Superconductivity in compressed CaC_2

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Outline

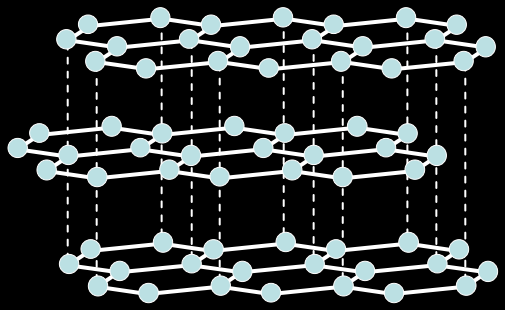
- Introduction
- Theoretical Methods
- Research Results
- Conclusion

Introduction

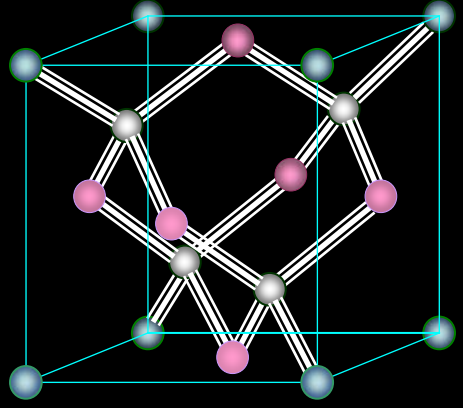
Carbon has many allotropes.

So many papers published.

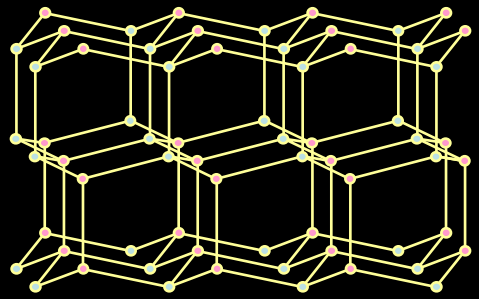
Charles Kittel, Introduction to solid states physics, 8th version.
M. D. Knuson, et al. Science **322**, 1822 (2008)
Q. Li, et al. PRL **102**, 175506 (2009)
Q. Zhu, et al. PRB **85**, 201407 (2012)
H. Niu, et al. PRL **108**, 135501(2012)
S. E. Boulfelfel, et al . Sci. Rep. **2**, 471 (2012)
Y. Wang, et al. Sci. Rep. **2**, 520 (2012)
……..



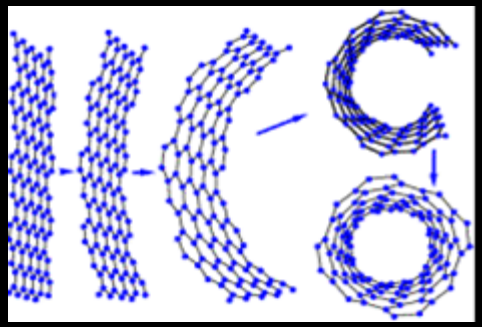
graphite



diamond (cubic)



