

Superconductivity in compressed CaC_2

Yan-Ling Li (李延齡)

School of Physics and Electronic Engineering



Outline

- Introduction
- Theoretical Methods
- Research Results
- Conclusion

Introduction

Carbon has many allotropes.

So many papers published.

Charles Kittel, Introduction to solid states physics, 8th version.

M. D. Knuson, et al. Science **322**, 1822 (2008)

Q. Li, et al. PRL **102**, 175506 (2009)

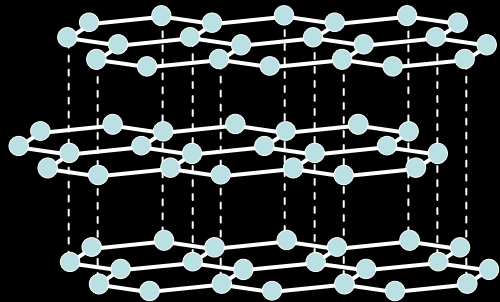
Q. Zhu, et al. PRB **85**, 201407 (2012)

H. Niu, et al. PRL **108**, 135501(2012)

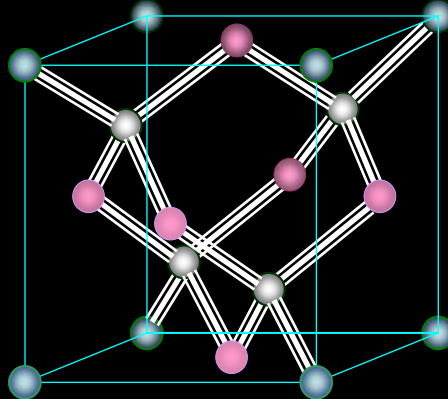
S. E. Boulfelfel, et al . Sci. Rep. **2**, 471 (2012)

Y. Wang, et al. Sci. Rep. **2**, 520 (2012)

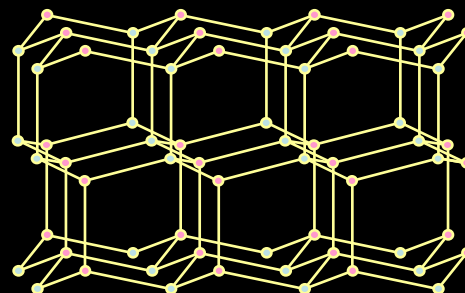
.....



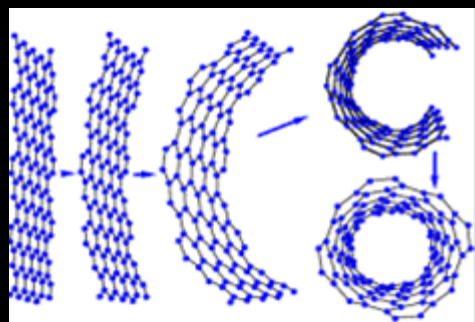
graphite



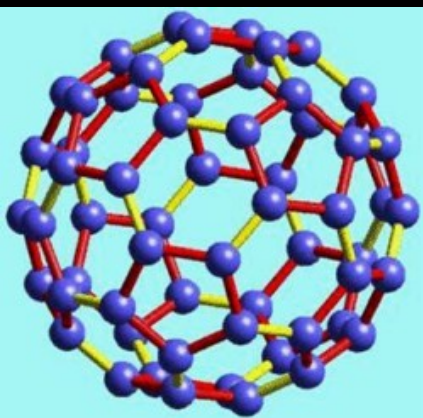
diamond (cubic)



h-diamond

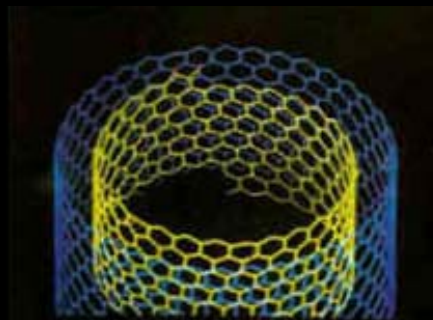


Graphene - CNT



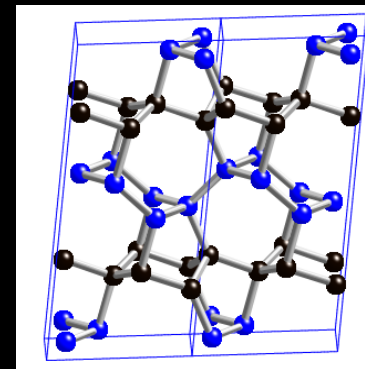
C60

Carbon
sp⁻、 sp²⁻、 sp³⁻



Carbon nanotube (CNT)

Amorphous carbon
Nanoporous Carbon



M-carbon

Calcium has rich phase diagram.

The phase diagram of compressed calcium solid arouses many people's interests due to early inconsistency between theory and experiment together with its peculiar physical behavior, such as superconductivity.

Hiroshi Fujihisa, *et al.* PRL **101**, 095503 (2008)

Y. Yao, *et al.* PRL **103**, 055503 (2009)

W. L. Mao, *et al.* PNAS **107**(22),9965 (2010)

ARO, *et al.* PNAS **107**(17),7646 (2010)

