

High Pressure and Materials Research



Chandrabhas Narayana

Chemistry and Physics of Materials Unit

Jawaharlal Nehru Centre for Advanced Scientific Research

Jakkur P.O. Bangalore 560 064

*Lecture delivered at Indus for future Users – January 24-25, 2012
January 24, 2012*

Investigation of Materials

- 'Disturbing the materials'
 - applying electric field, magnetic field, changing volume.
- To change volume
 - temperature variation
 - pressure variation
- Changing temperature
 - change in phonons along with V
- Changing Pressure
 - only changes V -----> Cleaner probe
- Changes are stronger with pressure
 - V of Si changes 5% for 100 kbars
 - 1.8 % for 0 K to melting.

PRESSURE

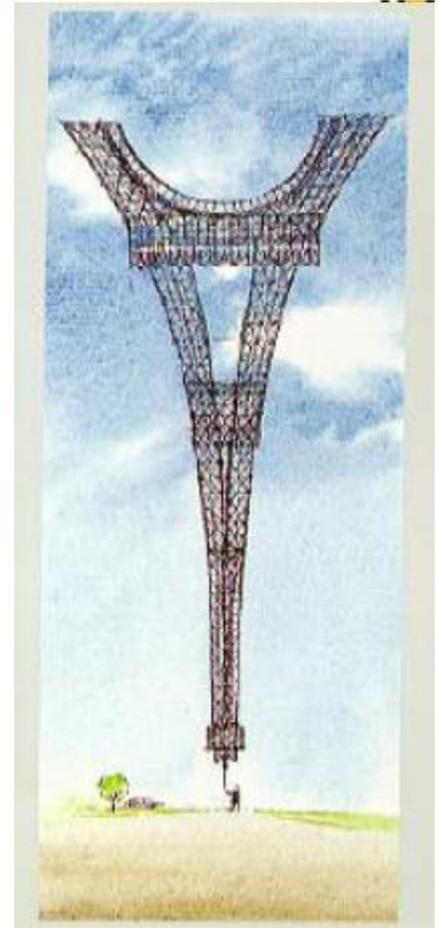
Pressure = Force/Area

- 1 atm = 14.7 psi
- 1 bar = 0.9869 atm
- 1 Pascal = 1N/m²
- 1 GPa = 10 kbars
- 100 GPa = 1 Mbar

Pressure at the center of

- Earth = 390 GPa
- Uranus = 600 GPa
- Saturn = 1400 GPa
- Jupiter = 2000 GPa

Highest static pressure achieved in lab ~ 3 -5 Mbars



PRESSURE

```
graph TD; A[PRESSURE] --> B[STATIC]; A --> C[DYNAMIC];
```

STATIC

T remains constant
Mechanical methods
No time limit
Small samples
Laboratory experiment
5 Mbar

DYNAMIC

T Changes with pressure
Shock wave
Short duration
Larger samples
Elaborate setup
25 Mbar

History - the HP forefathers

- Percy Bridgman's

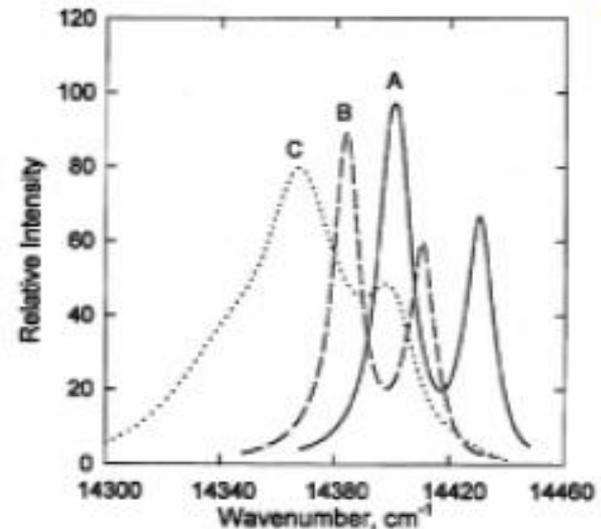
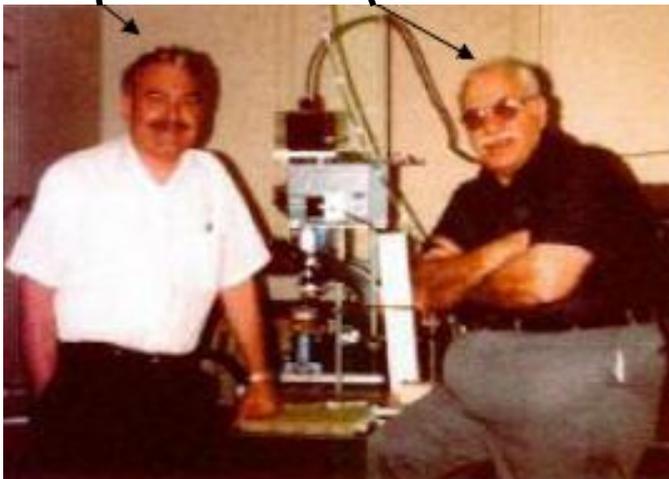
“....experimental work on static high pressures was begun in 1908. It was at first confined to pressures of about 6,500 atmospheres, but he gradually extended the range to more than 100,000 atmospheres and ultimately reached about 400,000 atmospheres. In this unexplored field, he had to invent much of the equipment himself. His most important invention was a special type of seal, in which the pressure in the gasket always exceeds that in the pressurized fluid, so that the closure is self-sealing; without this his work at very high pressures would not have been possible. Later he was able to make full use of the new steels and of alloys of metals with heat-resistant compounds such as carboloy (tungsten carbide cemented in cobalt).”



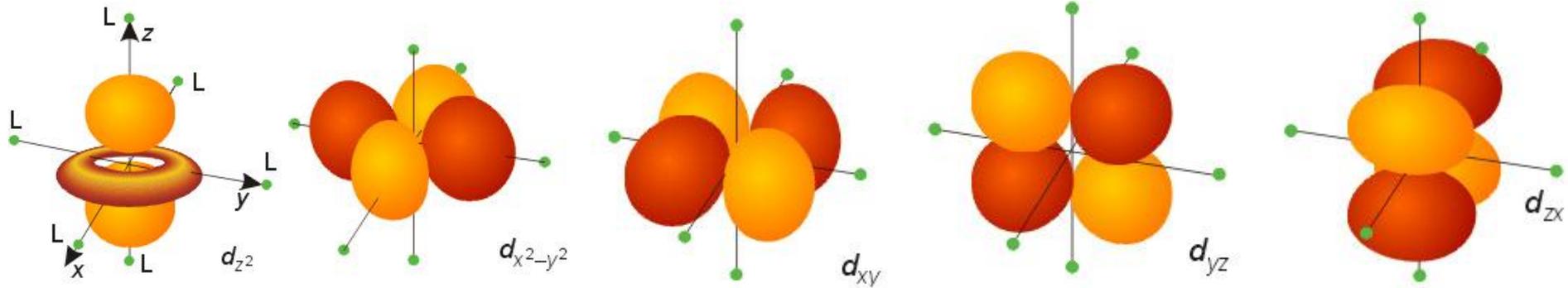
Nobel prize in 1946

History - important breakthroughs

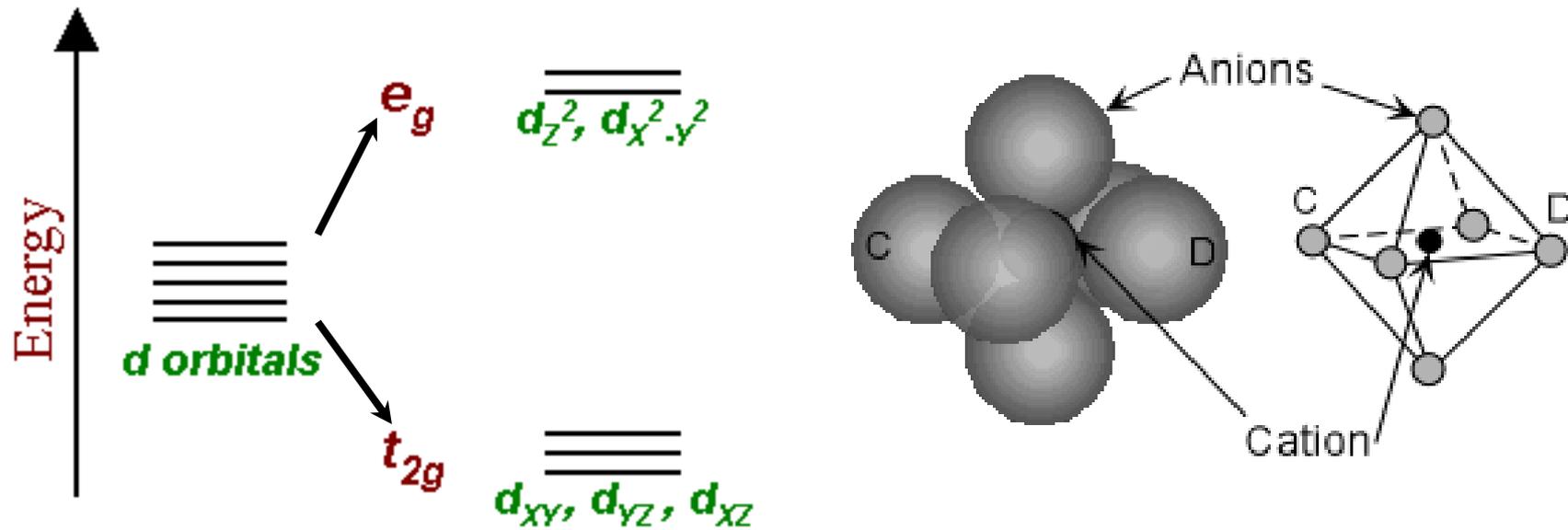
- Invention of diamond anvil cell 1958
 - Weir, Lippincott, Van Valcanberg and Bunting
J. Res. Natl. Bur. Stand. **63A**, 55 (1959)
- Pressure calibration with ruby lines 1975
 - Piermarini, Block, Barnett and Forman
J. Appl. Phys. **46**, 2774 (1975)



Crystal Field Splitting

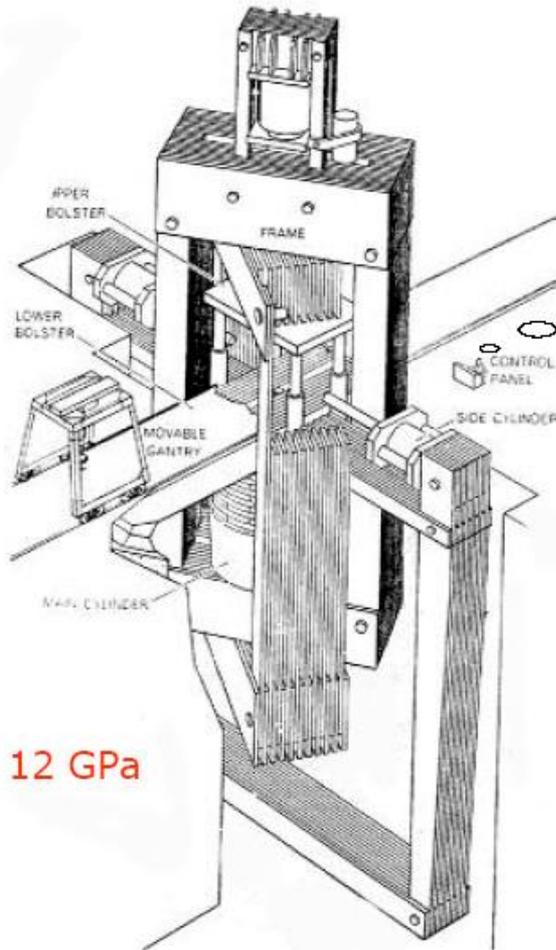


Octahedral Coordination



Crystal Field Splitting

Development of HP

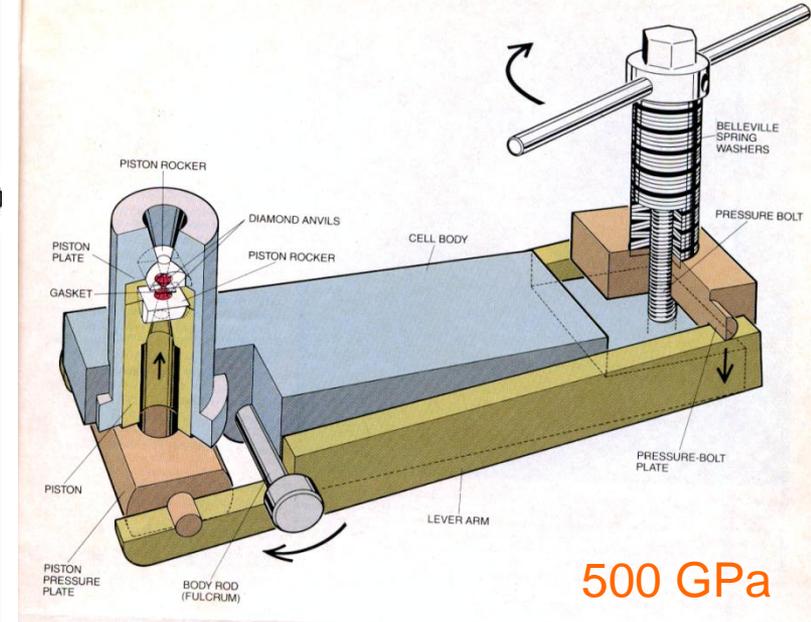


12 GPa

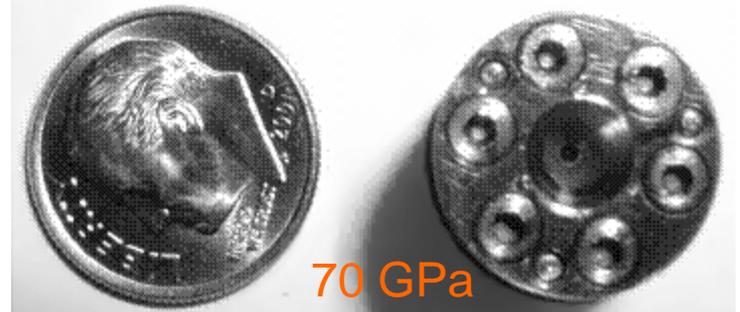
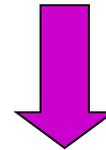
A high-pressure Ph.D student