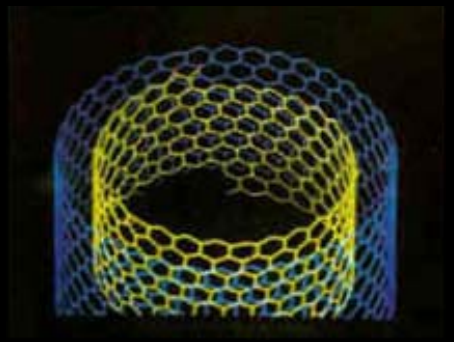
h-diamond



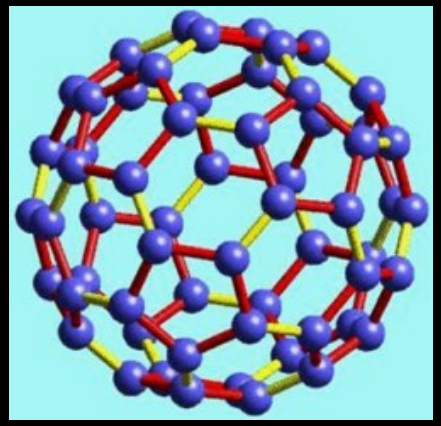
Graphene - CNT

Carbon

sp-、 sp^2-、 sp^3-

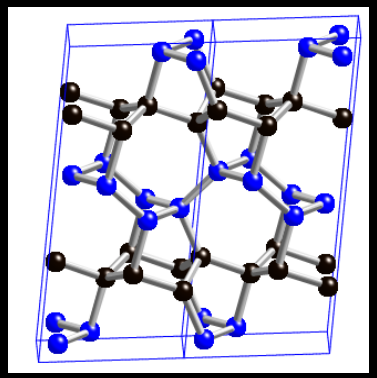


Carbon nanotube (CNT)



C60

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)

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

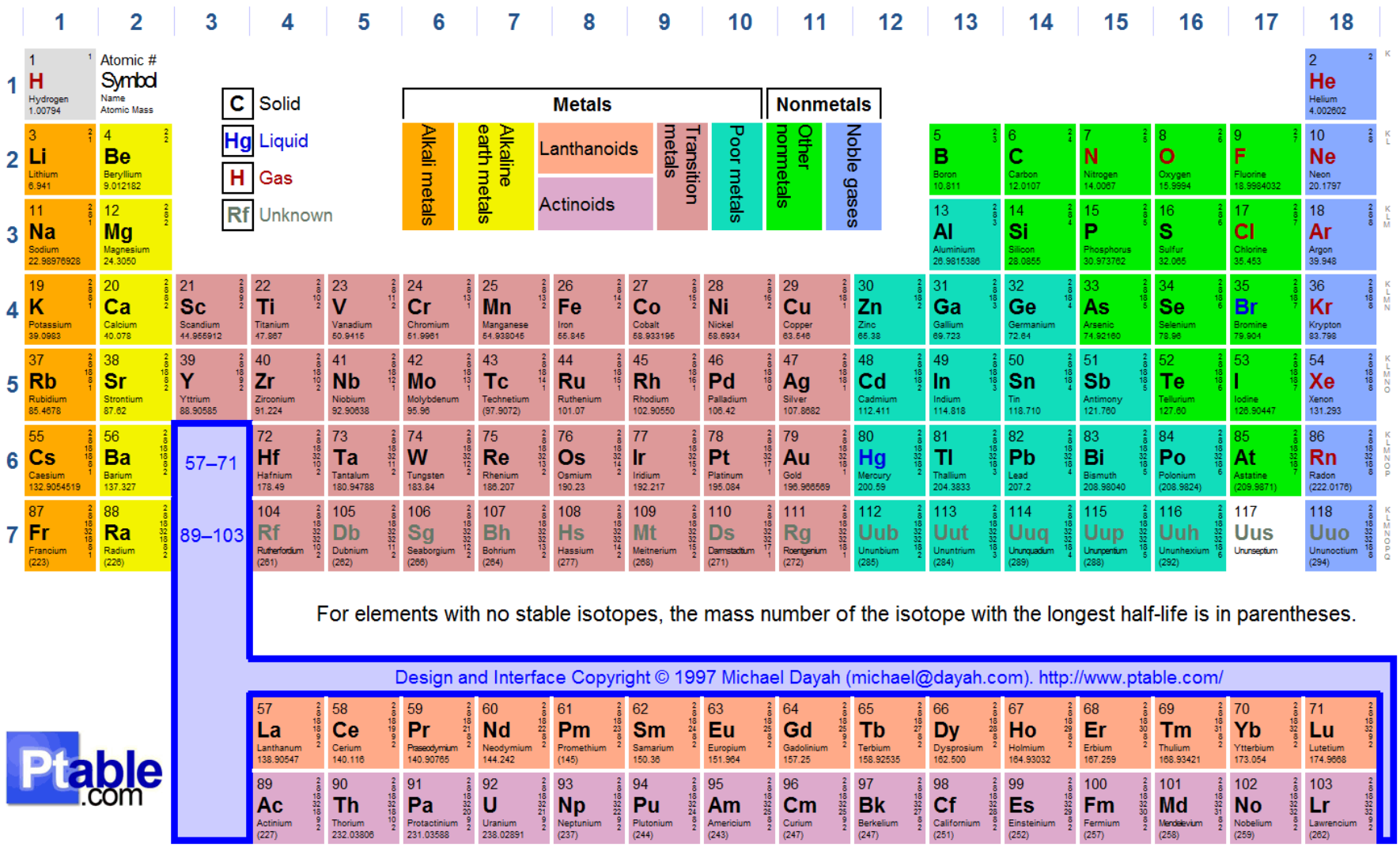
J. S. Tse, et al. Sci. Rep. **2**,372 (2012)