PRB, others

B. Li, *et al.* PNAS **109**(41),16459 (2012)

J. S. Tse, *et al.* Sci. Rep. **2**,372 (2012)

H. Fujihisa, *et al.* PRL **110**, 235501 (2013)

M. D. Gennaro, *et al.* PRL **111**, 025503 (2013)

Periodic Table of Elements

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18																												
1	H Hydrogen 1.00794	Atomic # Name Symbol Atomic Mass																	2	He Helium 4.002602																										
2	Li Lithium 6.941	Be Beryllium 9.012182	<table border="1"> <tr> <td>C Solid</td> <td colspan="3">Metals</td> <td colspan="3">Nonmetals</td> </tr> <tr> <td>Hg Liquid</td> <td>Alkali metals</td> <td>Alkaline earth metals</td> <td>Lanthanoids</td> <td>Transition metals</td> <td>Poor metals</td> <td>Other nonmetals</td> </tr> <tr> <td>H Gas</td> <td></td> <td></td> <td>Actinoids</td> <td></td> <td></td> <td>Noble gases</td> </tr> <tr> <td>Rf Unknown</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> </tr> </table>										C Solid	Metals			Nonmetals			Hg Liquid	Alkali metals	Alkaline earth metals	Lanthanoids	Transition metals	Poor metals	Other nonmetals	H Gas			Actinoids			Noble gases	Rf Unknown							B Boron 10.811	C Carbon 12.0107	N Nitrogen 14.0067	O Oxygen 15.9994	F Fluorine 18.9984032	Ne Neon 20.1797
C Solid	Metals			Nonmetals																																										
Hg Liquid	Alkali metals	Alkaline earth metals	Lanthanoids	Transition metals	Poor metals	Other nonmetals																																								
H Gas			Actinoids			Noble gases																																								
Rf Unknown																																														
3	Na Sodium 22.98976928	Mg Magnesium 24.3050	Al Aluminum 26.9815386	Si Silicon 28.0855	P Phosphorus 30.973762	S Sulfur 32.065	Cl Chlorine 35.453	Ar Argon 39.948																																						
4	K Potassium 39.0983	Ca Calcium 40.078	Sc Scandium 44.955912	Ti Titanium 47.887	V Vanadium 50.9415	Cr Chromium 51.9961	Mn Manganese 54.938045	Fe Iron 55.845	Co Cobalt 58.933195	Ni Nickel 58.6934	Cu Copper 63.546	Zn Zinc 65.38	Ga Gallium 69.723	Ge Germanium 72.64	As Arsenic 74.92160	Se Selenium 78.96	Br Bromine 79.904	Kr Krypton 83.798																												
5	Rb Rubidium 85.4678	Sr Strontium 87.62	Y Yttrium 88.90585	Zr Zirconium 91.224	Nb Niobium 92.90638	Mo Molybdenum 95.96	Tc Technetium (97.9072)	Ru Ruthenium 101.07	Rh Rhodium 102.90550	Pd Palladium 106.42	Ag Silver 107.8682	Cd Cadmium 112.411	In Indium 114.818	Sn Tin 118.710	Sb Antimony 121.760	Te Tellurium 127.60	I Iodine 126.90447	Xe Xenon 131.293																												
6	Cs Caesium 132.9054519	Ba Barium 137.327	57-71		Hf Hafnium 178.49	Ta Tantalum 180.94788	W Tungsten 183.84	Re Rhenium 186.207	Os Osmium 190.23	Ir Iridium 192.217	Pt Platinum 195.084	Au Gold 196.966569	Hg Mercury 200.59	Tl Thallium 204.3833	Pb Lead 207.2	Bi Bismuth 208.98040	Po Polonium (208.9824)	At Astatine (208.9871)	Rn Radon (222.0176)																											
7	Fr Francium (223)	Ra Radium (226)	89-103		Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (266)	Bh Bohrium (264)	Hs Hassium (277)	Mt Meitnerium (268)	Ds Darmstadtium (271)	Rg Roentgenium (272)	Uub Ununbium (285)	Uut Ununtrium (284)	Uuq Ununquadium (289)	Uup Ununpentium (288)	Uuh Ununhexium (292)	Uus Ununseptium	Uuo Ununoctium (294)																											

For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

Design and Interface Copyright © 1997 Michael Dayah (michael@dayah.com). <http://www.ptable.com/>



57	La Lanthanum 138.90547	58	Ce Cerium 140.116	59	Pr Praseodymium 140.90765	60	Nd Neodymium 144.242	61	Pm Promethium (145)	62	Sm Samarium 150.36	63	Eu Europium 151.964	64	Gd Gadolinium 157.25	65	Tb Terbium 158.92535	66	Dy Dysprosium 162.500	67	Ho Holmium 164.93032	68	Er Erbium 167.259	69	Tm Thulium 168.93421	70	Yb Ytterbium 173.054	71	Lu Lutetium 174.9668
89	Ac Actinium (227)	90	Th Thorium 232.03806	91	Pa Protactinium 231.03688	92	U Uranium 238.02891	93	Np Neptunium (237)	94	Pu Plutonium (244)	95	Am Americium (243)	96	Cm Curium (247)	97	Bk Berkelium (247)	98	Cf Californium (251)	99	Es Einsteinium (252)	100	Fm Fermium (257)	101	Md Mendelevium (258)	102	No Nobelium (259)	103	Lr Lawrencium (262)

How about carbon-based compounds?

- **Carbon-based compounds investigated widely due to their peculiar behavior, such as high hardness (C_3N_4 , BC_x), and high T_c (CaC_6 , BC_5)**

J. He, *et al.* APL 88, 101906 (2006)

M. Calandra, *et al.* PRL 101, 016401 (2008).

V. L. Solozhenko, *et al.* PRL 102, 015506 (2009).

T. E. Weller, *et al.* Nature Phys. 1, 39 (2005).

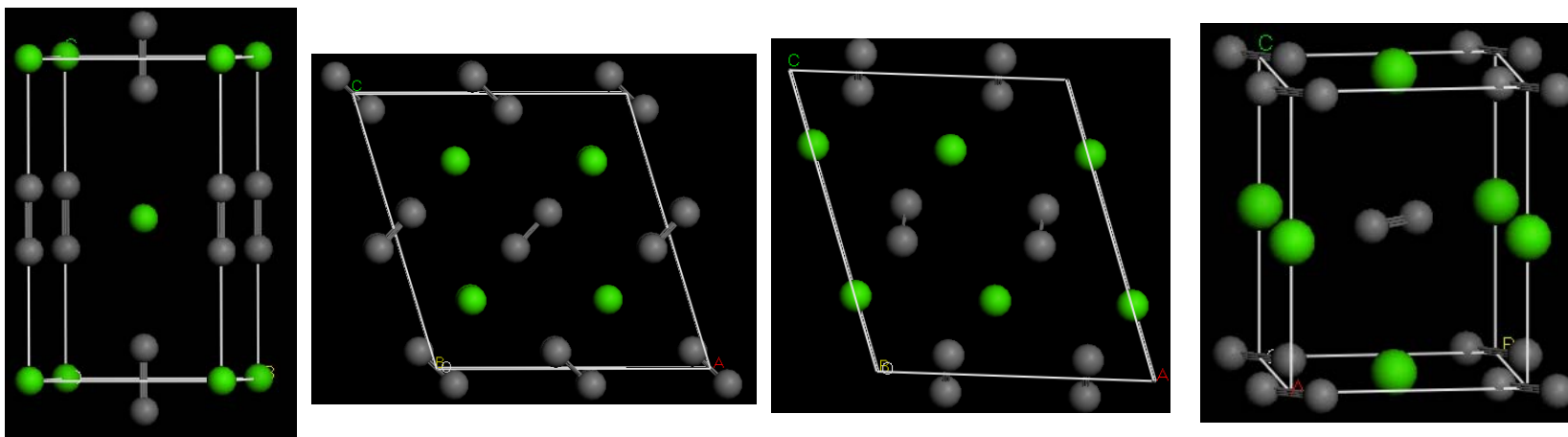
G. Csanyi, *et al.* Nature Phys. 1, 42 (2005).