Diamond anvil Cell (DAC)

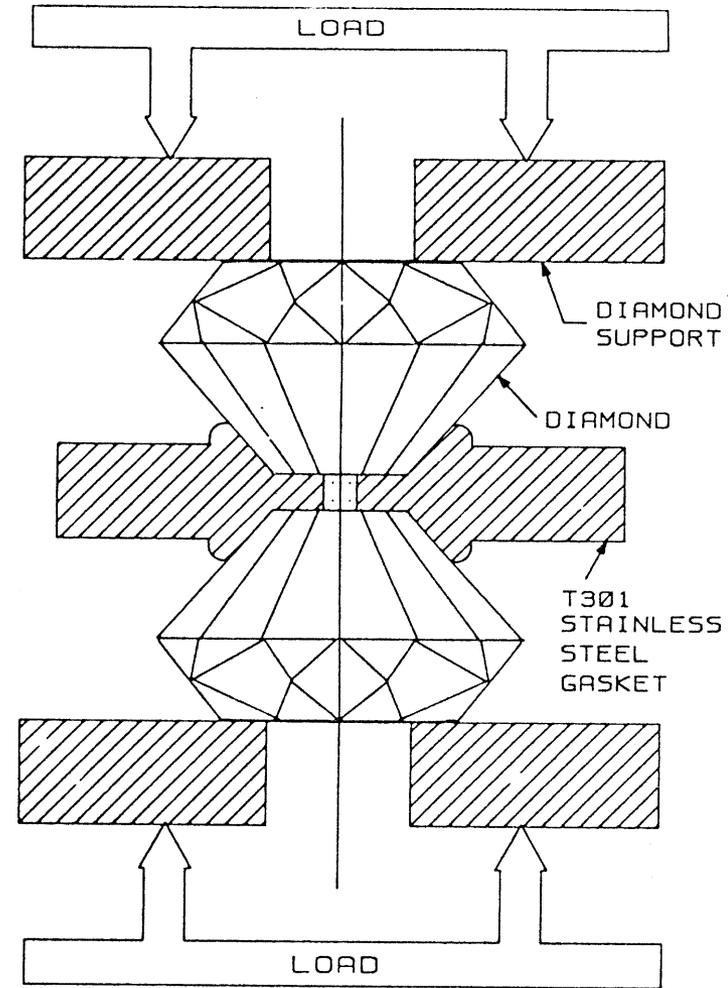
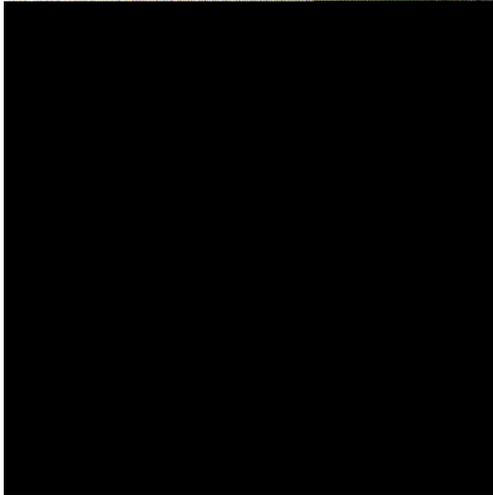


500 GPa



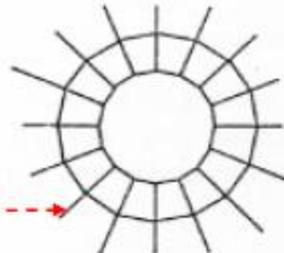
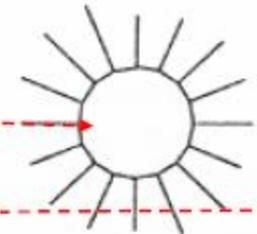
70 GPa

Principle of DAC



SINGLE CULET

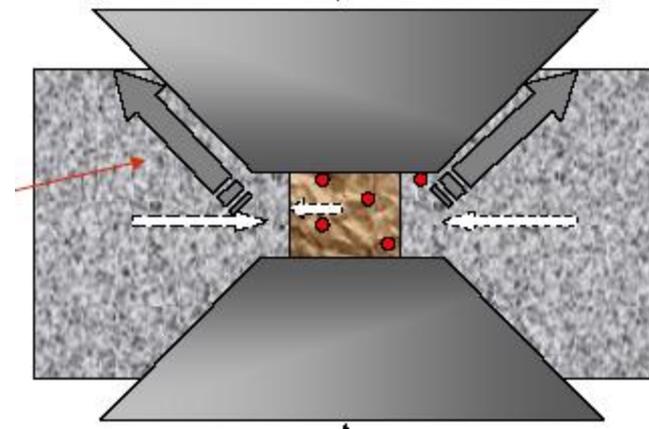
DOUBLE CULET



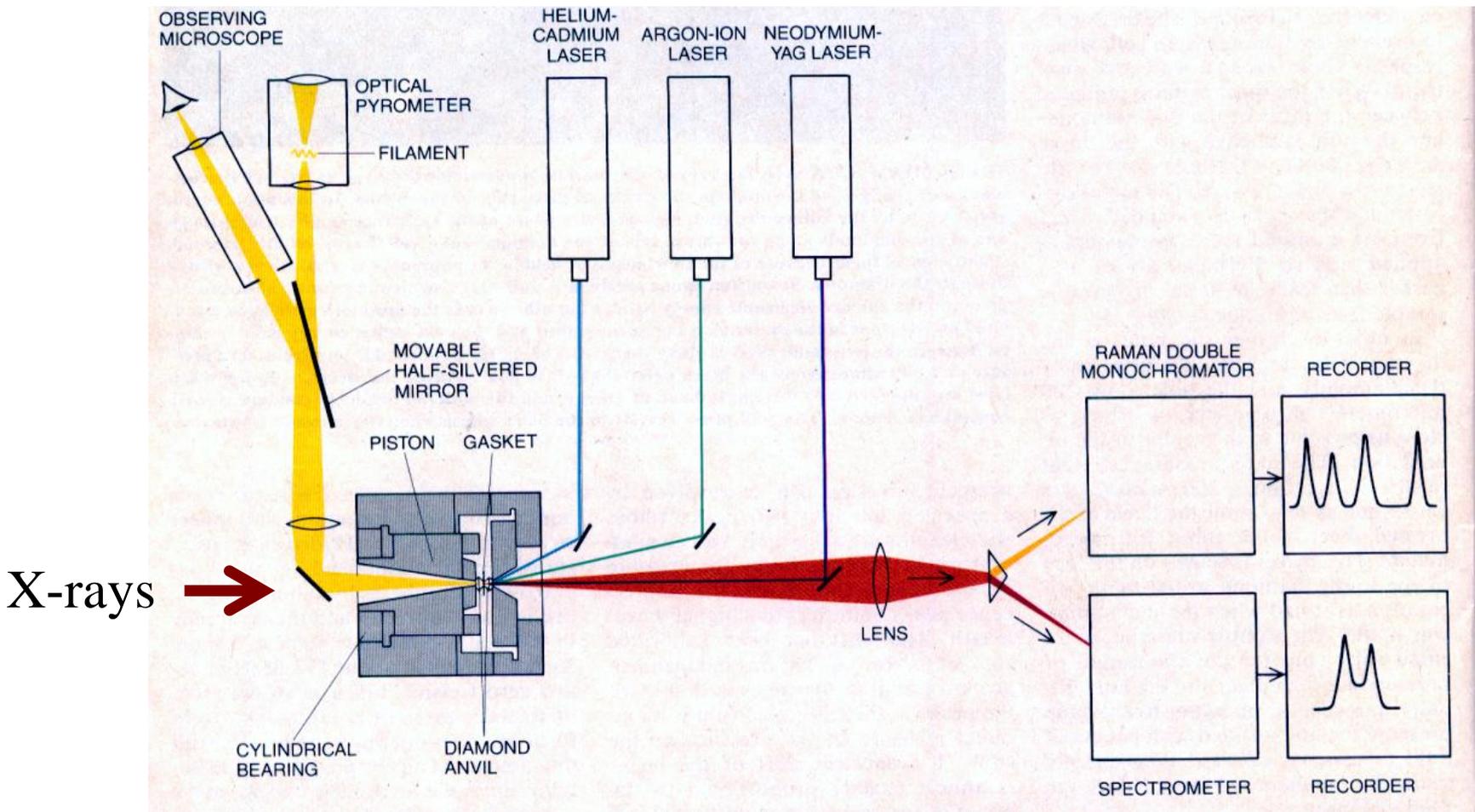
moderate pressures

very high pressures

Gasketing



- Provides containment for pressure medium
- Extrudes around the diamonds acting as a supporting ring
- Prevents failure of anvils due to concentration of stresses at the edge
- It's introduction made DAC a quantitative tool



Schematic diagram for Possible Measurements

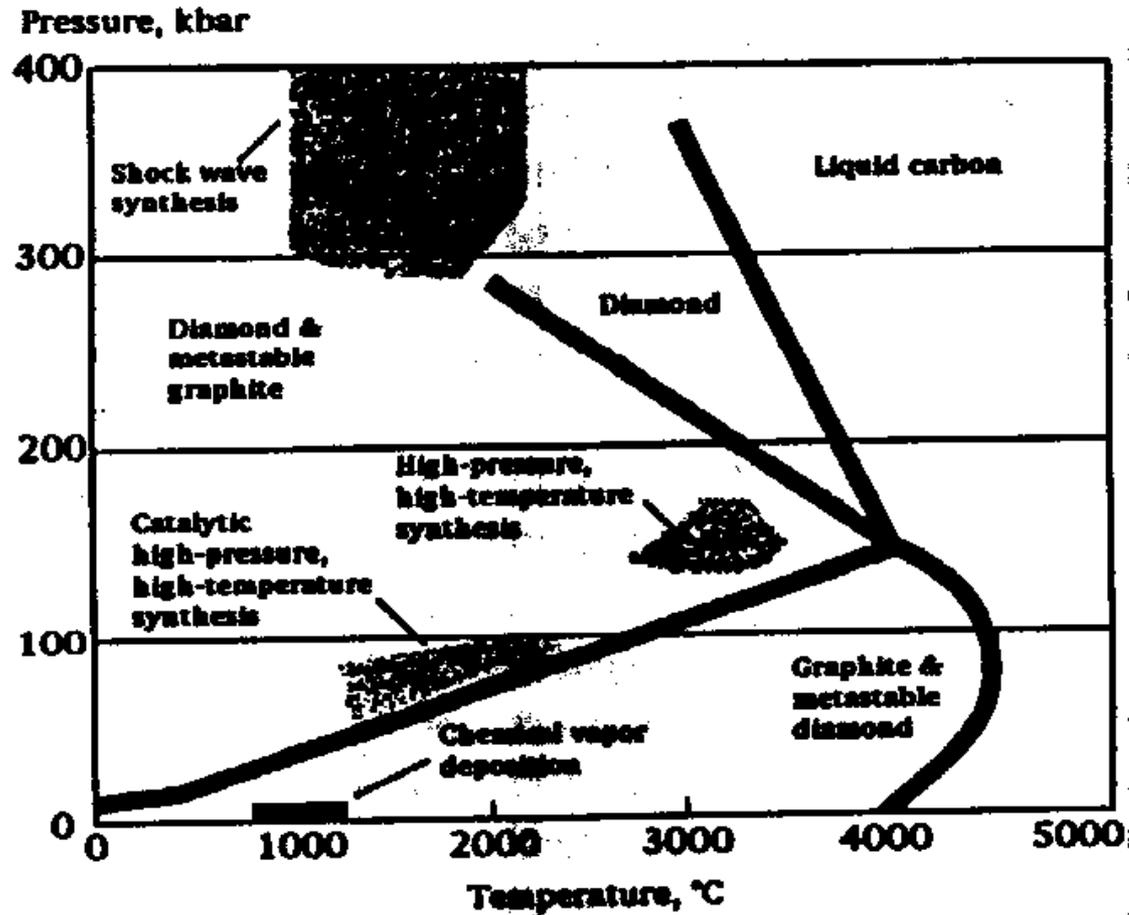
High Pressure in Materials Research

- New state of matter with novel properties
- Unearthing new phenomena
- Led to discovery of exotic and industrially useful materials.
 - classic example is synthetic diamond and cubic BN_3 .