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

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

PRB, others

Periodic Table of Elements



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

Ptable.com

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).

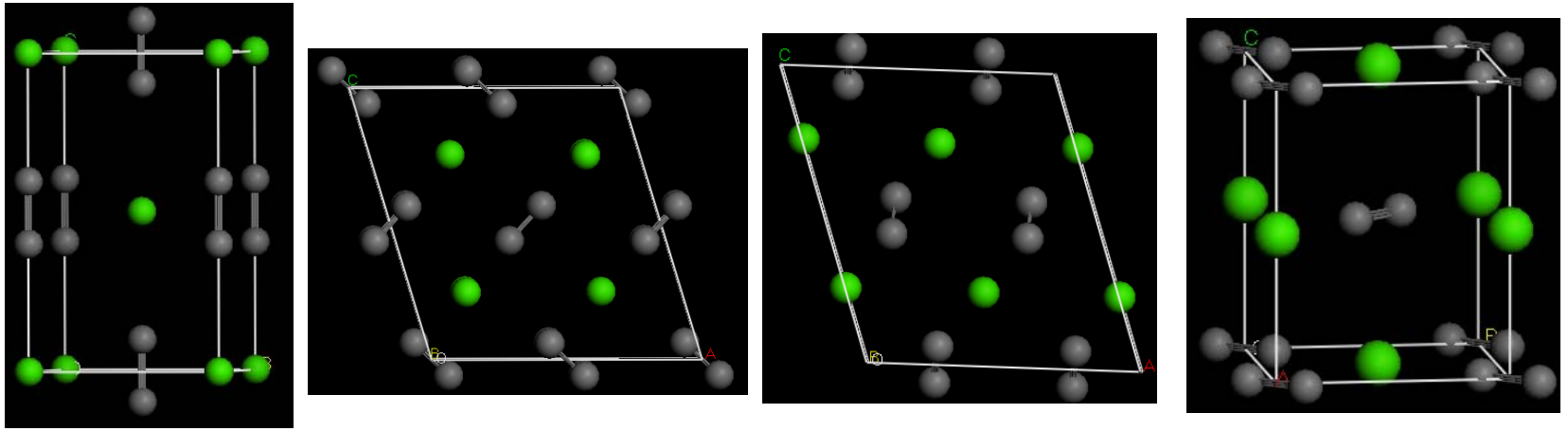
G. Csanyi, et al. Nature Phys. 1, 42 (2005).