N. Emery, *et al.* PRL 95, 087003 (2005).

A. Gauzzi, *et al.* PRL 98, 067002 (2007).

- Alkali-Earth metal dicarbides, including C_2 dumbbell at ambient pressure.

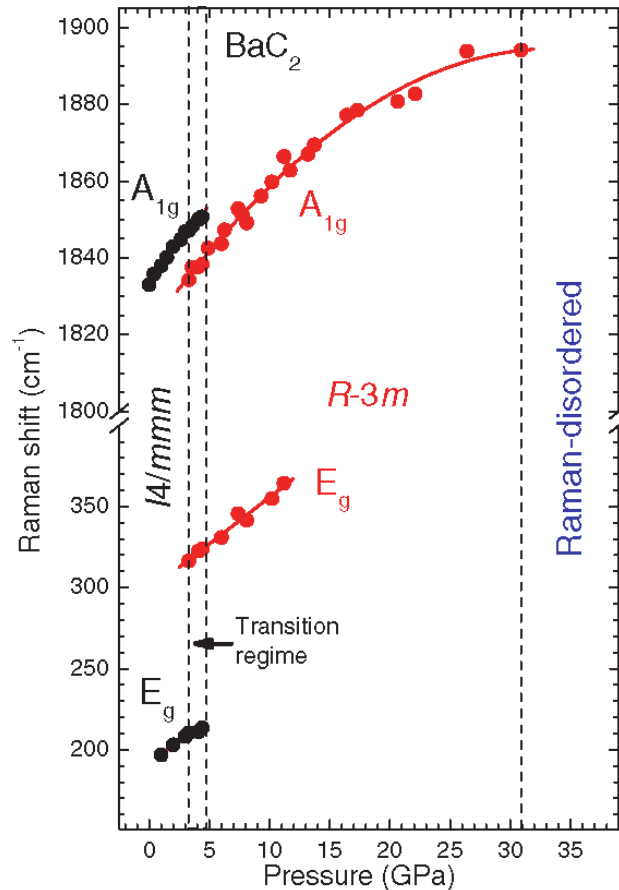
Temperature-modulated phases Semiconductor



C_2 units in them have different orientation.

Experimentally, BaC_2 and CaC_2

BaC_2



PRB **85**, 054105 (2012)

CaC_2

At pressures above 18 GPa Raman spectra become featureless, and remain featureless upon decompression which suggests an irreversible amorphization of the acetylide carbides.

JCP **137**, 224507 (2012)

Research Motivation

Open question for di-carbides:

- Polymerization?
- Metallization?
- Superconducting?

**Evolution of C₂ dimer with pressure increase;
Enrich data base for compressed carbon;
Explore novel carbon existence form.**

sp, sp², sp³

Research Methods

- **Stable structures: USPEX**
- **Total energy calculation: VASP, PAW**

Hard PP, high dense k-point grid.

- **Phonon:**

Phonopy: Phys. Rev. Lett. 78, 4063 (1997)

Phys. Rev. B, 78, 134106 (2008)

Supercell approach with the finite displacement method.

Quantum Espresso (QE):

DFPT: S. Baroni, et al. Rev. Mod. Phys. 73, 515 (2001).

Superconductivity: BCS theory, QE

$$T_c = \frac{\omega_{\log}}{1.2} \exp\left(-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right)$$

Result



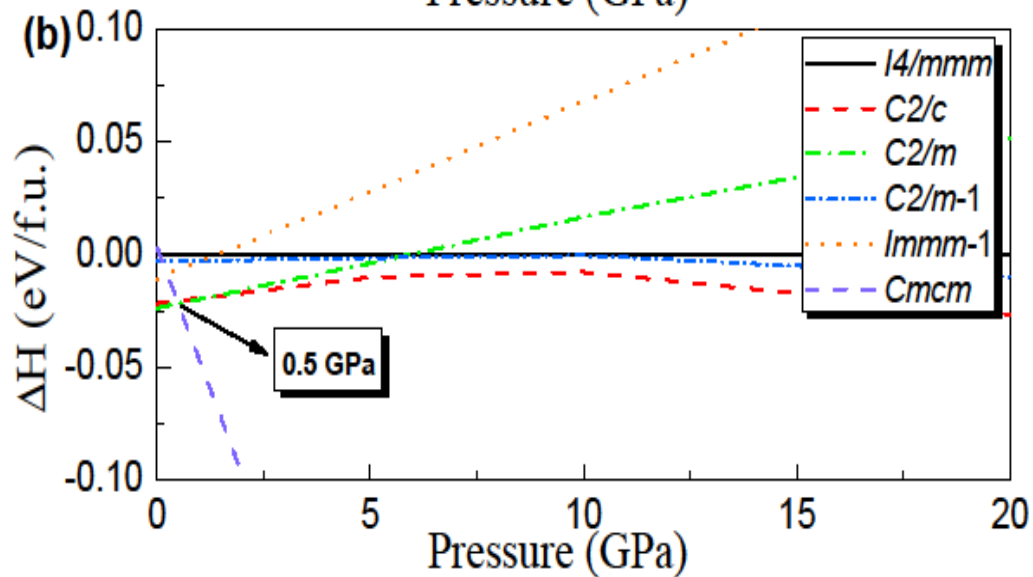
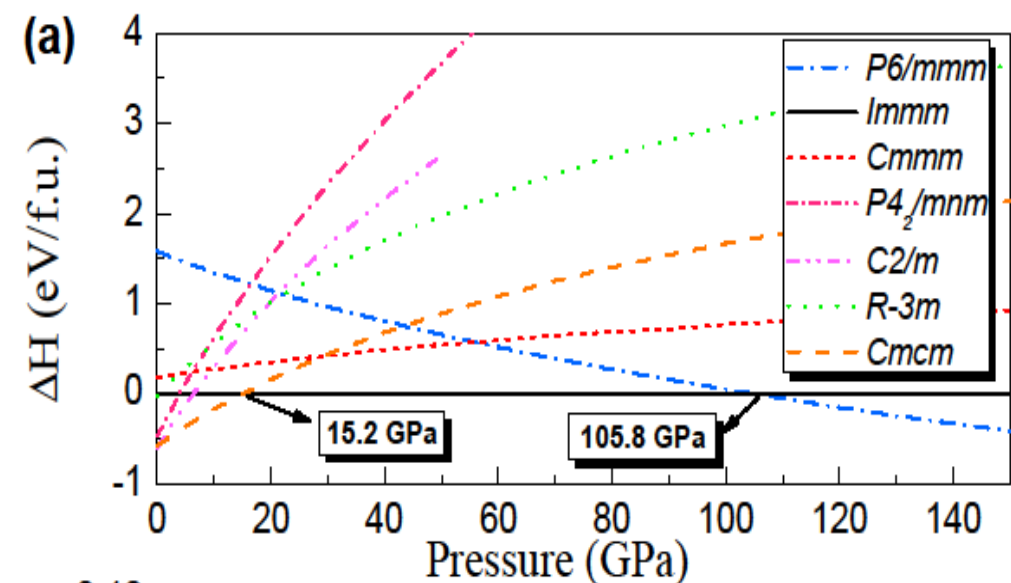
Pressure induced superconductivity in CaC_2