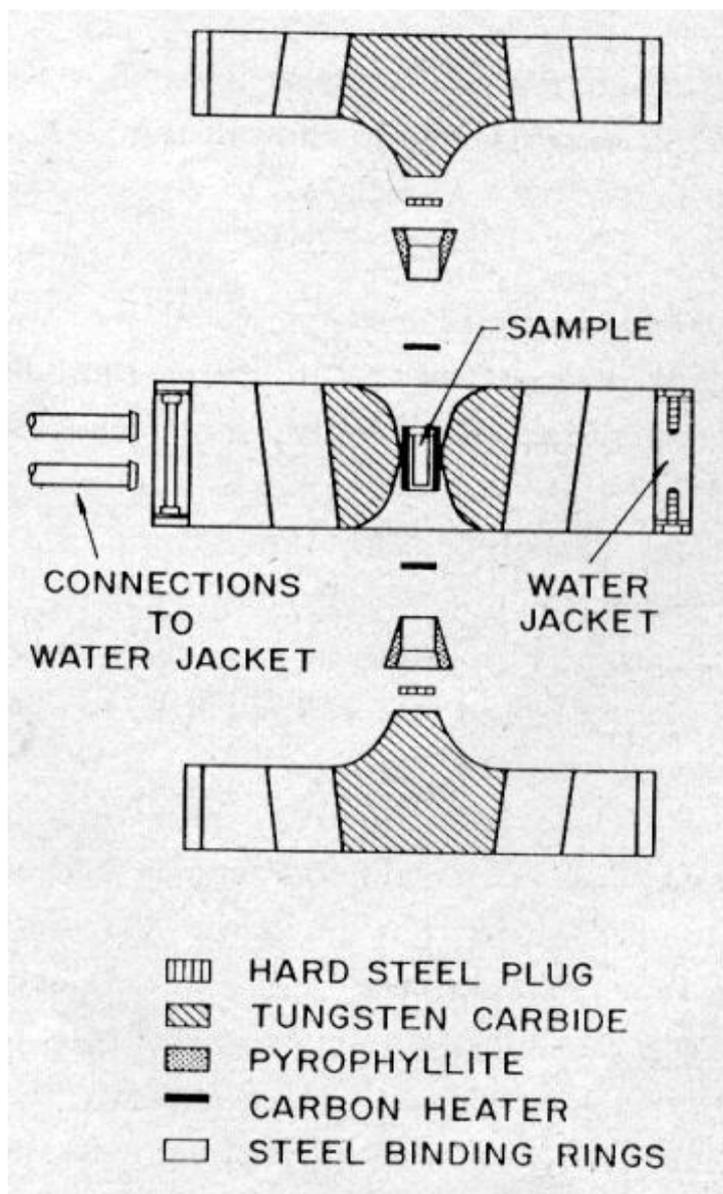
Diamond Synthesis

- Diamond synthesis had to wait for two development
 - An accurate thermodynamic stability field
 - High pressure-high temperature apparatus
- Diamond was first synthesized in early fifties by scientists in G E laboratory, USA
- Actual synthesis of diamond was achieved without a detailed knowledge of the phase diagram of carbon

Phase diagram of carbon



Belt Apparatus



Pressure around 70 kbar
Temperature 1800 K



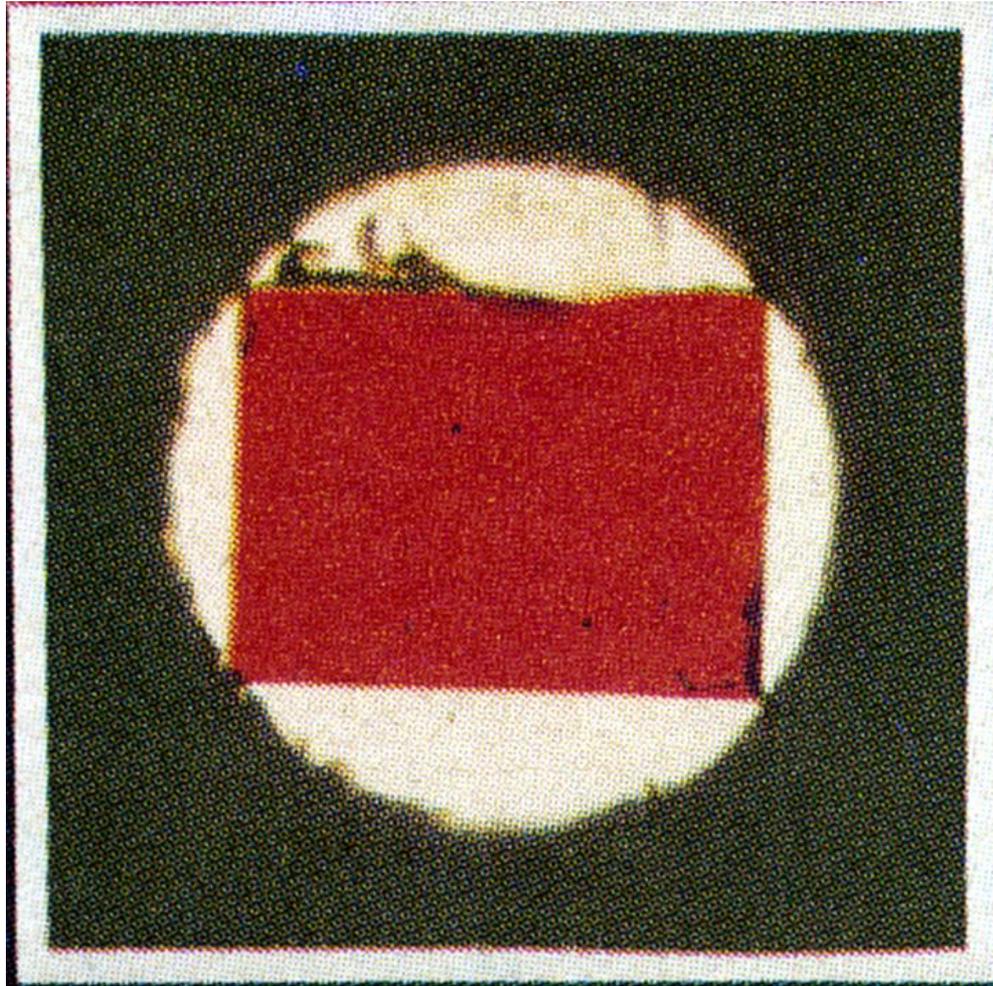
Synthetic diamonds



Natural diamonds

Invented by Hall

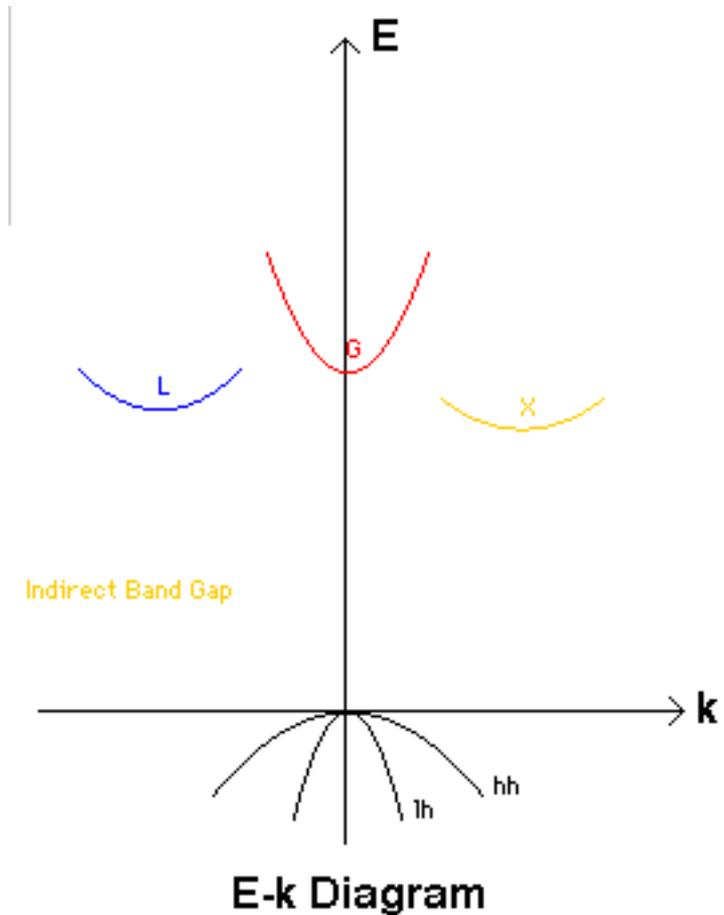
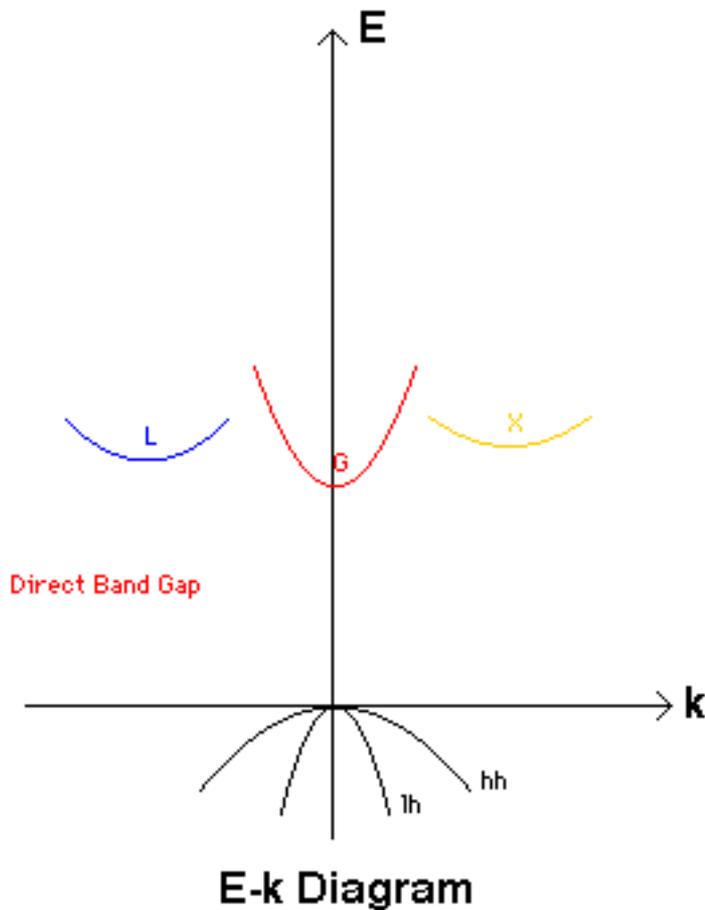
H.T. Hall, Rev. Sci. Instrum, **31**, 125 (1960)

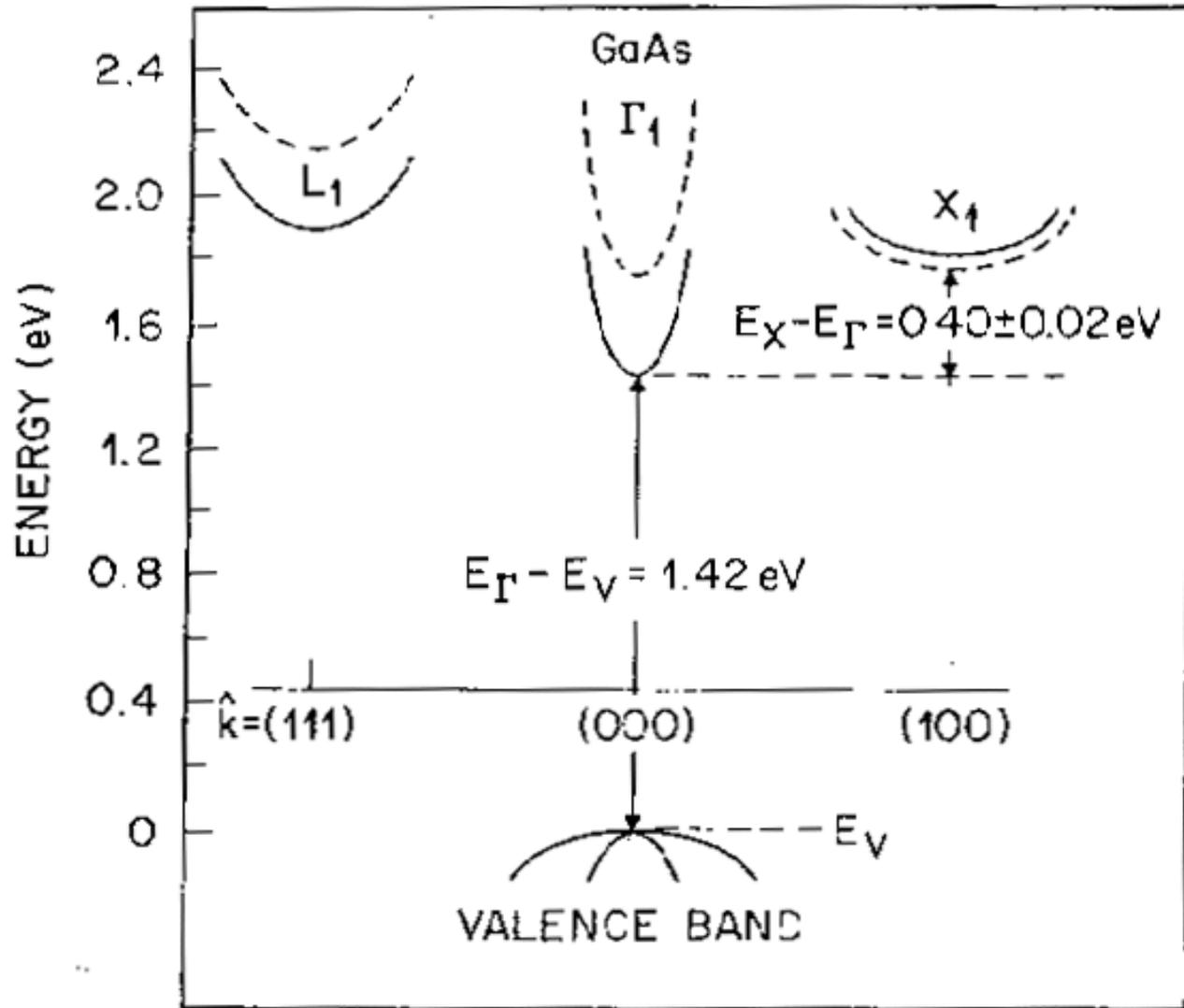


Pressure-induced transparency in GaAs

A.Jayaraman, Metals Materials and Processes, **2**, 1 (1990)