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.**

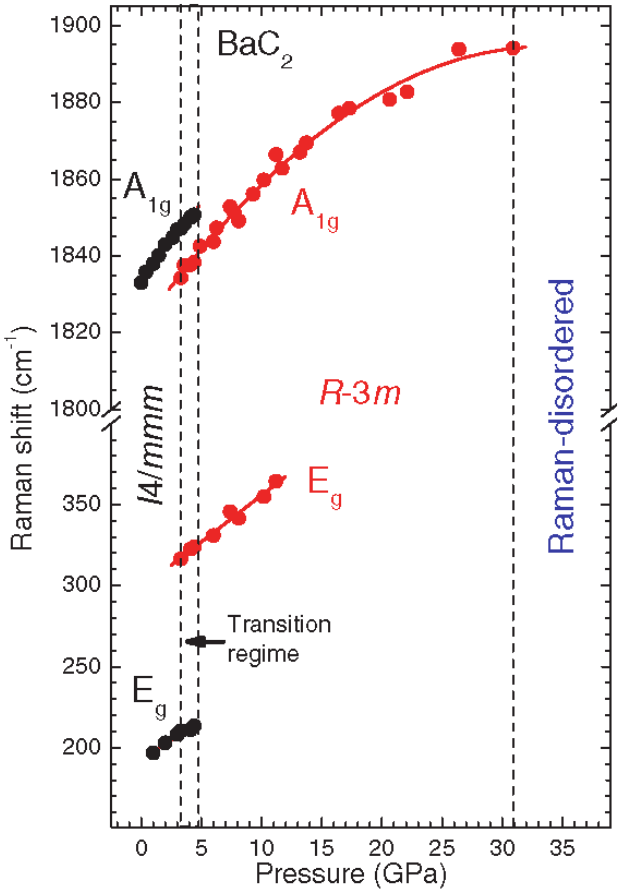
Temperature-modulated phases Semiconductor



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 C_2 dimmer with pressure increase;

Enrich data base for compressed carbon;

Explore novel carbon existence form.

sp, sp^2, sp^3

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

CaC_2

Pressure induced superconductivity in CaC_2

Y. L. Li, W. Luo, Z. Zeng, H. Q. Lin, H.-k. Mao,,and R. Ahuja

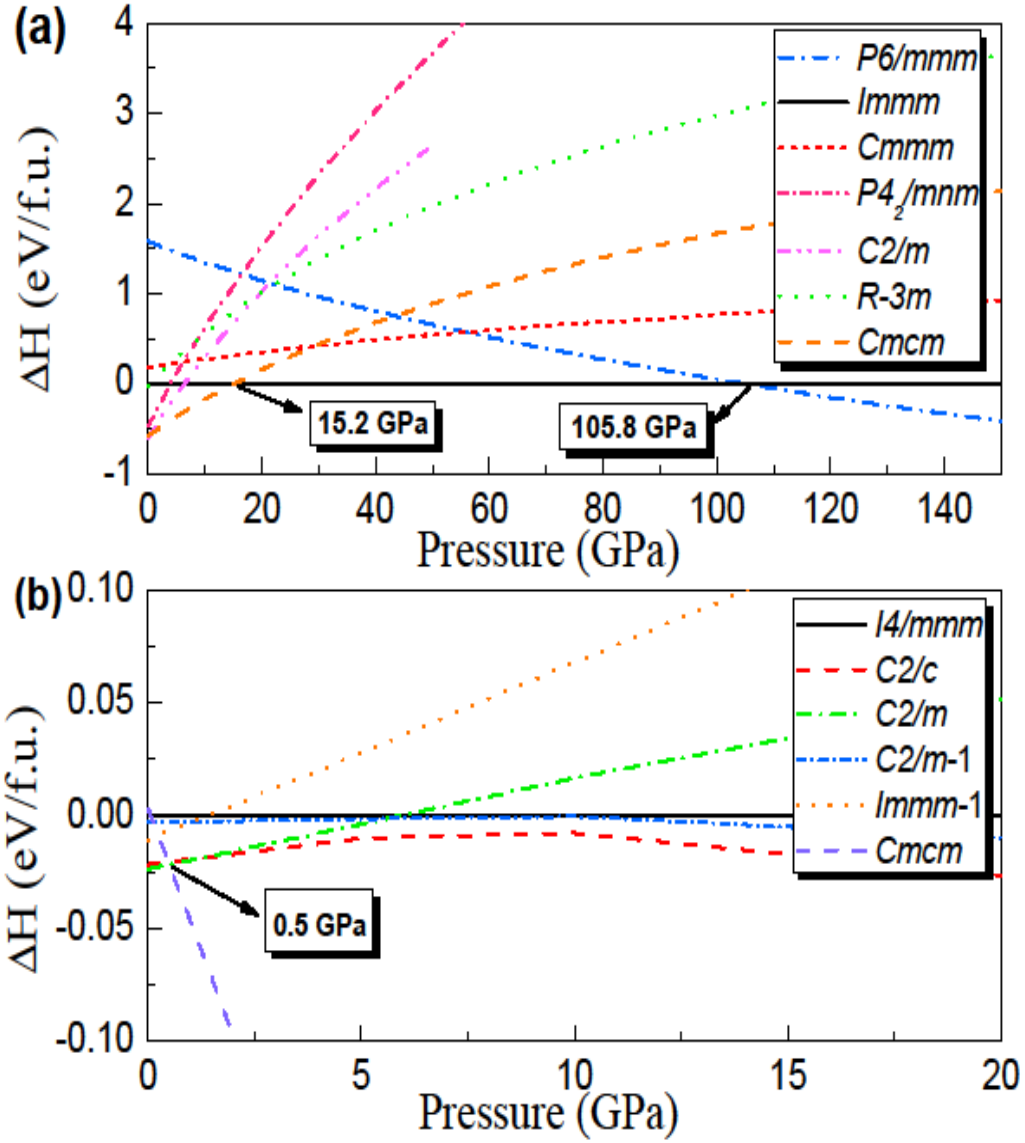
PNAS, USA 110, 9289-9294 (2013)