Y. L. Li, W. Luo, Z. Zeng, H. Q. Lin, H.-k. Mao, and R. Ahuja
PNAS, USA 110, 9289-9294 (2013)

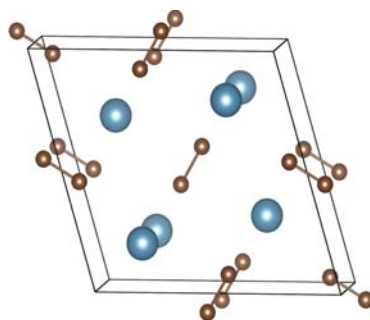
Lithium and calcium carbides with polymeric carbon structures

D. Benson, Y. L. Li, W. Luo, R. Ahuja, G. Svensson, and U. Häussermann
***Inorganic Chemistry* 52, 6402-6406 (2013)**

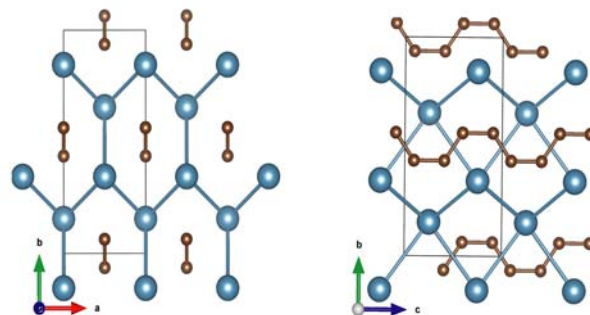
Enthalpy vs. pressure for CaC_2



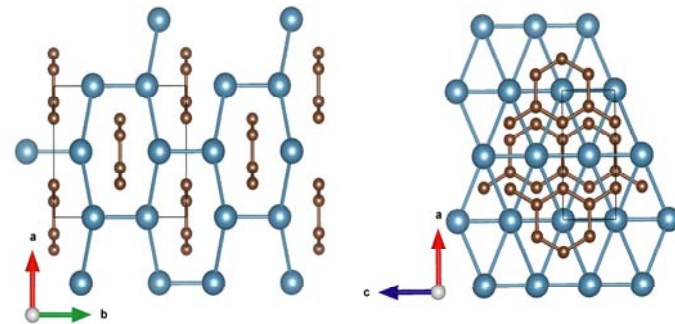
I



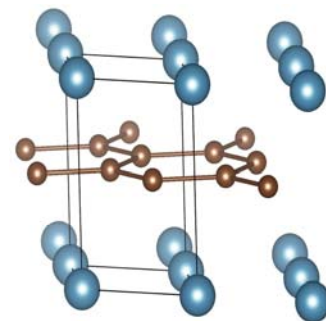
II



III



IV



Structural Stability Criteria

1. Low Enthalpy:

Total Energy calculation plus Equation of State (EOS)

2. Mechanical stability:

Elastic constants

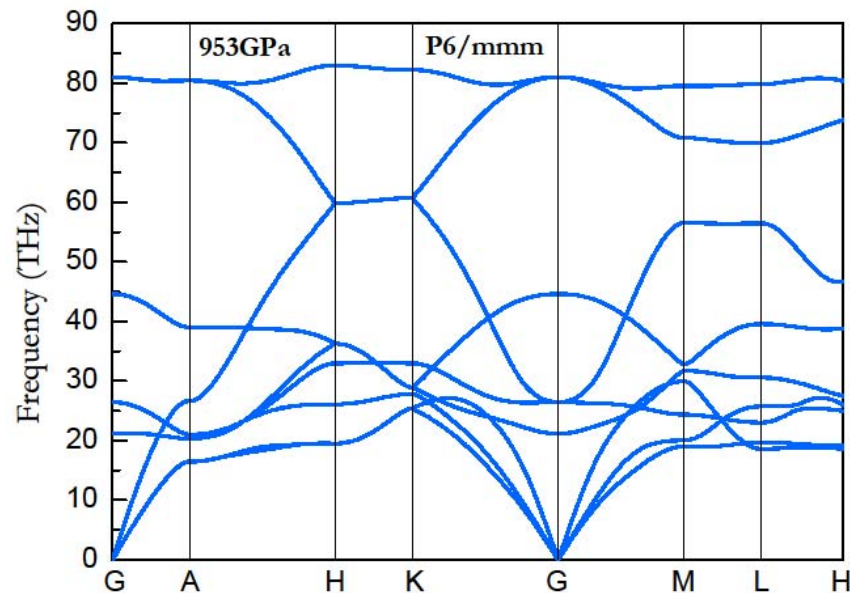
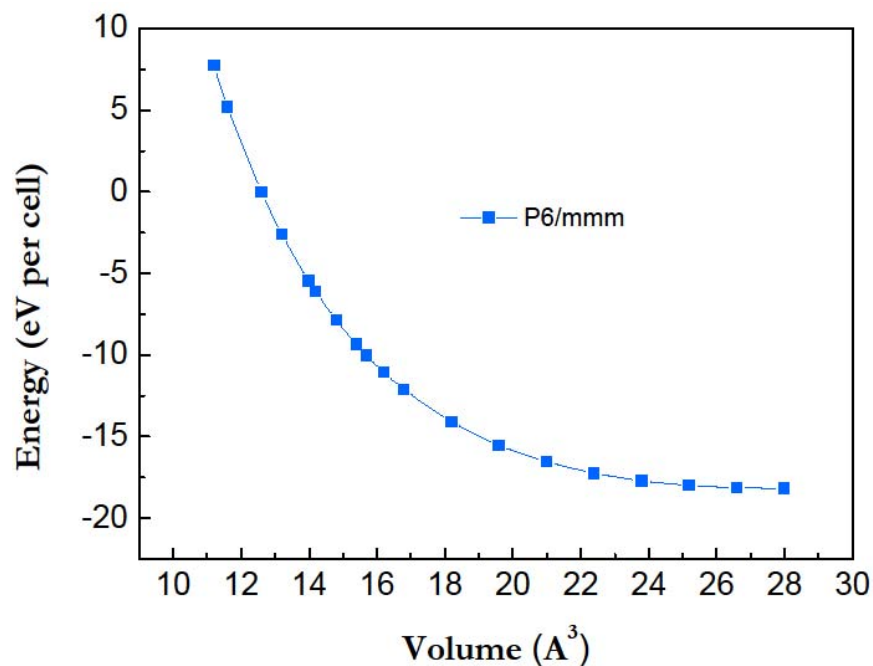
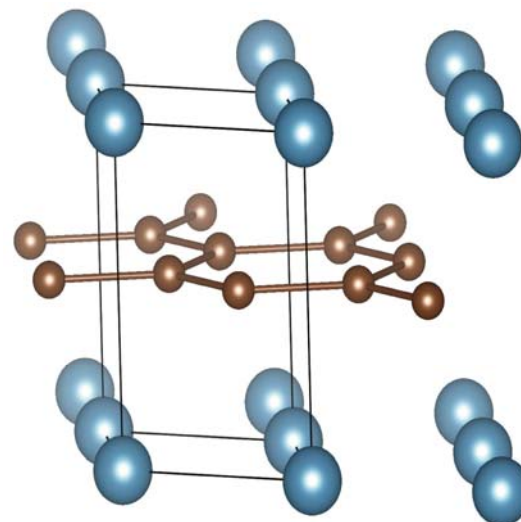
3. Dynamical stability:

Phonon

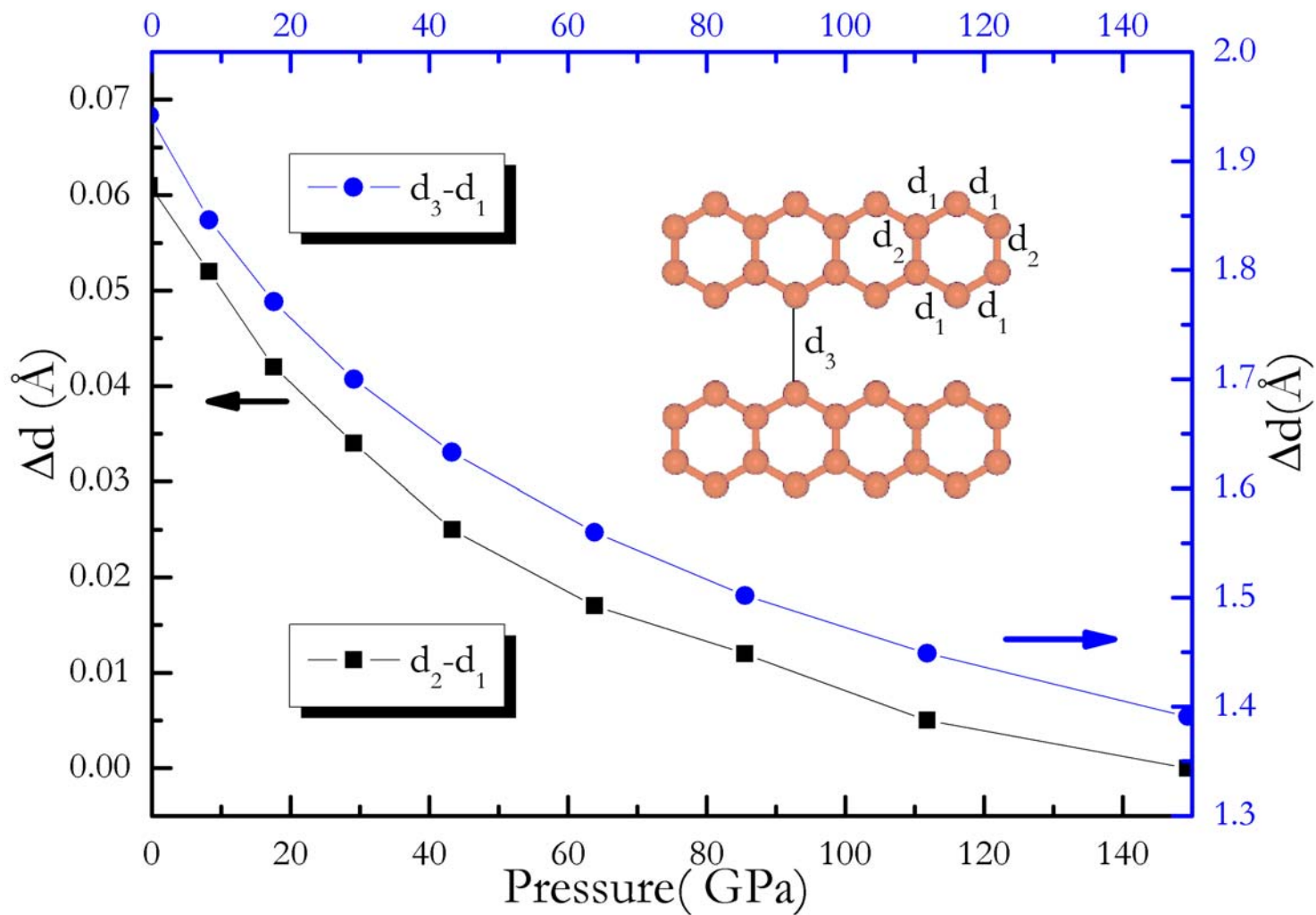
3D polymerized carbon in CaC_2 ??