Direct and Indirect Bandgap

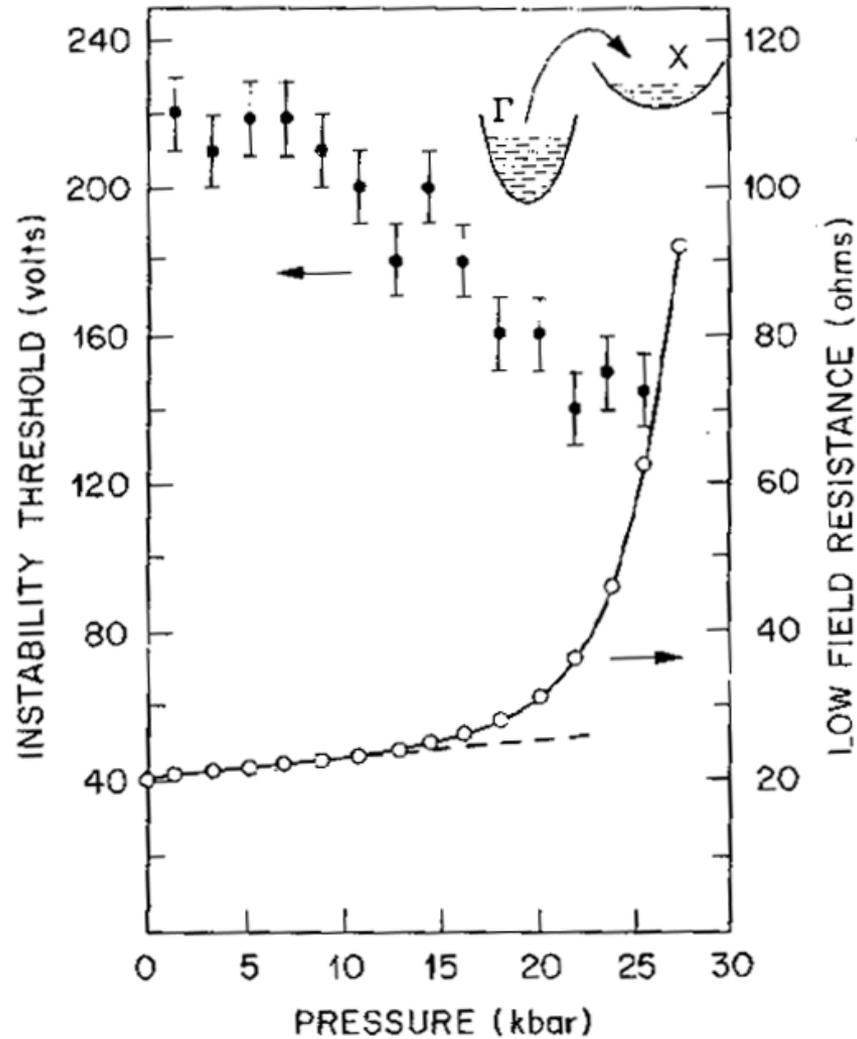




Electronic band structure of GaAs at ambient pressure (solid line) and at 35 kbar (dashed line)

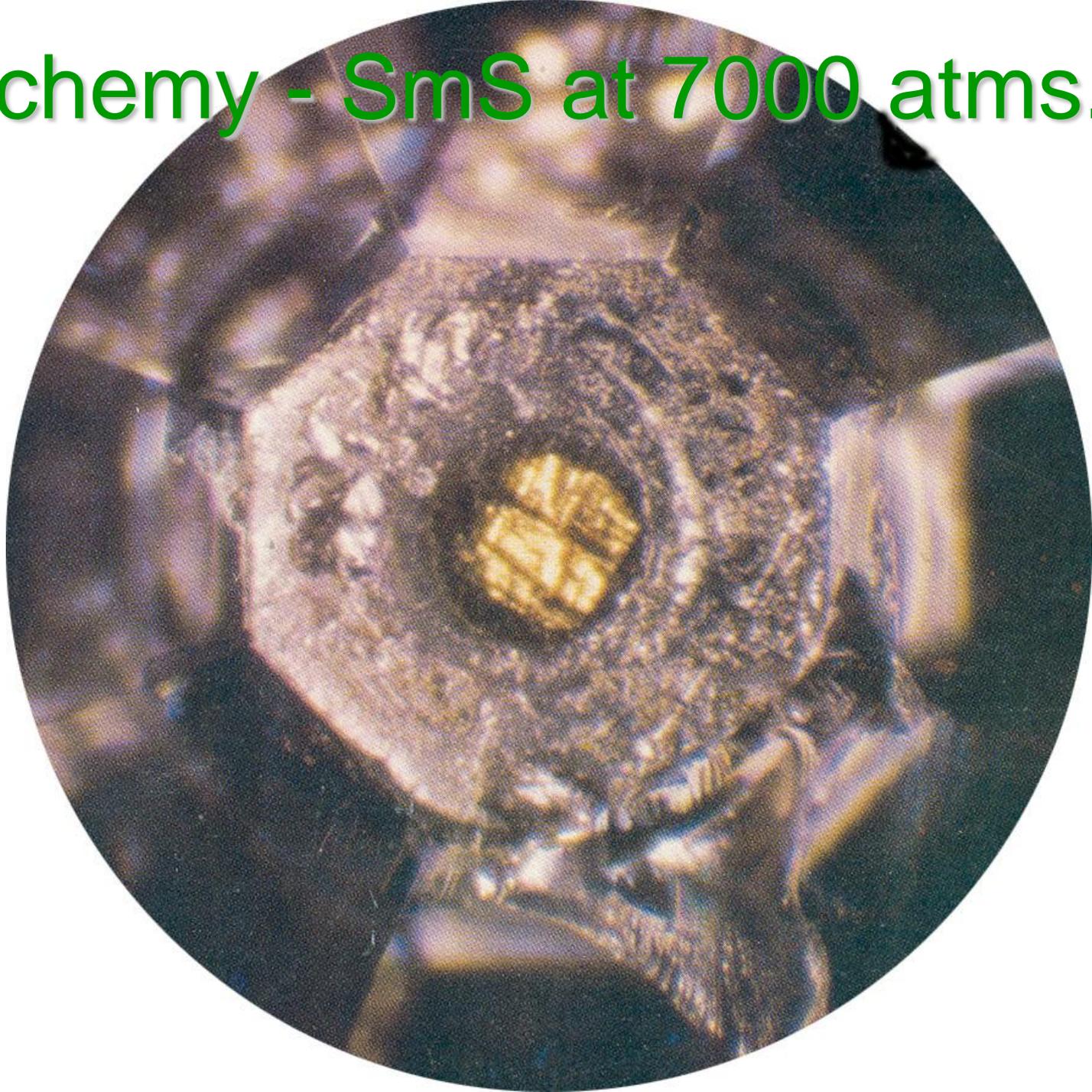
Pressure effects on GaAs

- Pressure increases (direct) band gap in GaAs up to 40 kbar
- Above 40 kbar, transforms from direct to indirect band gap material.
- Pressure effects on GaAs helped understand the **Gunn effect** - negative conductance effect
 - threshold voltage decreases with pressure
 - when the energy separation is sufficiently low the effect vanishes.



Effect of pressure on the Gunn threshold voltage and low field resistance

Alchemy - SmS at 7000 atms.



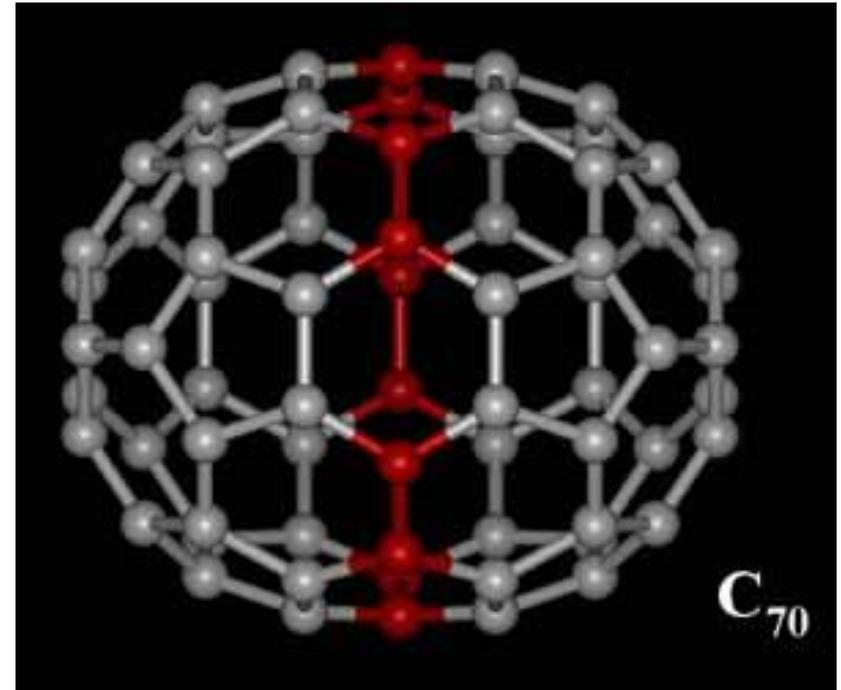
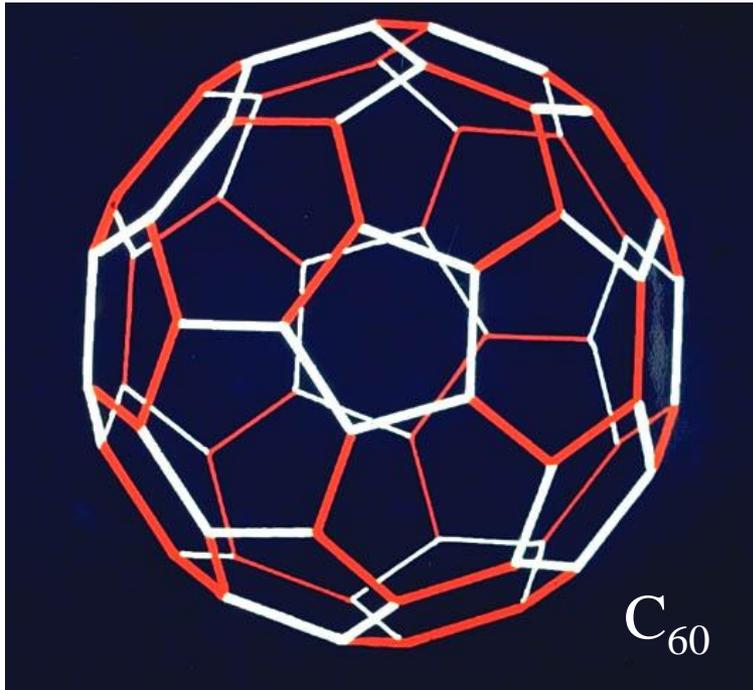
Pressure effects on SmS

- An abrupt anomalously large decrease in volume at 6.5 kbar
- No change in structure associate with this volume change (remains NaCl)
- High pressure resistivity studies shows a semiconductor to metal transition
- Rare-earth monochalcogenides are metal or semi-conducting depending on the trivalent or divalent state, respectively

Pressure effects on SmS

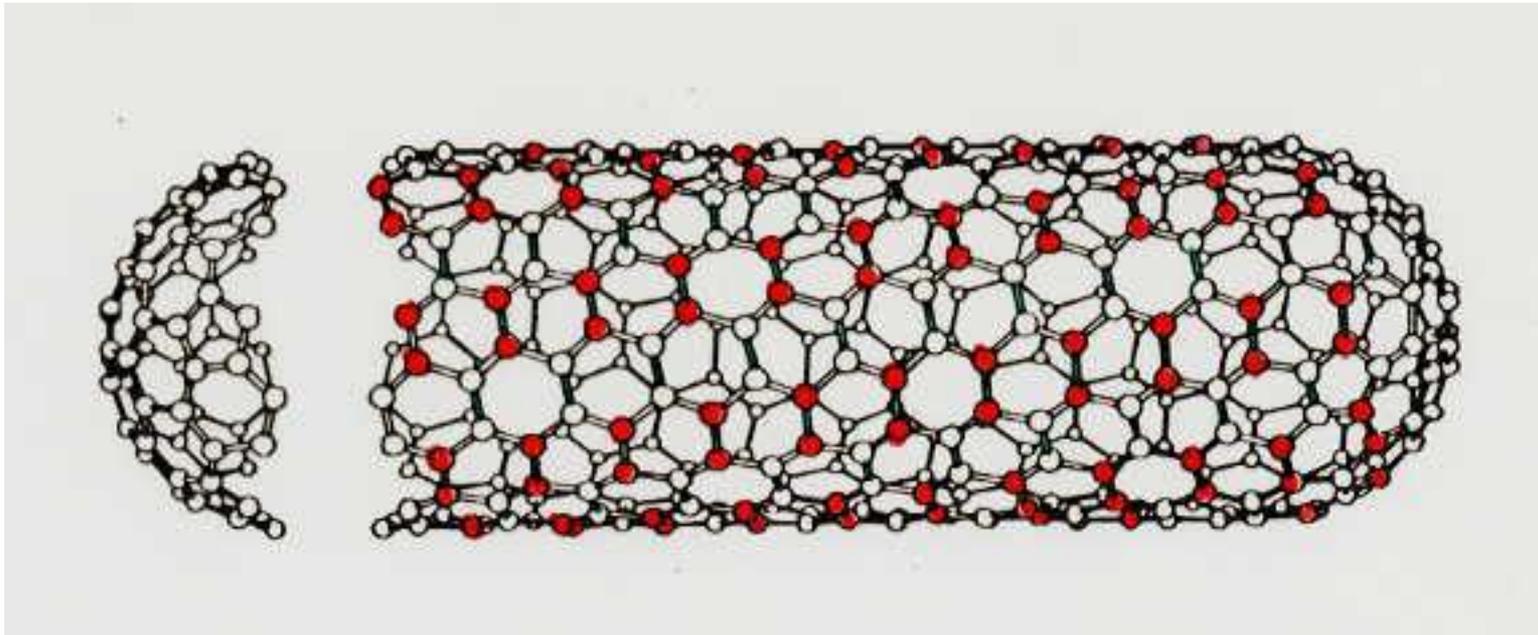
- Promotion of 4f electron to 5d conduction band
- The band gap at ambient conditions is 0.4 eV
- High pressure phase of SmS shows electrical resistivity of $10^{-4} \Omega\text{cm}$
- High pressure phase show metallic luster
- One electron per formula unit is released when the divalent rare-earth ion becomes $\text{Sm}^{2.7+}$ and not Sm^{3+} . (heavy fermion Superconductivity)