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

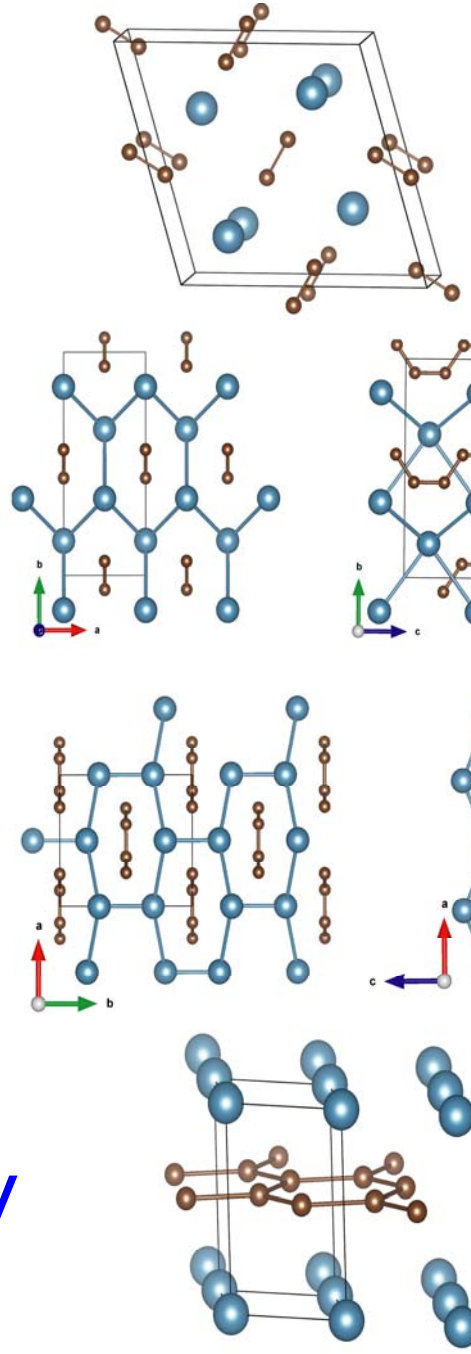


I

II

III

IV



Structural Stability Criteria

1. **Low Enthalpy:**

   Total Energy calculation plus Equation of State (EOS)

