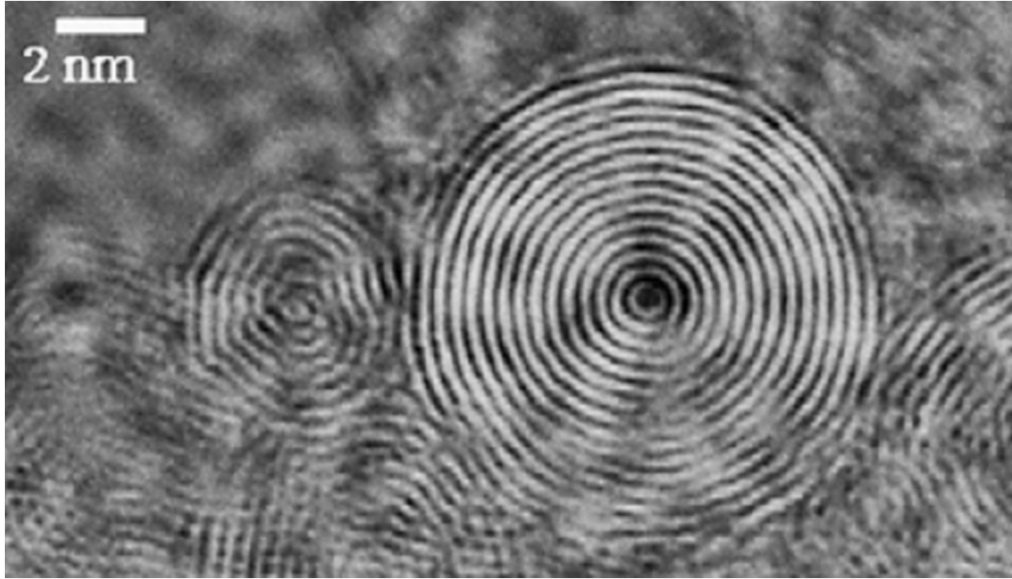
◆ Carbon onions, electron irradiation of graphite, concentric spherical graphite layers, spacing decreases from 3.4 Å to 2.2 Å in the onion center, 100 GPa, 200 keV beam, in several hours, pressureless conversion to diamond

◆ 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

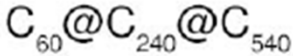
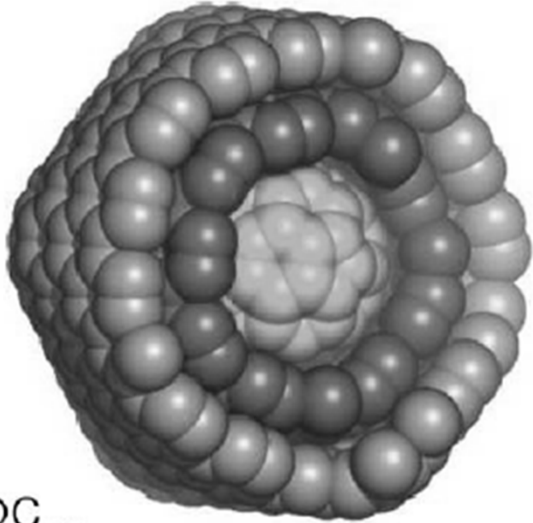
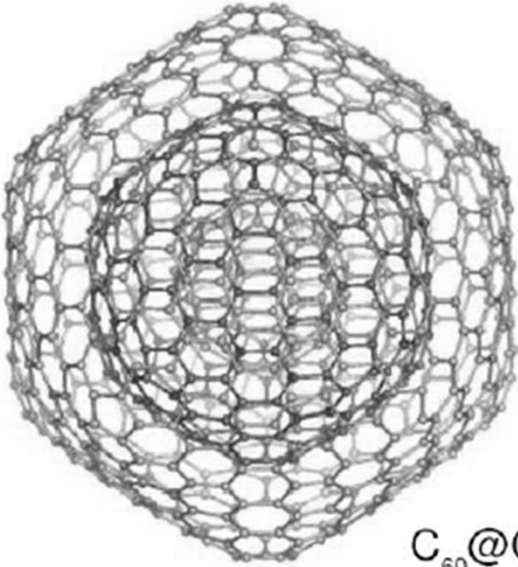
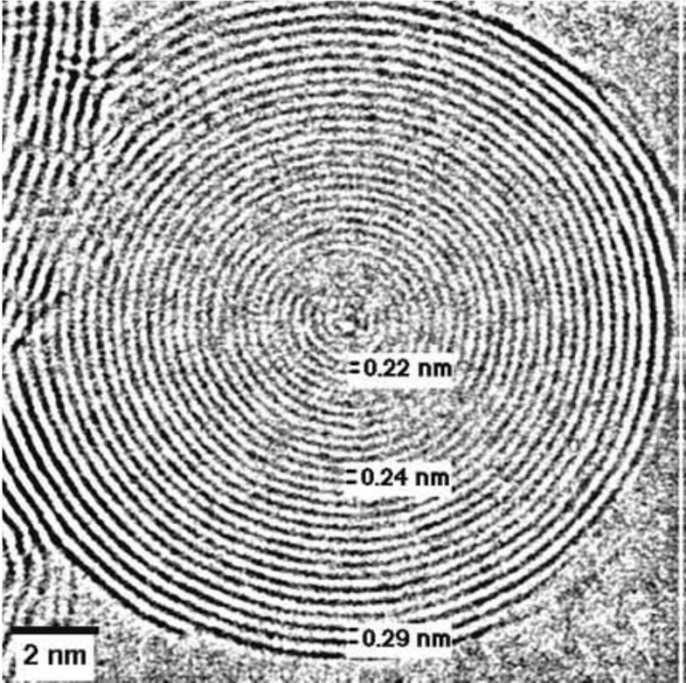