Fullerenes under pressure



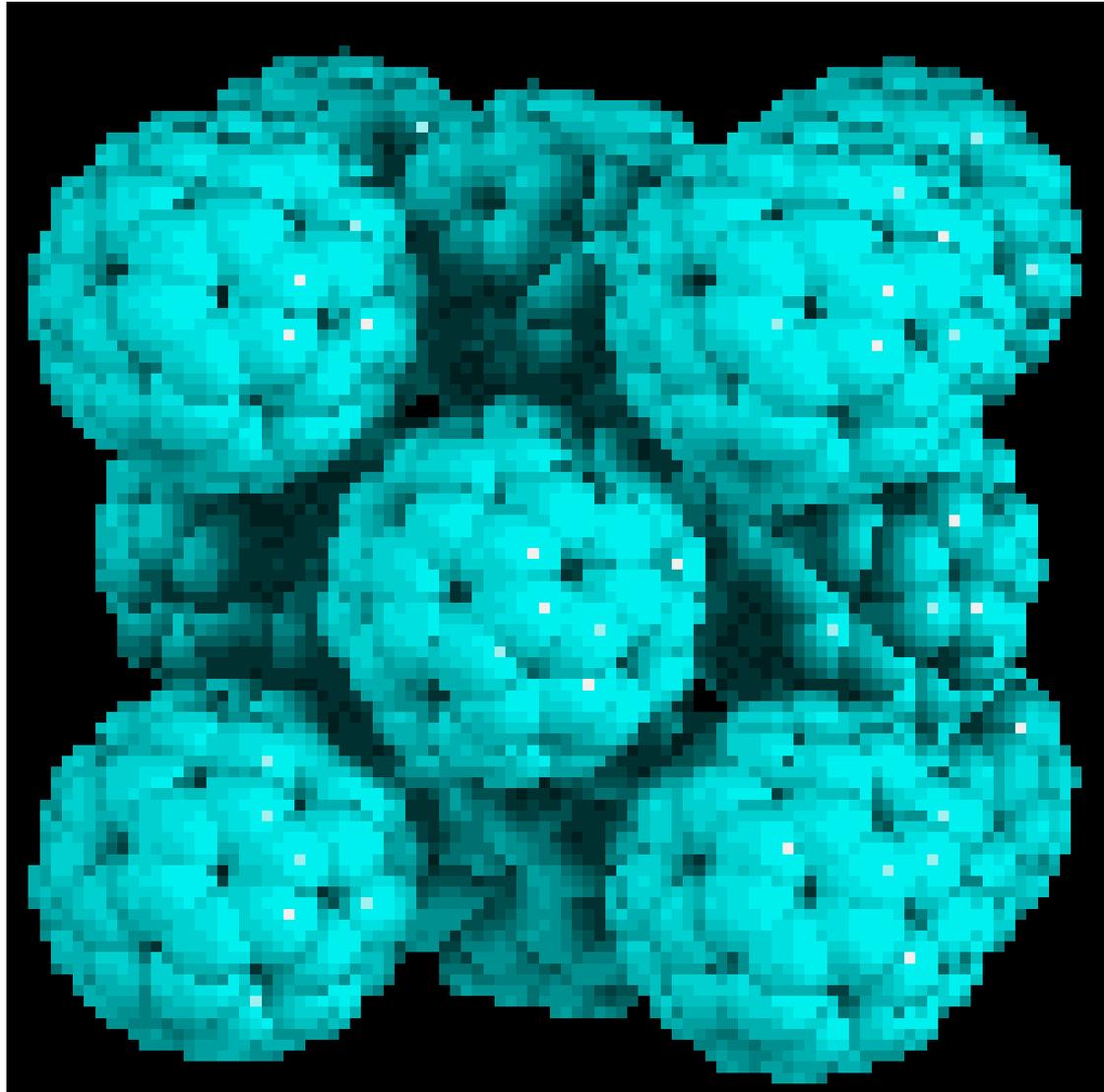
All closed fullerene have 12 pentagons and rest of them as hexagons.

Carbon Nanotubes

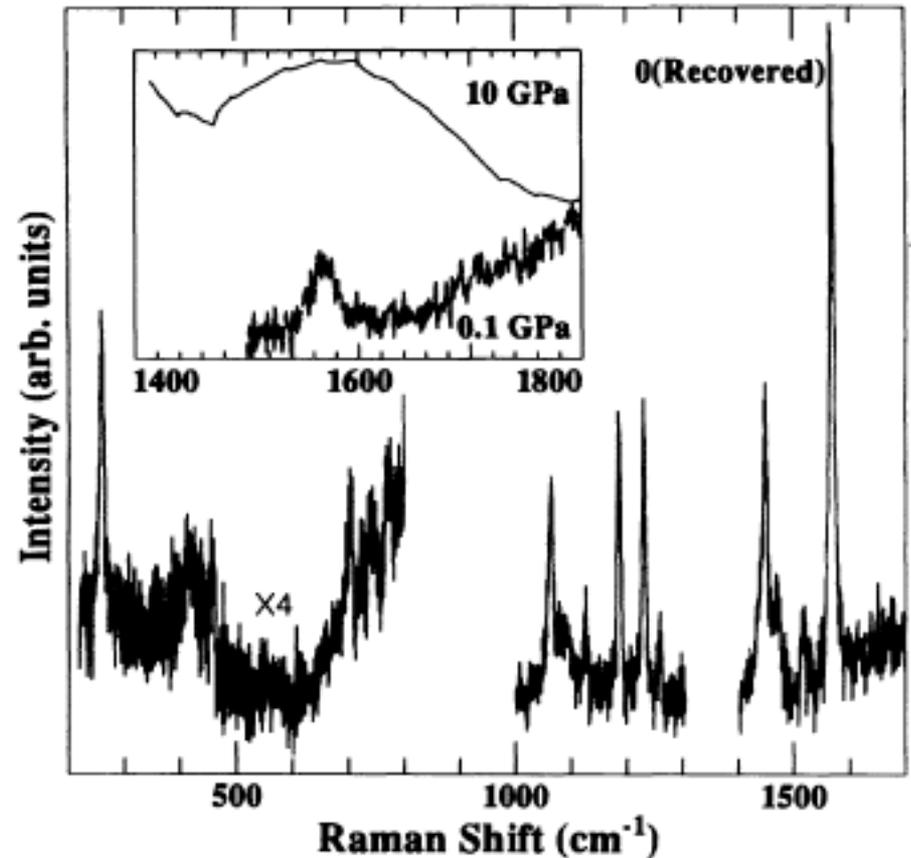
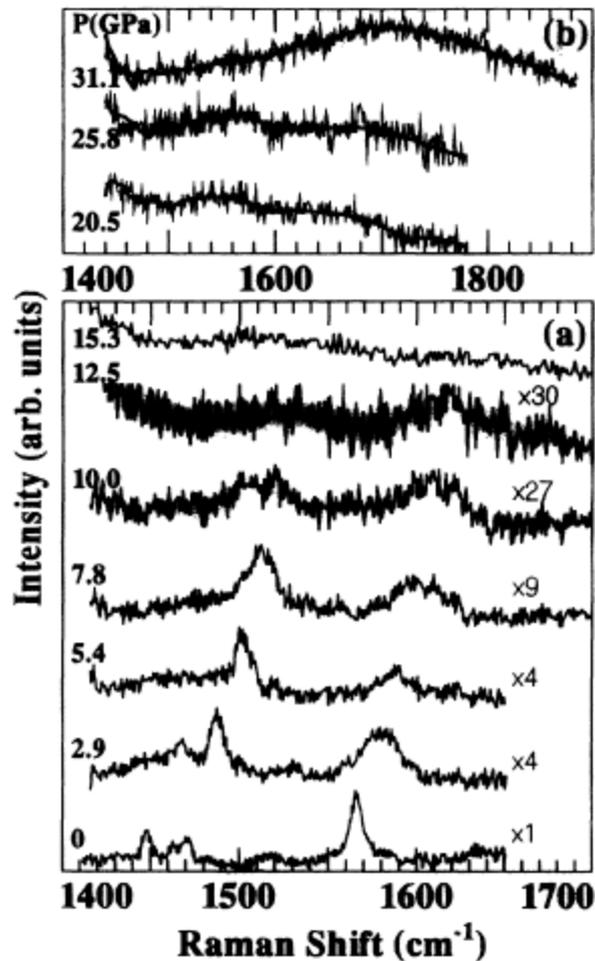


Can be thought of in simple terms as a combination of buckyball hemispheres with roles of graphite

Solid Fullerene



Pressure-induced amorphization

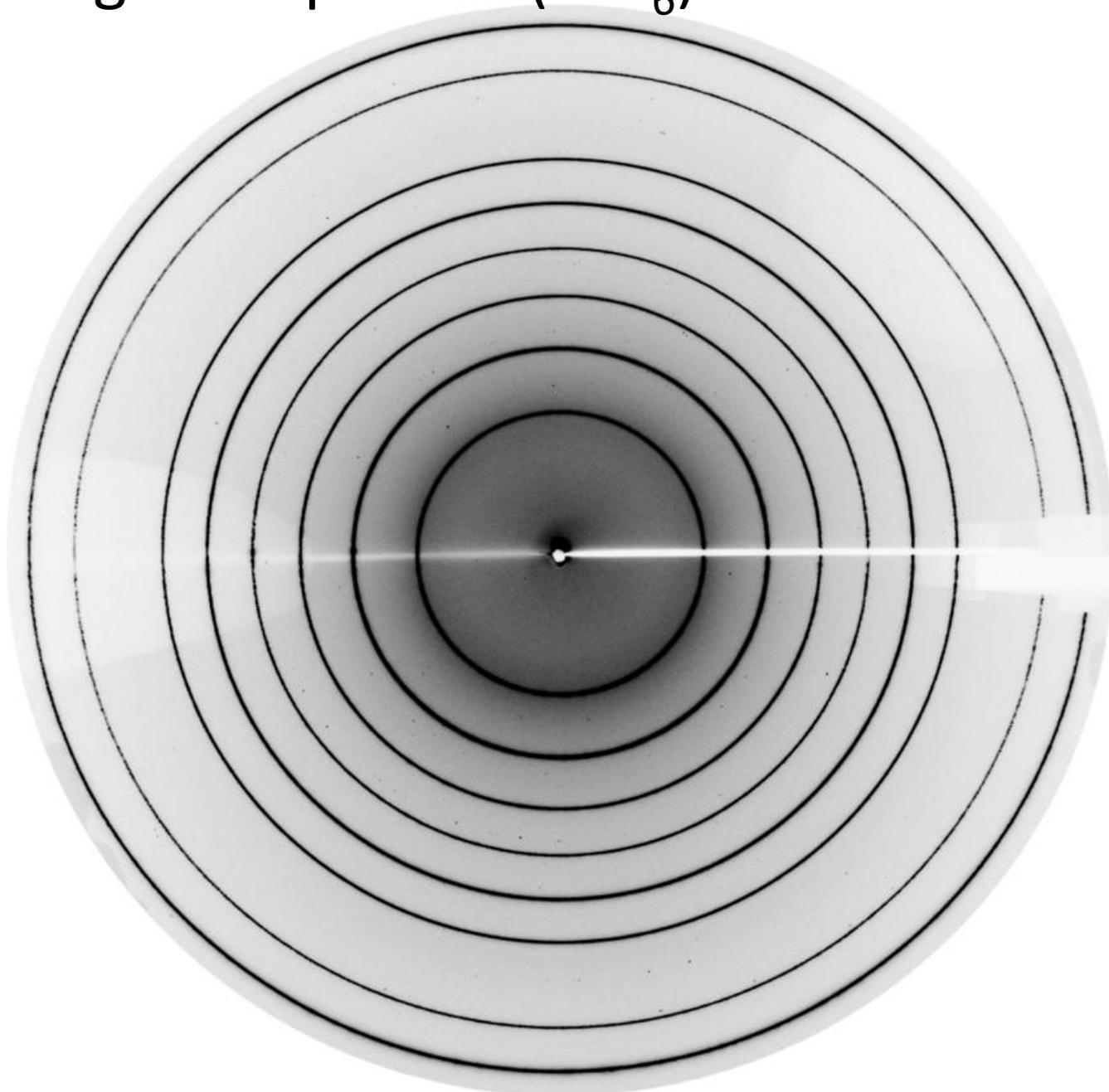


Chandrabhas et al Phys. Rev. Lett. 74, 3411 (1994)

C₇₀ At high pressures

- The Raman modes vanish and a broad peak appears.
- The broad peak resembles amorphous carbon.
- Polymerization of fullerenes at high pressure.
- It is reversible, all Raman modes appear at ambient conditions, unlike C₆₀
- Carbon carbon distances are quite far between inter molecular space in C₇₀ unlike C₆₀.

2D image of a powder(LaB_6) on a CCD detector



High Pressure Studies Sn_3N_4 and its implications

Acknowledgments to

*Umesh V. Waghmare, Gopal K.
Pradhan and Sudip K. Deb*

Elastic properties and stability of γ - A_3N_4 (A= Si, Ge, Sn) Nitrides

A_3N_4 polymorphs are promising candidates in the search for superhard materials

High bulk modulus is expected.