2. **Mechanical stability:**

   Elastic constants

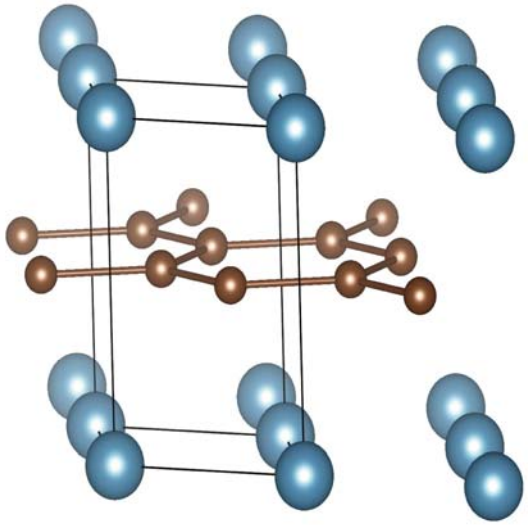
3. **Dynamical stability:**

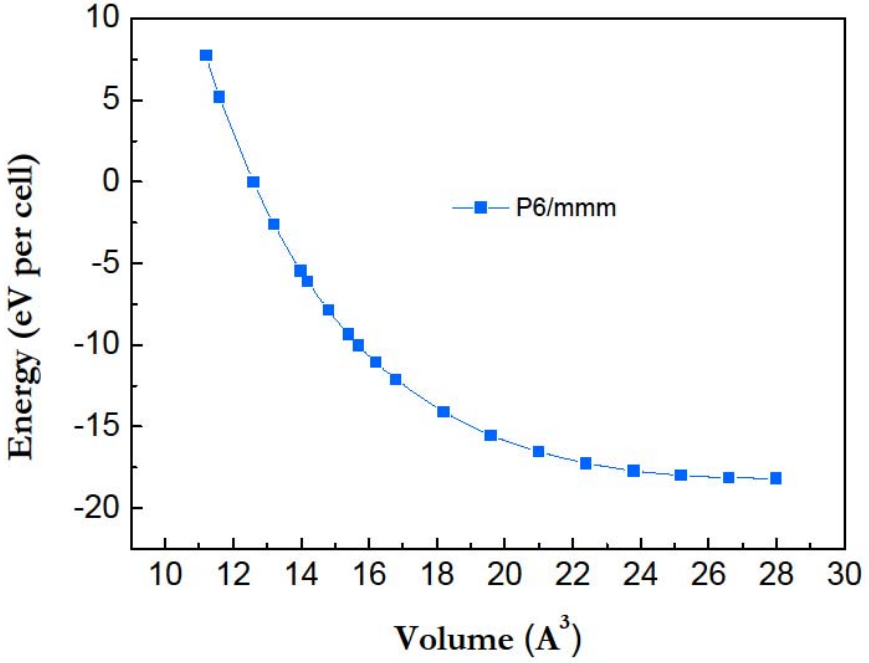
   Phonon

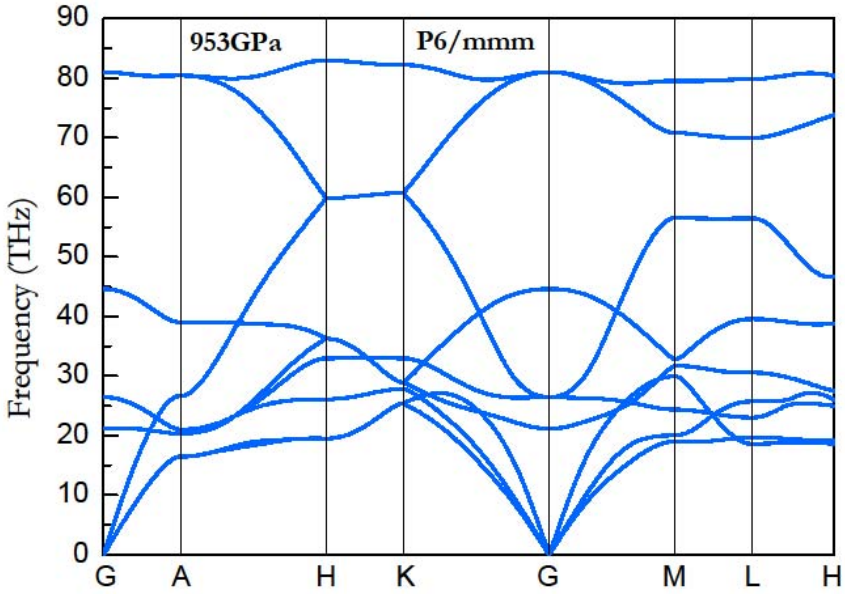
3D polymerized carbon in CaC_2 ??