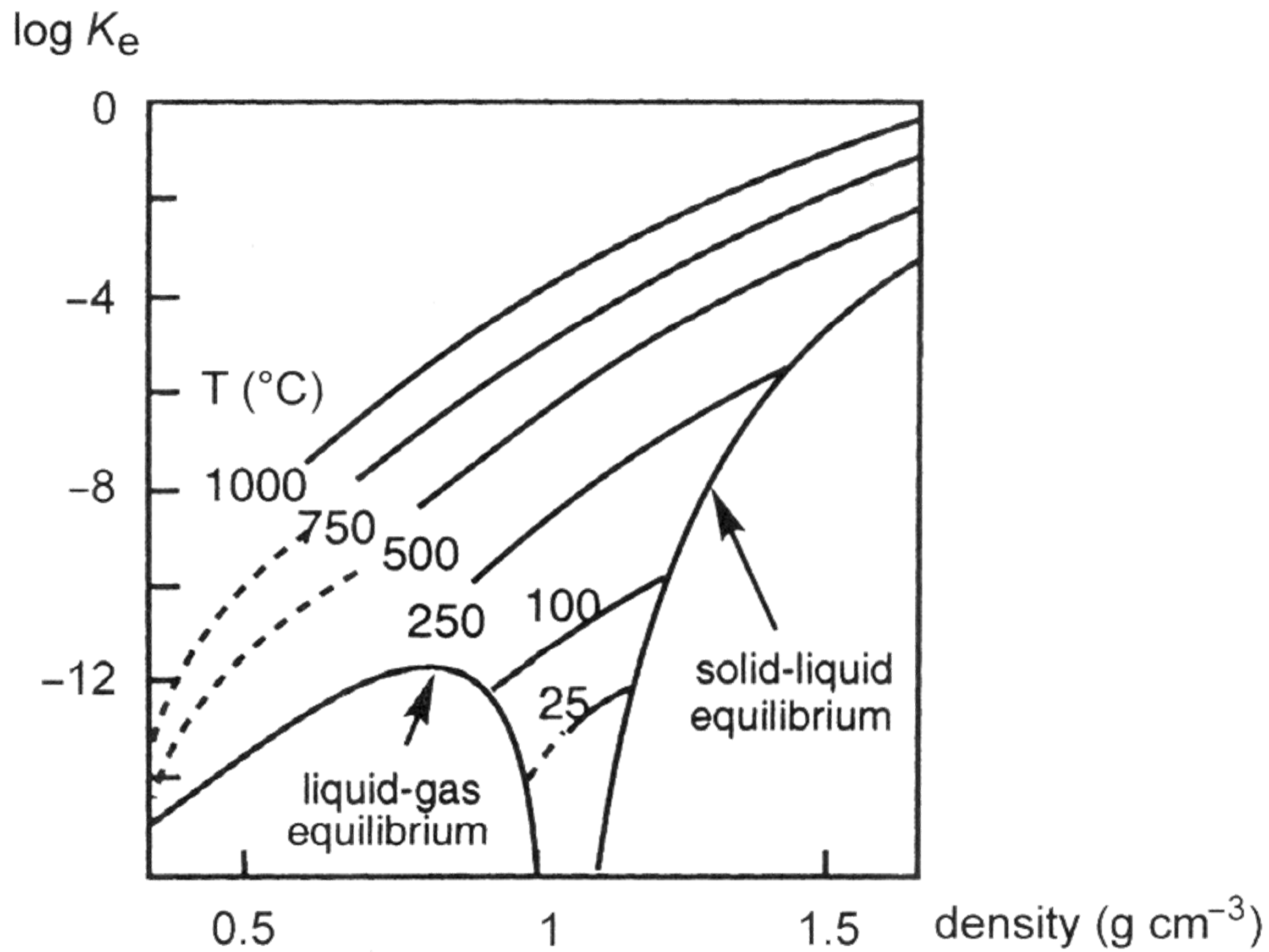
Graphite





Carbon onions





Organic molecule theory of diamond cleavage

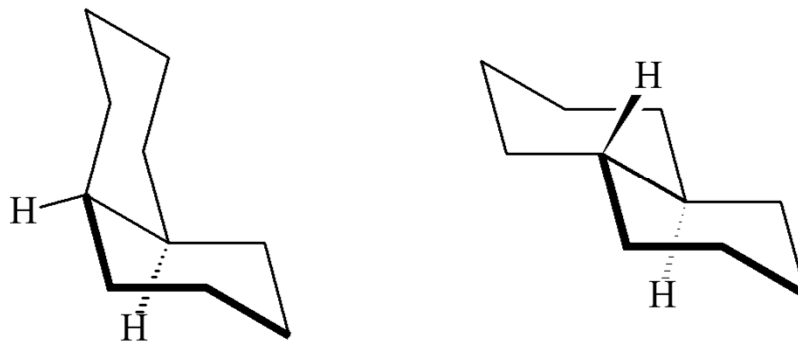
The jeweler's chisel if placed correctly on a diamond, with a well oriented blow, always cause cleavage along {111} greater than 90% of the time, imagine the cost of a mistake with a large crystal

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.

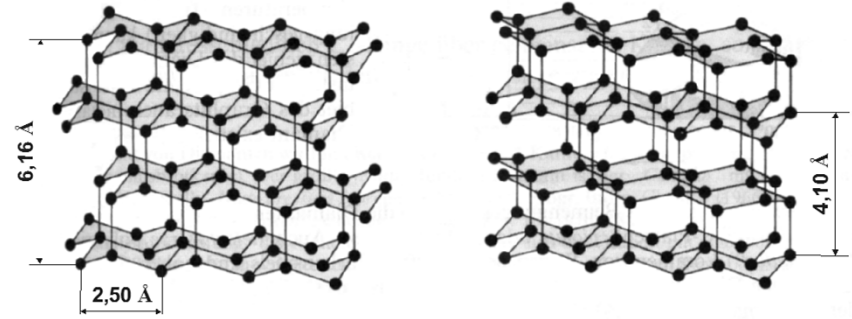


**A breaking molecule theory: axial-axial unfavorable interactions cause the mechanical energy of the jeweler's chisel to be funneled into preferential breakage of an axial C-C bond
This then induces a kind of domino effect whereby the adjacent axial C-C bonds break and C-C bonds throughout the entire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