300 GPa, 500 GPa, 700 GPa, 1TPa

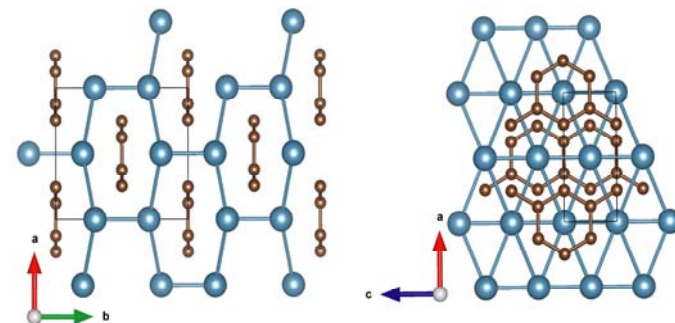
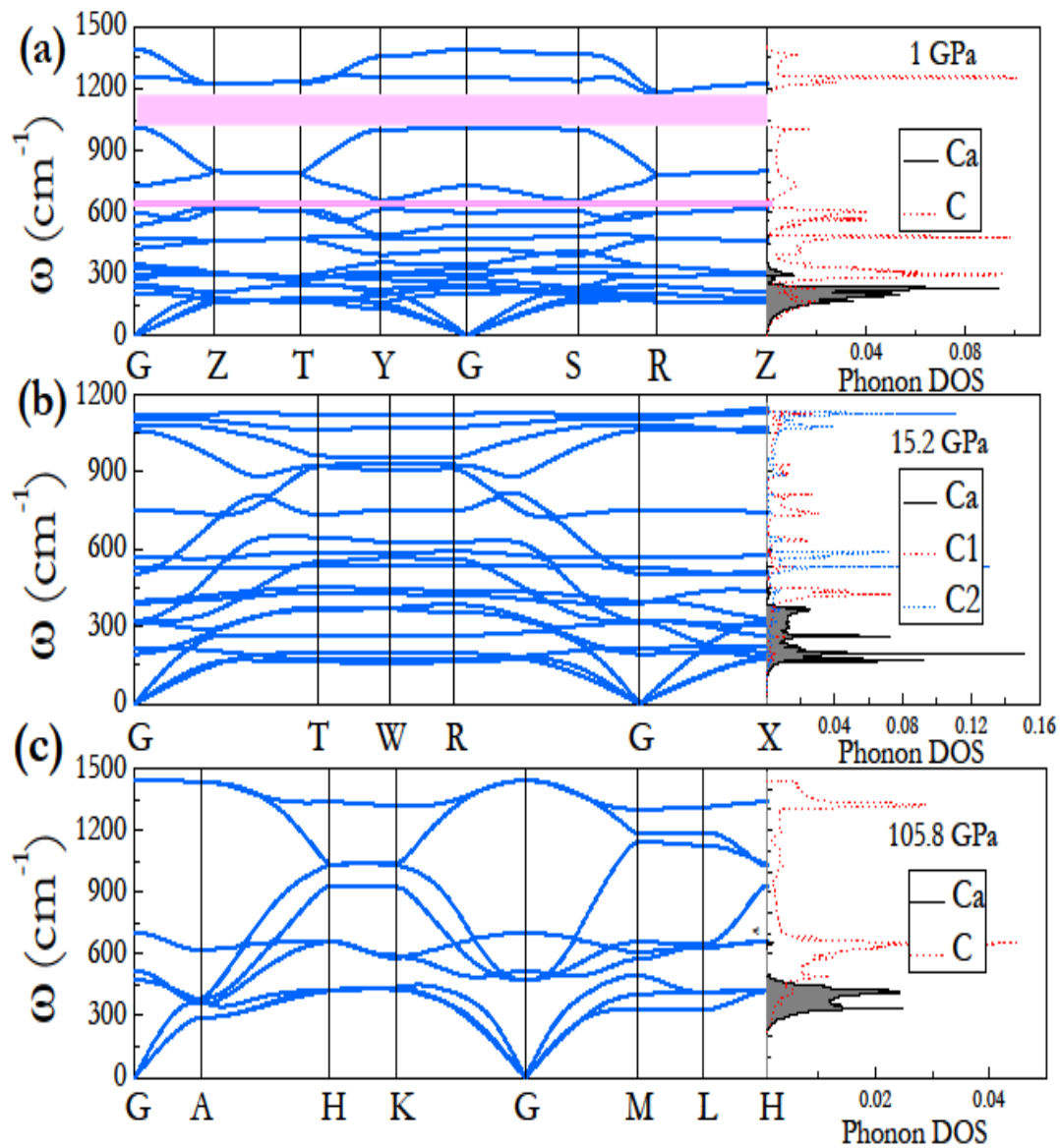
2 or 4 molecules per unit cell