Electronic band gap of γ - Si_3N_4 *has been predicted to be in an attractive range for optoelectronic applications .*

The existence of the heavier element spinel nitrides γ - Ge_3N_4 & γ - Sn_3N_4 *should open for a broad range of band gap- engineering and property-tailoring, similar to the III-V nitrides.*

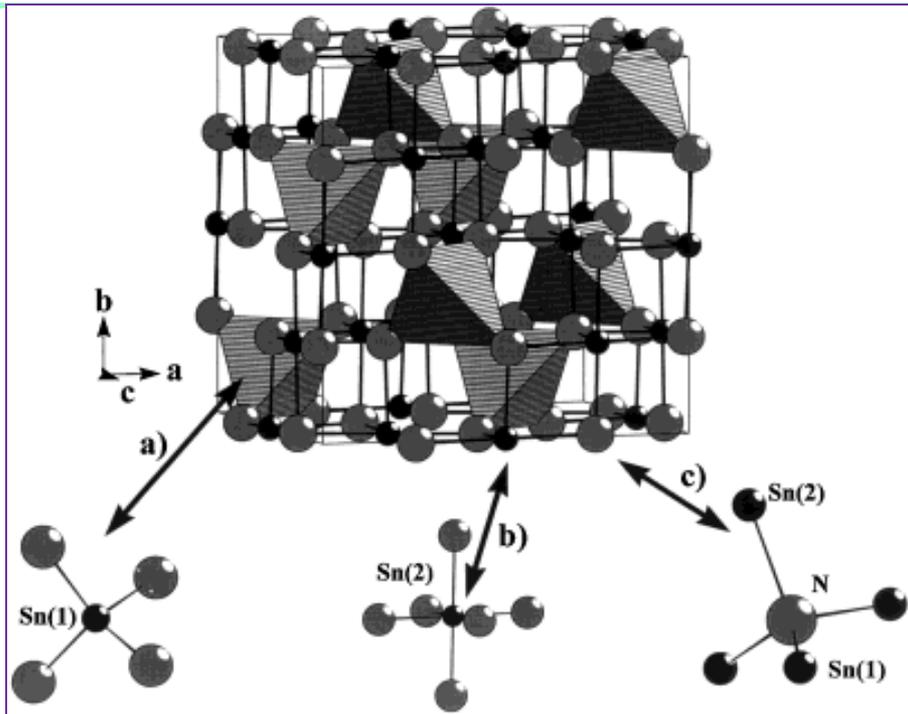
Hardness along with semiconducting nature makes them suitable for replacement of diamond.

Structure of γ - A_3N_4 (A= Si, Ge, Sn) Nitrides

Spinel type structure

The general formula of spinel is AB_2X_4 . Distorted *fcc* array of anions X. 1/8 of the *tetrahedral interstices* and 1/2 of the *octahedral ones* are occupied by cations A and B. In A_3N_4 , both A and B sites are occupied by the same element A = Si or Ge or Sn ($A^{\text{tet}}[A^{\text{oct}}]_2N_4$)

Space group $Fd\bar{3}m$, $Z=8$



Bulk modulus (B_0) is determined mainly by the nitrogen sublattice but modulated by the choice of cations.

$B_0 = 306 \text{ GPa}$ (Si_3N_4), 286 GPa (Ge_3N_4) [Expt.]

Shemkunas *et al*, J. Mater Res. **19**, 1392 (2004)

E. Soignard *et al*, J. Phys.: Condens. Matter **13**, 557 (2001)

$B_0 = 186 \text{ GPa}$ (Sn_3N_4) [Predicted]

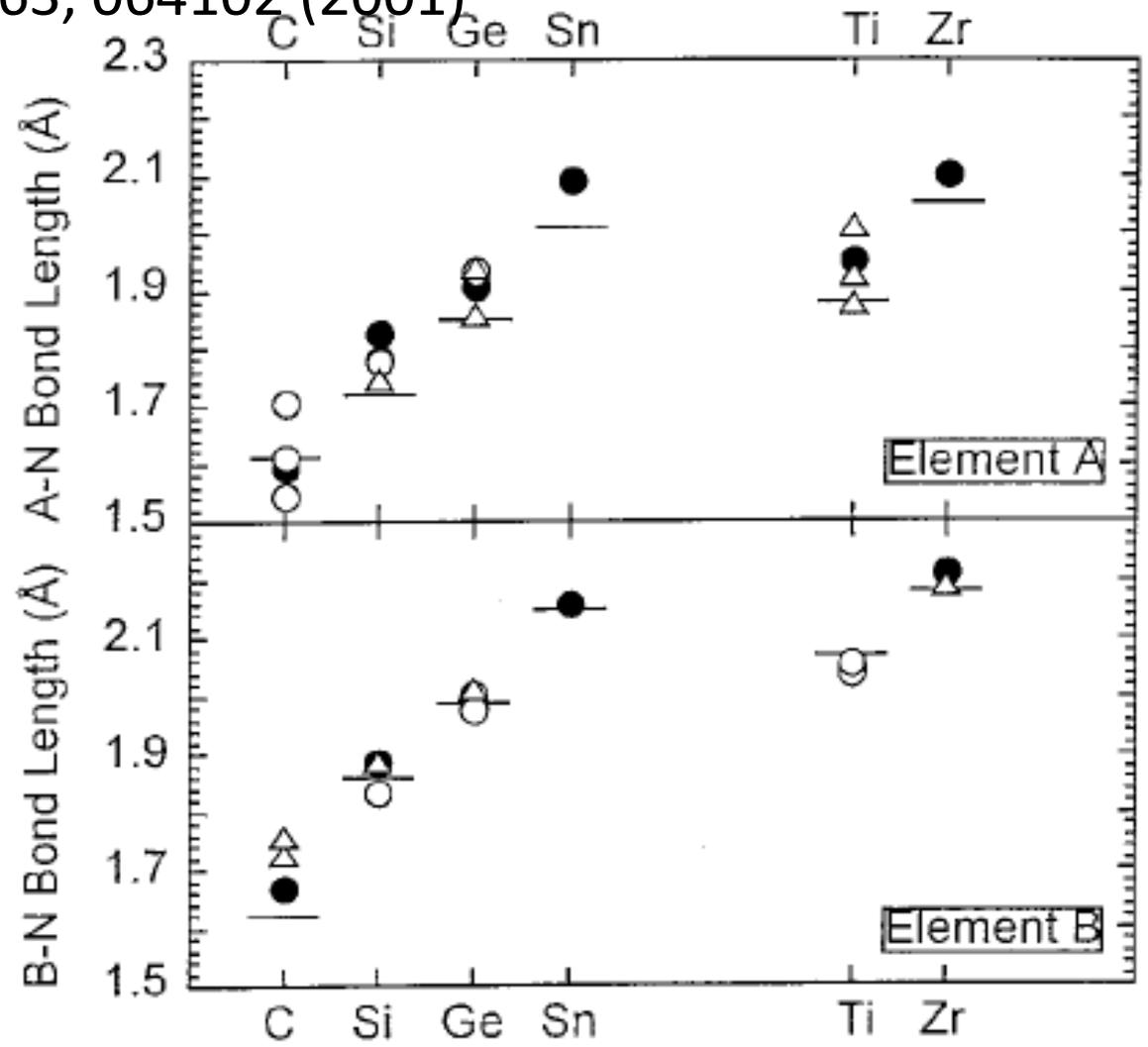
N. Scotti *et al* Z. Anorg. Allg. Chem. **625** (1999)

Calculated properties of Spinel Nitrides

Crystal	Lattice parameters		Band gap		Bulk modulus		Mulliken charge			Bond orders/length						
	a (Å)	u	ΔE (eV/ A_3N_4)	E_g	E_g	B (GPa)	B'	Q_{tet}^*	Q_{oct}^*	Q_N^*	Total bond order	Bond order A-N	Bond length A-N (Å)	Bond order B-N	Bond length B-N (Å)	
				direct	indirect											
c-C ₃ N ₄	6.8952	0.3833		1.14		377.6	3.36	3.70	3.63	5.27	8.647	0.358	1.592	0.241	1.669	
c-Si ₃ N ₄	7.8372	0.3844		3.45		280.1	3.76	2.65	2.58	6.05	8.670	0.362	1.824	0.241	1.889	
c-Ge ₃ N ₄	8.2110	0.3841		2.22		268.6	3.14	2.81	2.80	5.90	7.900	0.327	1.907	0.220	1.981	
c-Sn ₃ N ₄	8.9658	0.3845		1.29		203.6	4.98	2.71	2.70	5.97	6.958	0.284	2.089	0.195	2.160	
c-Ti ₃ N ₄	8.4459	0.3833		0.25	0.07	265.6	3.56	3.09	3.20	5.62	8.474	0.353	1.950	0.236	2.044	
c-Zr ₃ N ₄	9.1217	0.3830		0.40	0.23	225.3	4.17	3.06	3.17	5.65	8.609	0.356	2.101	0.240	2.210	
c-CSi ₂ N ₄	LF	7.5209	0.3811	-0.64	1.34	1.26	309.5	2.72	4.14	4.44	4.75	11.231	0.299	1.708	0.368	1.835
c-SiC ₂ N ₄	HE	7.2867	0.3885	3.09	Metal		327.7	4.69	2.45	3.71	5.53	8.260	0.359	1.748	0.225	1.729
c-CGe ₂ N ₄	0	7.7407	0.3701	0.00	1.36		266.0	3.53	3.67	2.79	5.68	8.284	0.361	1.610	0.225	1.974
c-GeC ₂ N ₄	HE	7.4284	0.3943	3.84	0.71		310.1	4.22	2.85	3.67	5.45	7.816	0.317	1.857	0.220	1.726
c-SiGe ₂ N ₄	LE	8.0871	0.3773	-0.26	1.85		277.1	3.02	3.10	2.91	5.77	9.999	0.564	1.783	0.229	2.003
c-GeSi ₂ N ₄	HE	8.0011	0.3899	0.44	2.64	2.55	258.3	2.04	3.02	2.53	5.98	8.260	0.320	1.939	0.238	1.889
c-CTi ₂ N ₄	LE	7.8351	0.3637	-1.95	Metal		300.3	3.99	3.71	3.23	5.46	9.005	0.383	1.543	0.248	2.051
c-TiC ₂ N ₄	HE	7.5400	0.3936	4.51	0.97	0.62	317.3	3.13	2.97	3.77	5.37	8.030	0.352	1.875	0.217	1.756
c-SiT ₂ N ₄	LE	8.2168	0.3749	-1.42	Metal		274.5	1.99	2.51	3.31	5.72	9.075	0.366	1.778	0.256	2.055
c-TiSi ₂ N ₄								Unstable								
c-GeTi ₂ N ₄	LE	8.4002	0.3829	-0.43	Metal		253.2	1.98	2.90	3.18	5.68	8.657	0.323	1.934	0.253	2.036
c-TiGe ₂ N ₄	HE	8.3158	0.3837	0.90	2.27	1.87	266.6	2.82	3.08	2.91	5.77	8.231	0.378	1.926	0.217	2.009
c-TiZr ₂ N ₄	HE	8.9276	0.3800	0.95	0.32	0.15	227.5	2.46	3.14	3.14	5.64	8.482	0.339	2.010	0.240	2.188
c-ZrTi ₂ N ₄								Unstable								

Calculated Bond Distances at both A and B Sites

Phys. Rev. B, 63, 064102 (2001)



Motivation

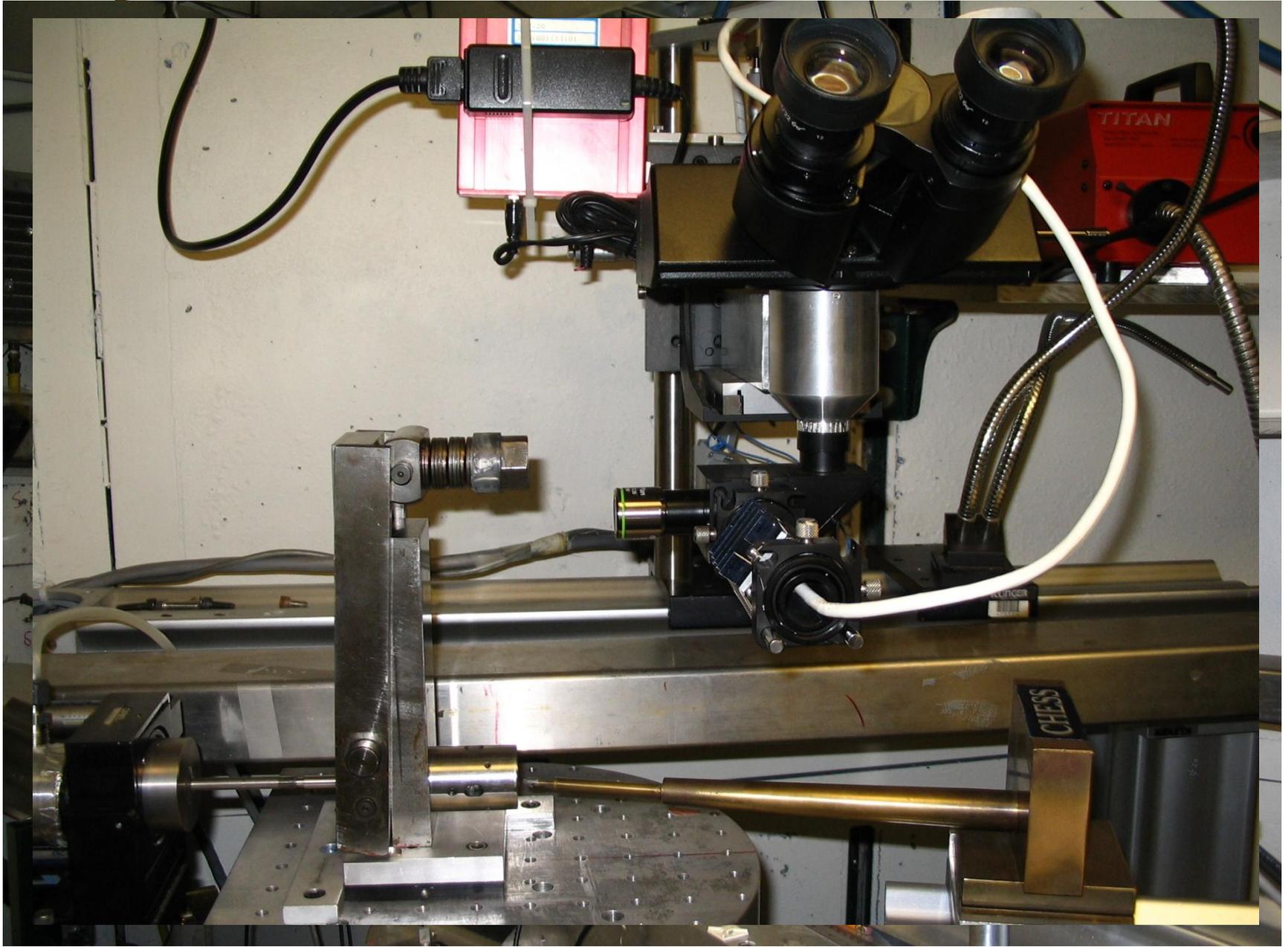
The structure and electronic properties of tin nitride has not been as extensively studied as its lighter congeners (Si_3N_4 , Ge_3N_4)

To search for other Sn_3N_4 polymorphs that may be stable at higher pressure than the spinel structure.