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

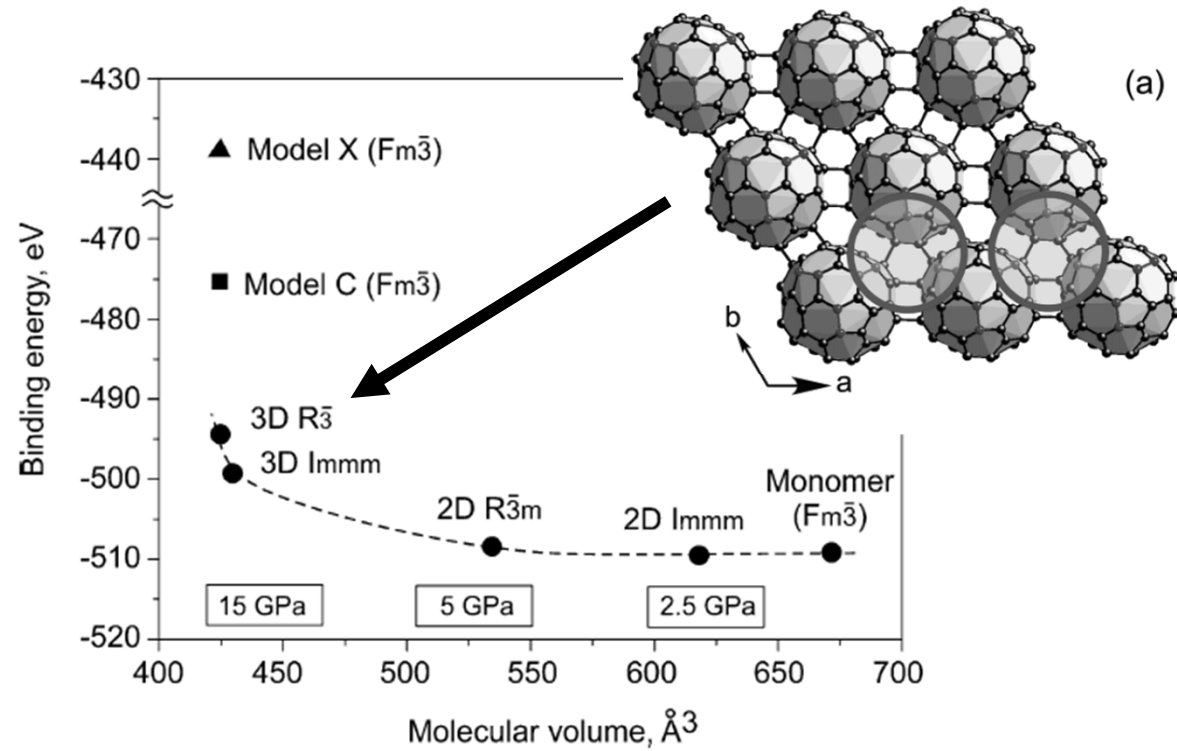
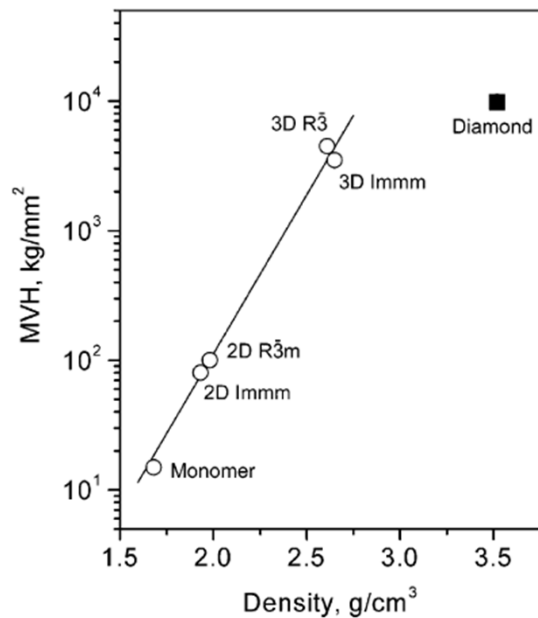


Synthesized in the laboratory at static pressure of 130 kbar and temperature over 1000 °C from well-crystallized graphite in which the *c* axes of the crystallites are parallel to each other and to the direction of compression

The crystal structure is hexagonal with $a = 2.52 \text{ \AA}$ and $c = 4.12 \text{ \AA}$.