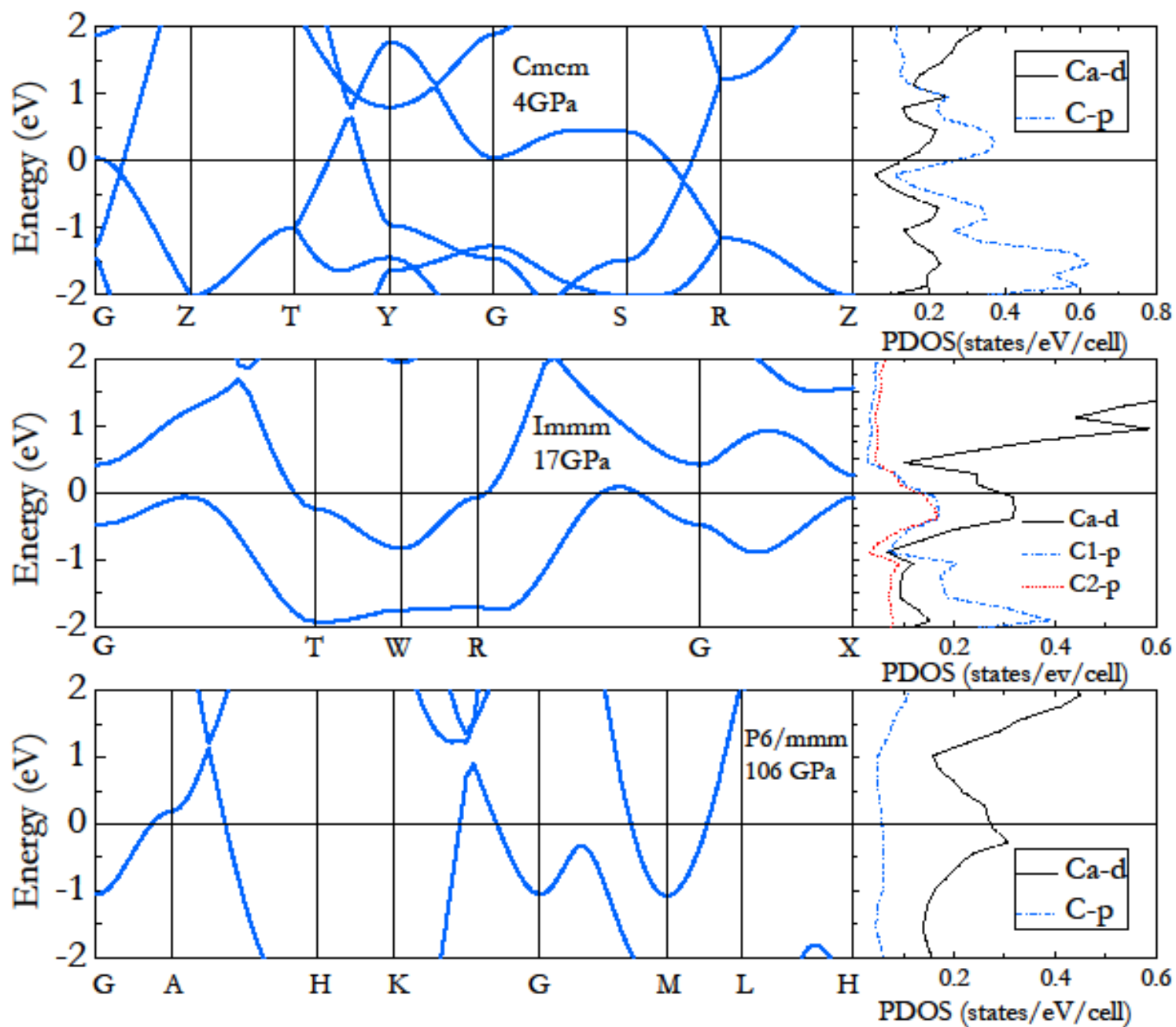
Phase III

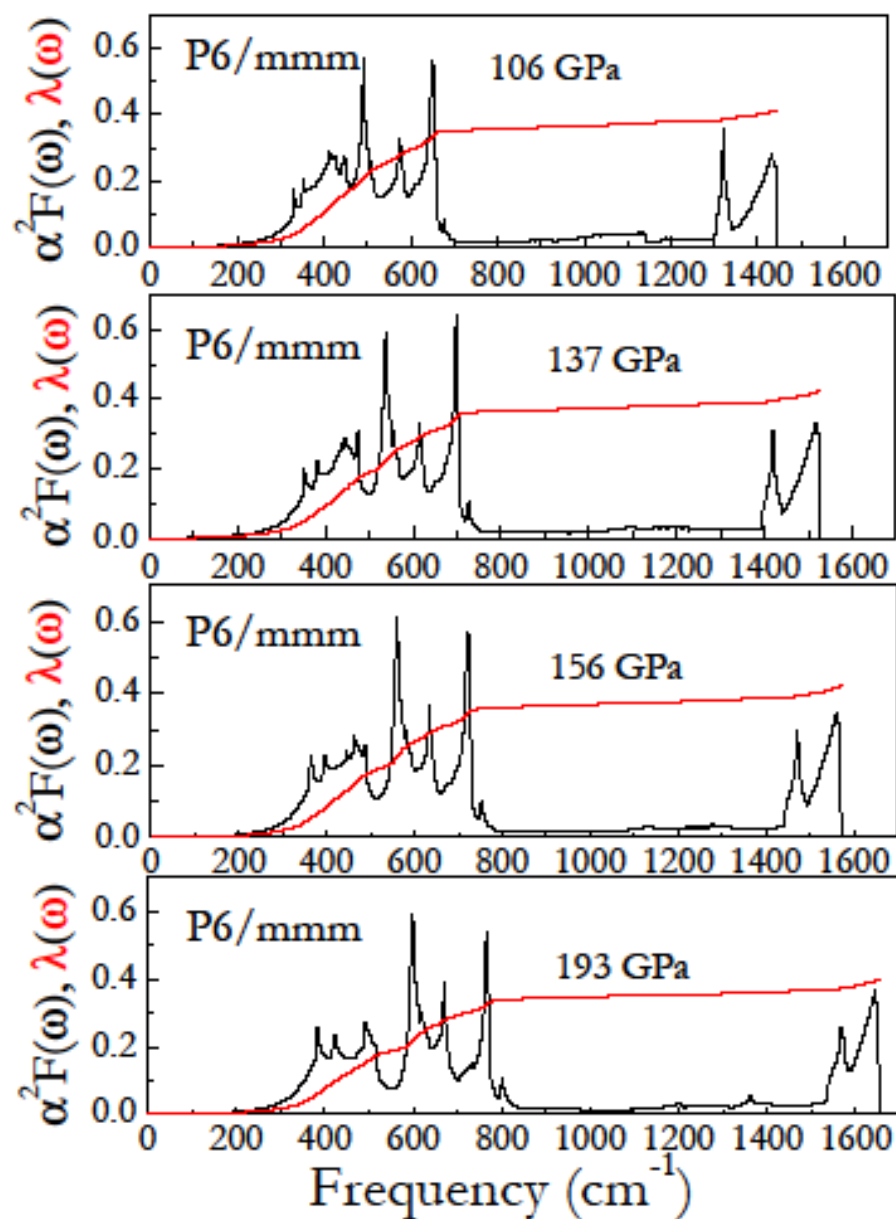
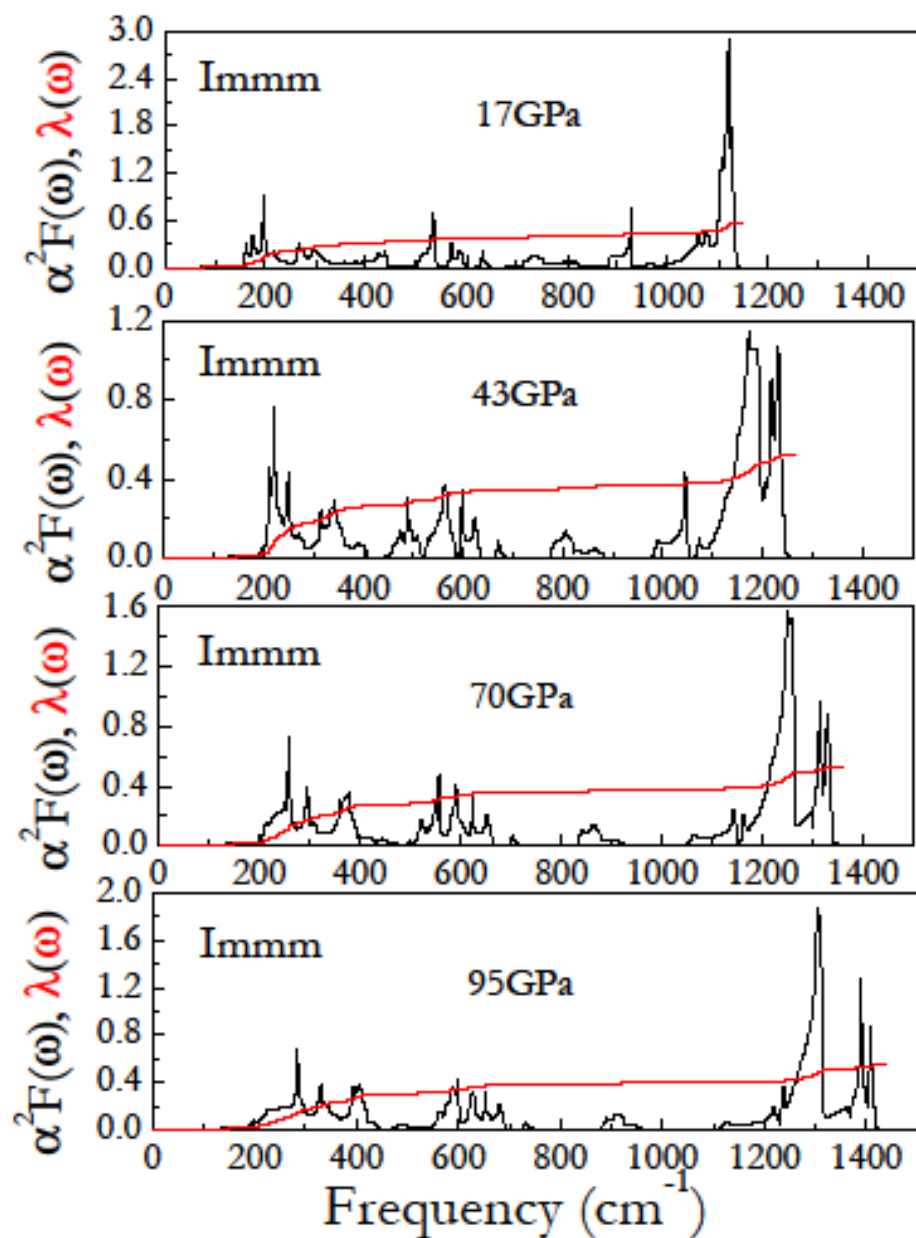