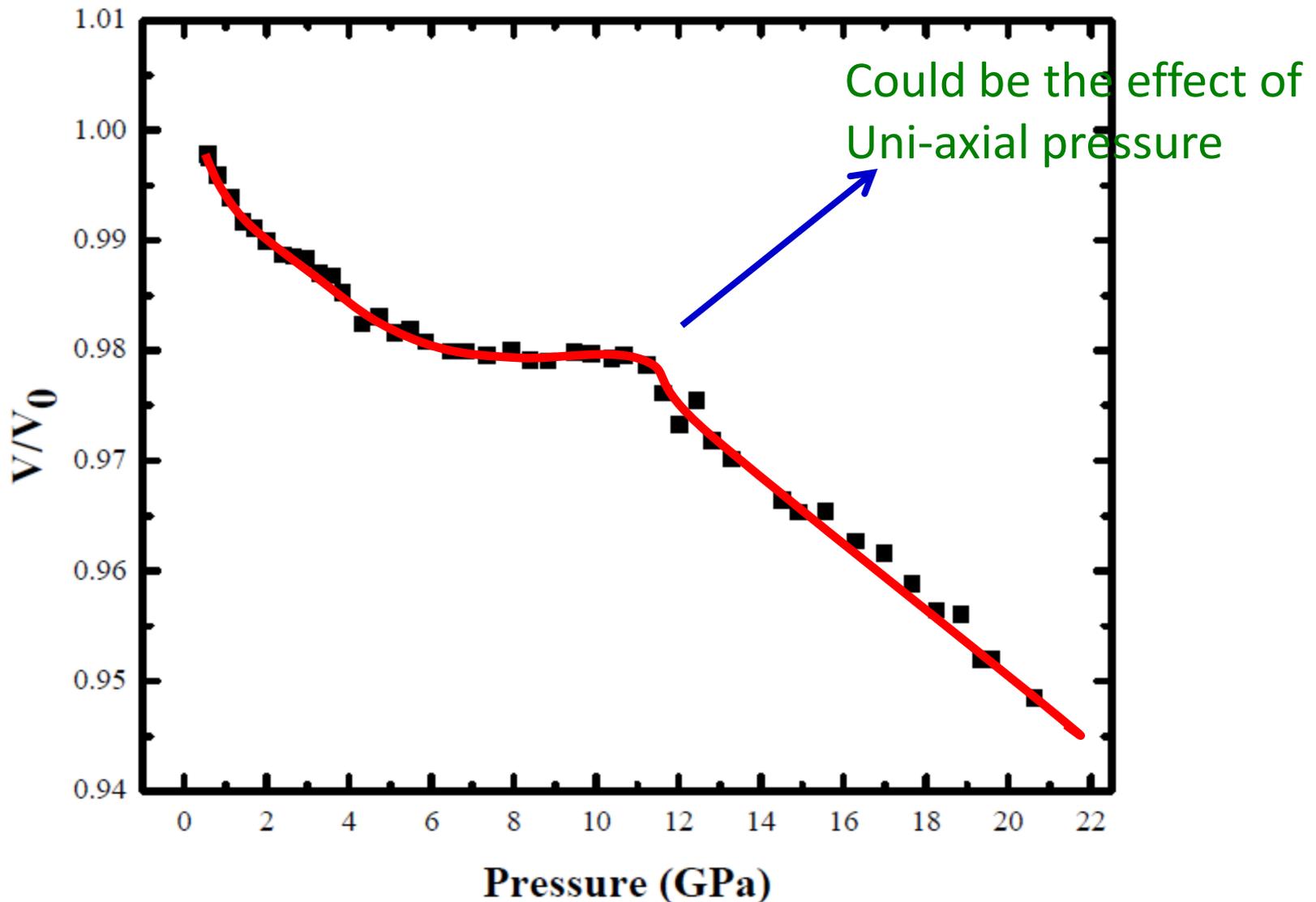
Structural transition in A_3N_4 & AB_2N_4 systems is interesting in understanding the electronic behavior with cationic size substitution

Accurate determination of EOS and Bulk Modulus

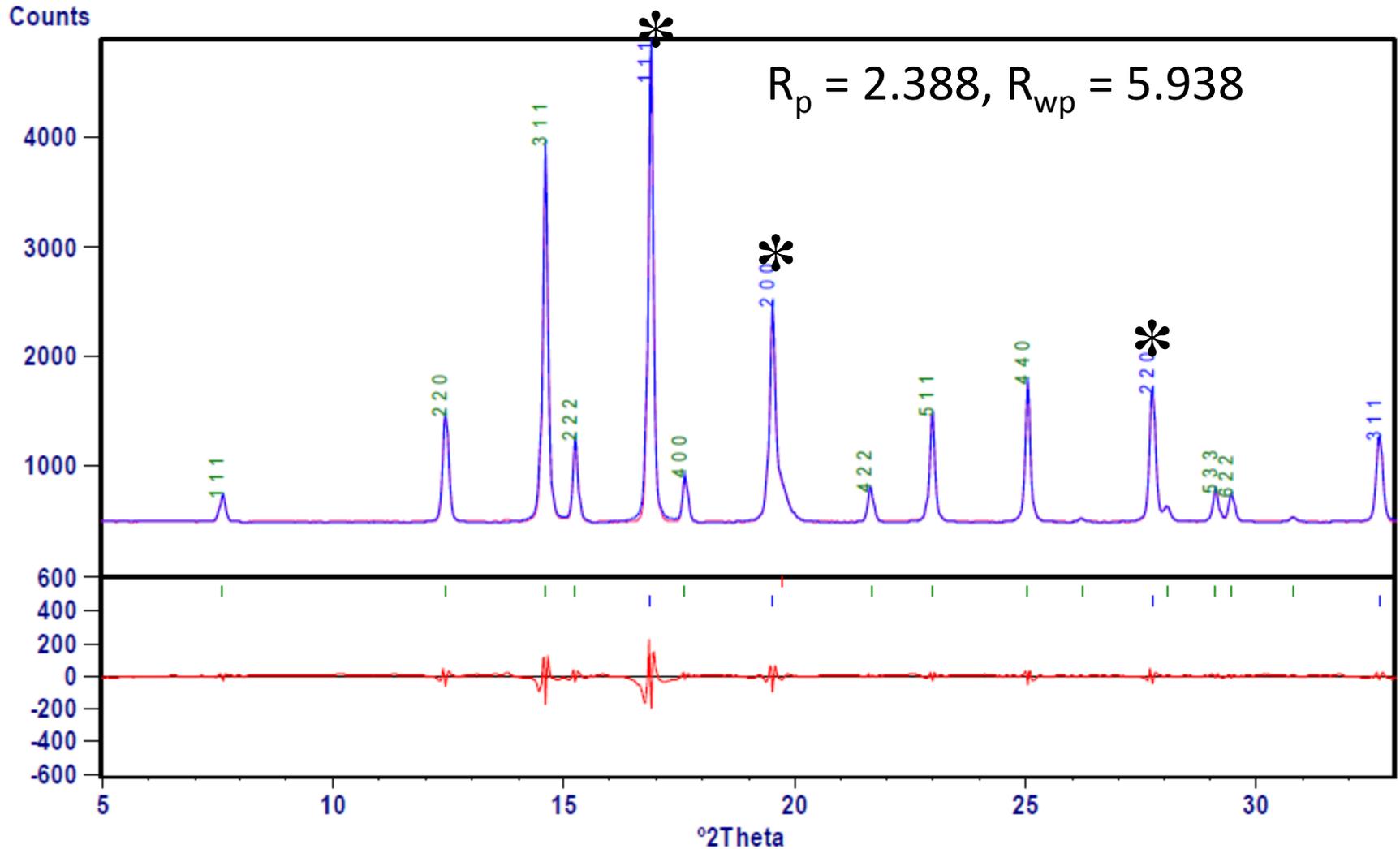
Experiments at B1 station of CHESS



Non-Hydrostatic Pressure Evolution of EDXRD @B1-CHESS

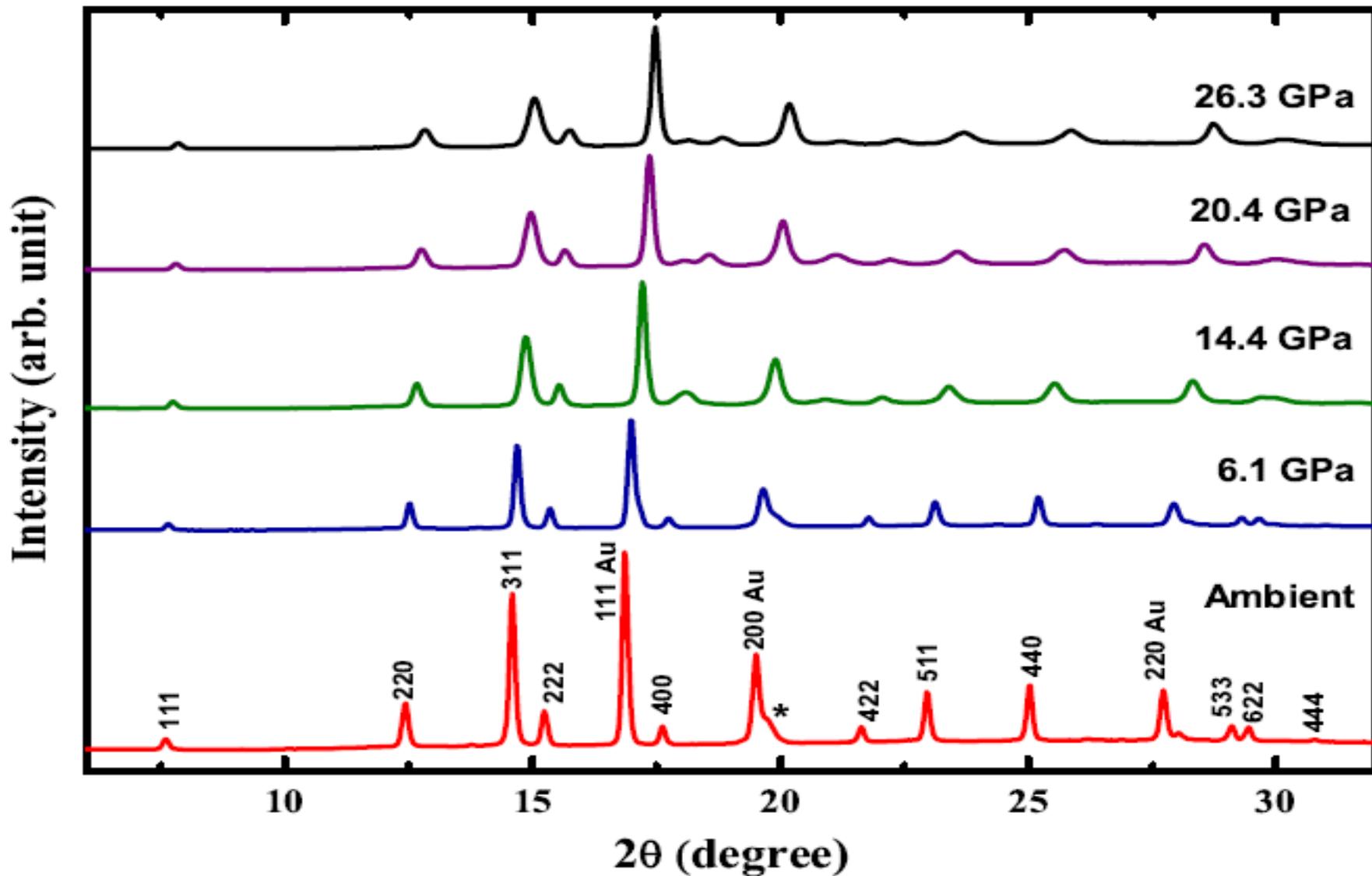


ADXRD Pattern of γ - Sn_3N_4 @Elettra XRD1



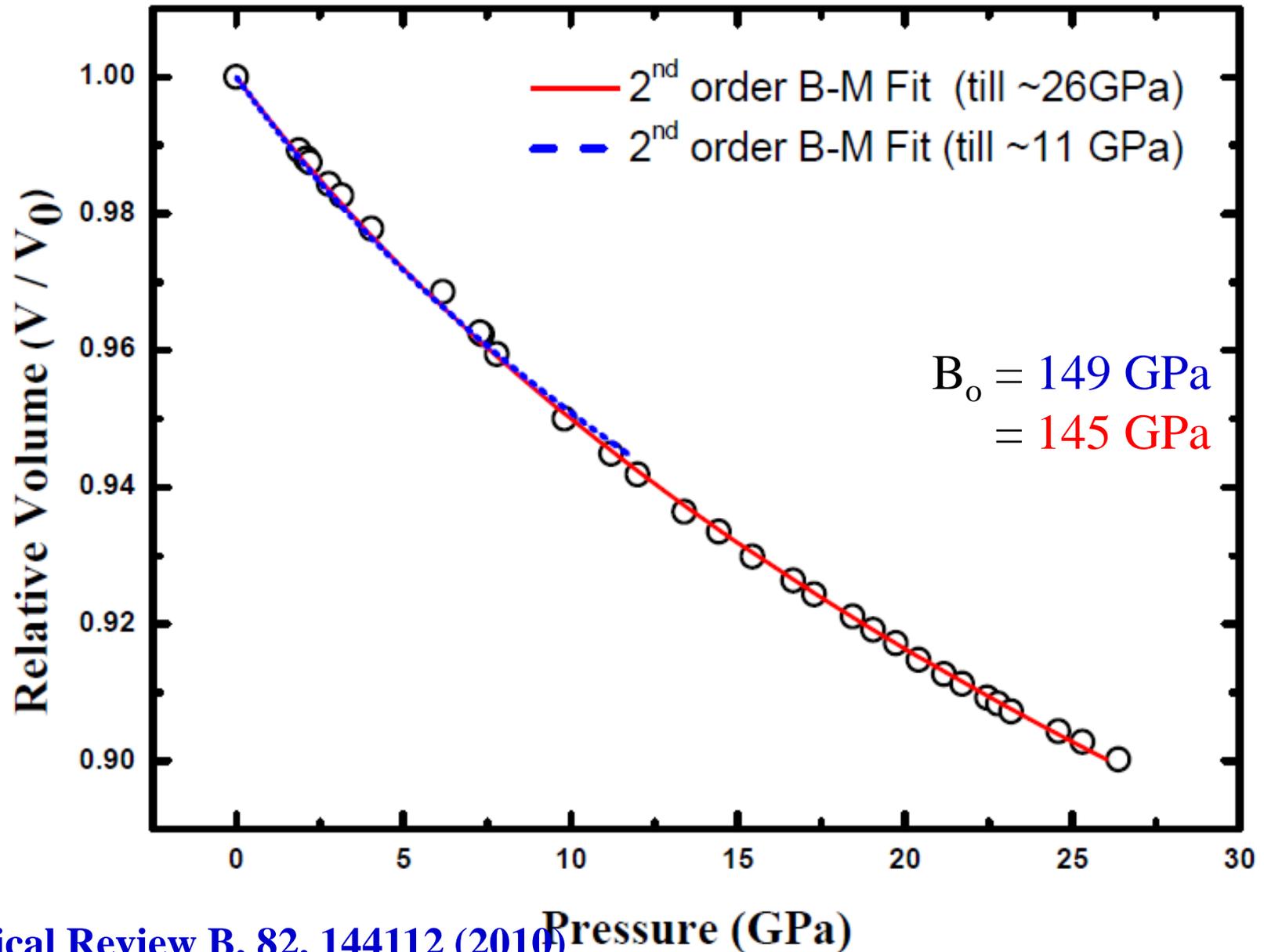
lattice constant, $a = 9.008 \text{ \AA}$