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

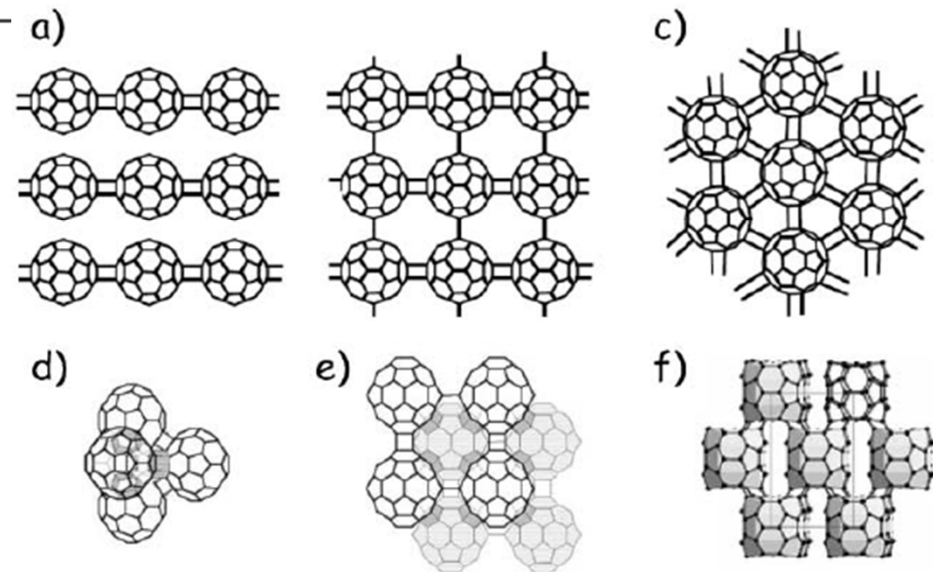
Topochemical 3D Polymerization of C_{60} under High P and T



Micro-Vickers hardness (MVH)

Polymerization of C₆₀

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 <i>Immm</i>	4	80	1.936	1.93
2D <i>R$\bar{3}m$</i>	6	100	2.004	1.98
3D <i>Immm</i>	8	3,500	2.78	2.65
3D <i>R$\bar{3}$</i>	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!**