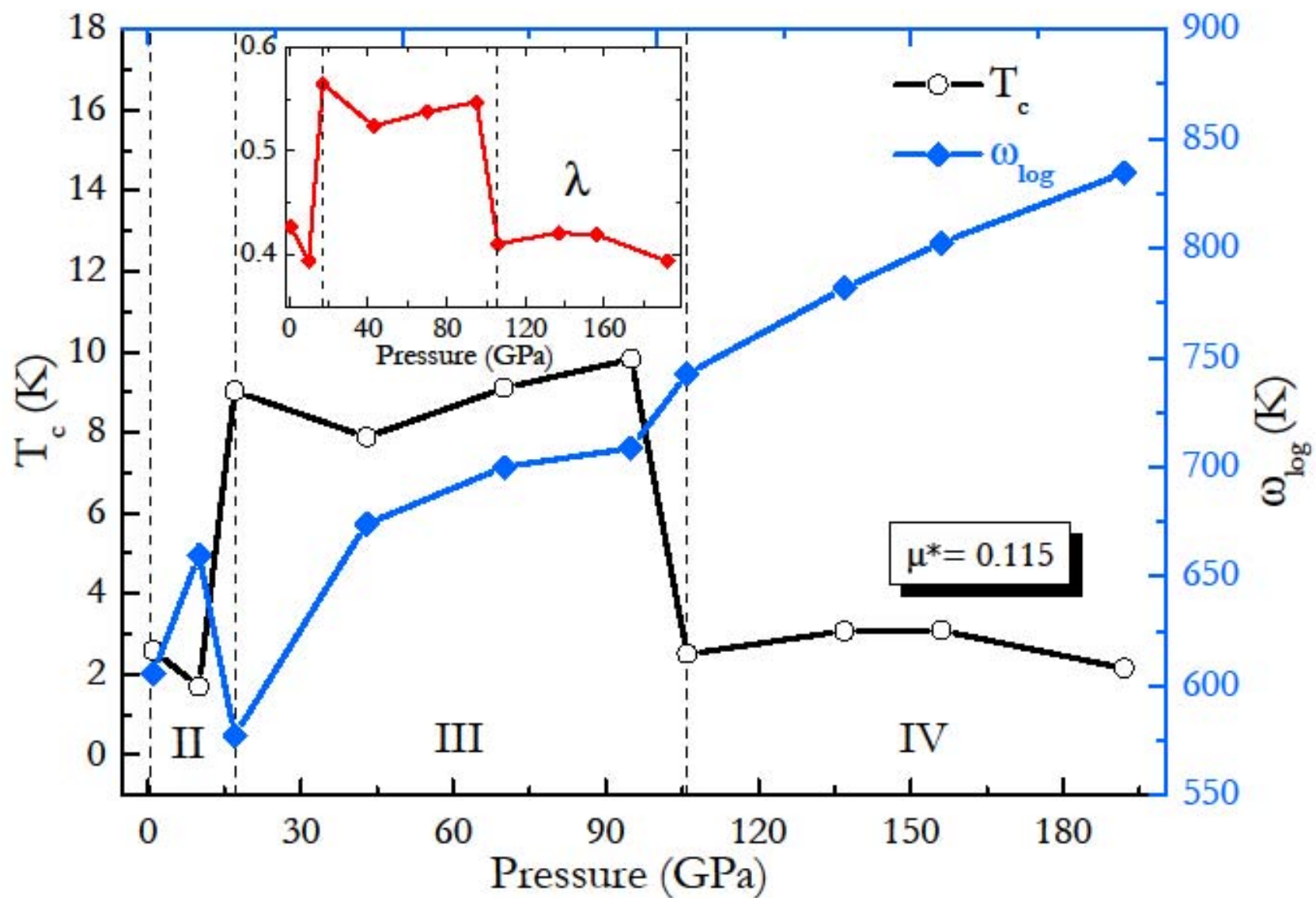
Phonon



Soft modes







Conclusion

- Localized dimer to 1D chain to quasi-1D ribbon to 2D-sheet (stability up to 1TPa).
- Metallization predicted.
- Superconductivity predicted.
- Superconducting mechanism similar to CaC_6 .
- Both SrC_2 and BaC_2 are similar to CaC_2 , but no superconductivity.
- Carbon polymerized observed in Li_2C_2 .

Summary

1. Three E. “Energy, enthalpy, entropy”

$$H=E+PV$$

$$G=E+PV-TS$$

For CaC_2 and BaC_2 ,

Can free energy **G** give consistent results with experiment?

2. Carbon evolution rules in AEM carbides obtained.

Acknowledgements

Prof. Hai-Qing Lin

CSRC, P. R. China

Prof. Zhi Zeng

ISSP, P. R. China

Prof. Rajeev Ahuja

Uppsala University, Sweden

Prof. Ho-kwang Mao

Carnegie Institution of Washington, USA

Thank you for your attention.