Pressure (QH) Evolution of ADXRD Pattern



No transition till 26 GPa

Equation of State by Birch-Murnaghan EOS

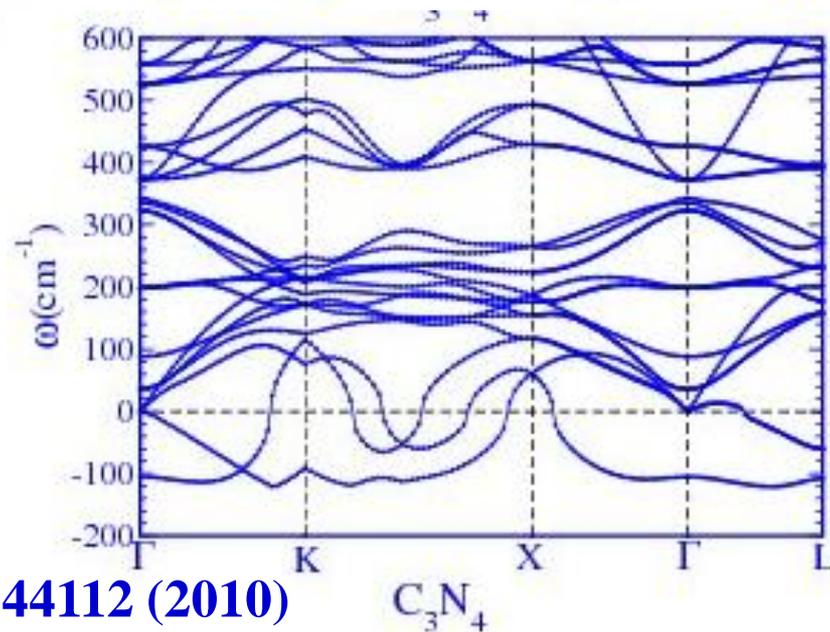
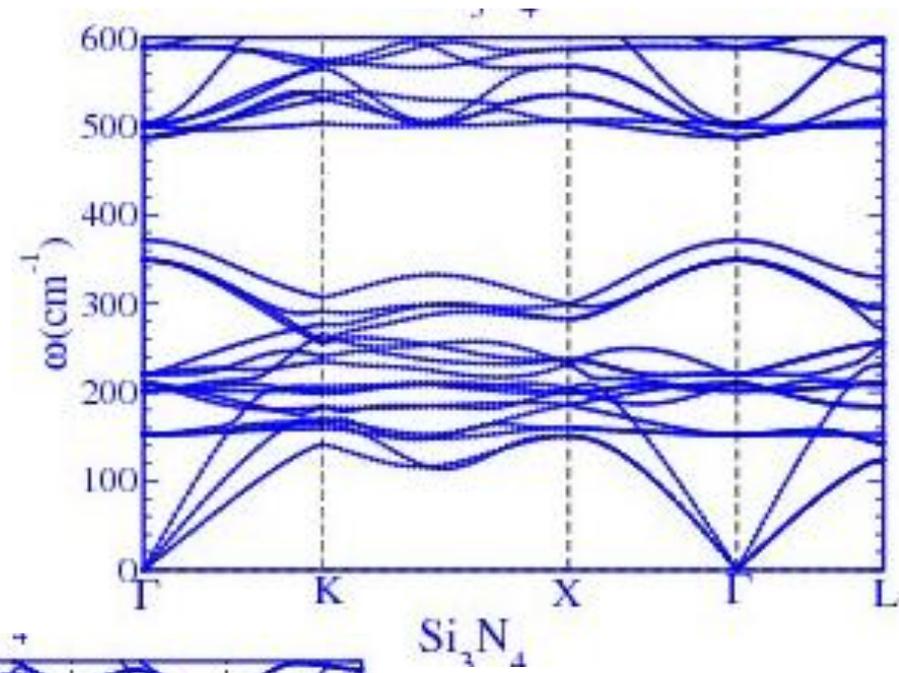
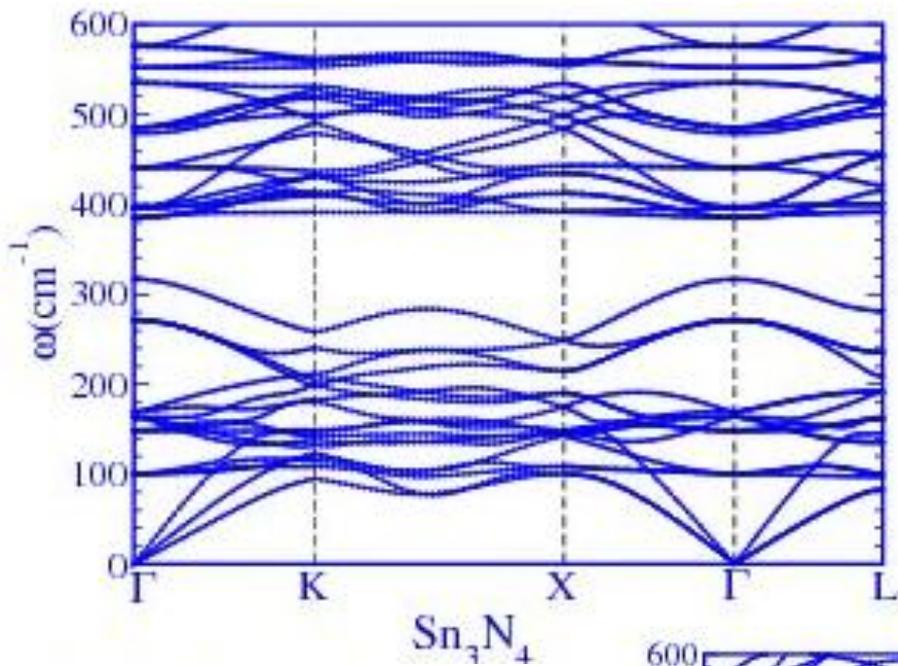


Theoretical Calculations

First Principle Density Functional Theory calculation in the Generalized Gradient Approximation.

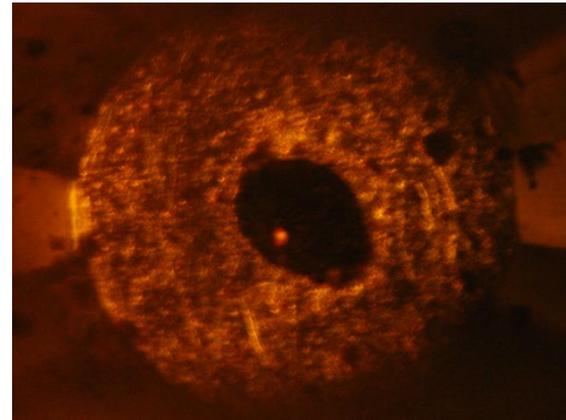
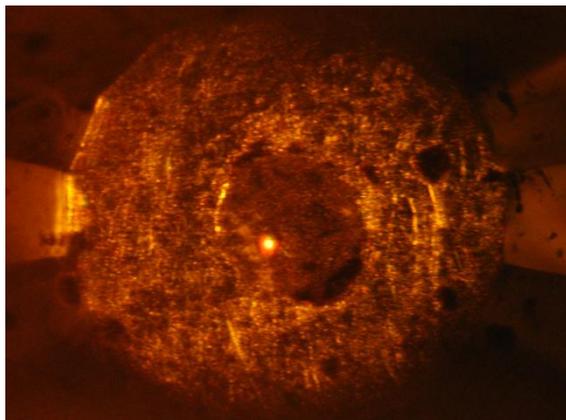
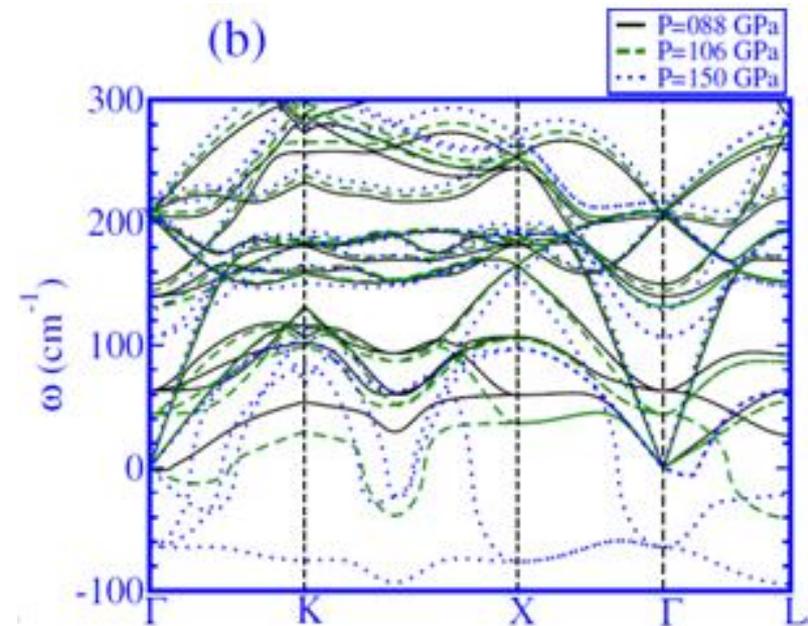
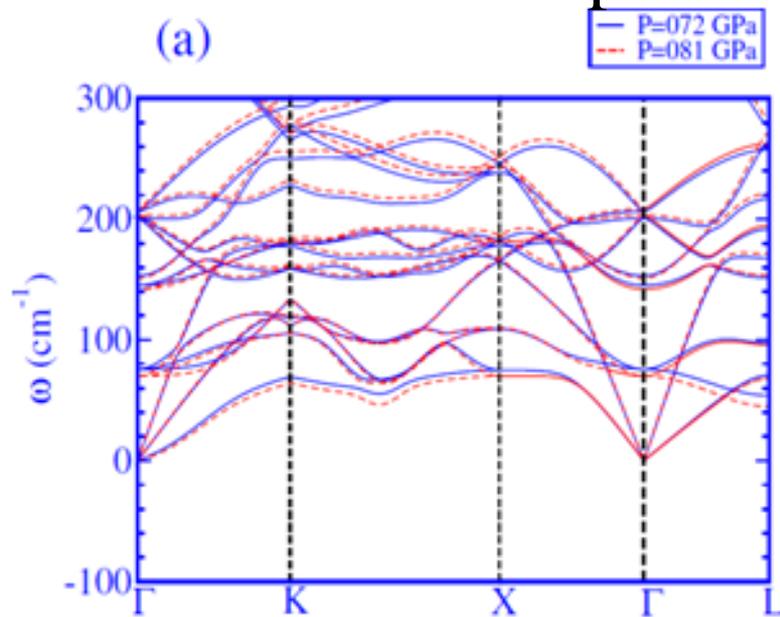
	Calc. a_0 (Å)	Expt. a_0 (Å)	Calc. B (GPa)	Expt. B (GPa)	Band Gap (eV)	Internal parameter (u)
γ -Sn ₃ N ₄	9.136	9.0205 9.0144 ¹⁸ 9.037 ¹	158	149 (± 1.2)	0.2	0.2592
γ -Si ₃ N ₄	7.792	7.7381(2) ¹² 7.7339(1) ¹¹	292	308(± 5) ¹²	3.4	0.2575
γ -C ₃ N ₄	6.796	Yet to be synthesized	379		1.02	0.2559

Stability of γ - A_3N_4



Pressure Effects on Sn_3N_4

The Bandgap of Sn_3N_4 changes from 0.2 eV at ambient pressures to 2.0 eV at 50 GPa



Summary

- γ - Sn_3N_4 doesn't undergo any transition till 26 GPa under hydrostatic conditions.
- The Bulk modulus for γ - Sn_3N_4 is much smaller ($B_0 = 149$ GPa)
- Uni-axial pressures have a distinct effect on the structure and needs to be investigated.
- Higher pressure experiments in Argon or Neon atmosphere need to be performed to see the theoretical predicted transition pressures are at 88 GPa to CaFe_2O_4 and CaTi_2O_4 -type structures
- Theoretical predicted B_0 of γ - Sn_3N_4 is 158 GPa.
- The stability of all the A_3N_4 have been studied and γ - C_3N_4 is found to be unstable.