300 GPa, 500 GPa, 700 GPa, 1TPa

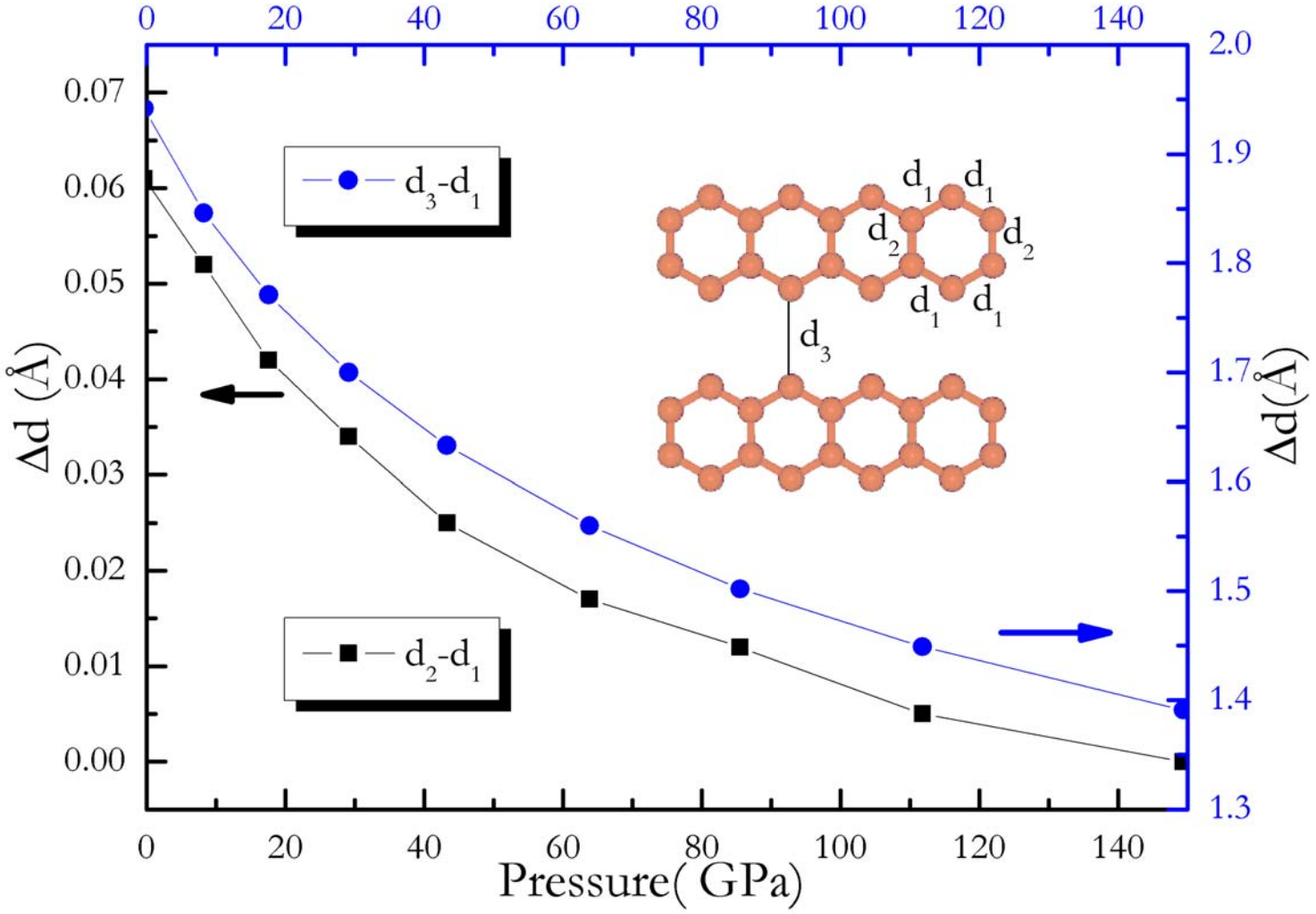
2 or 4 molecules per unit cell



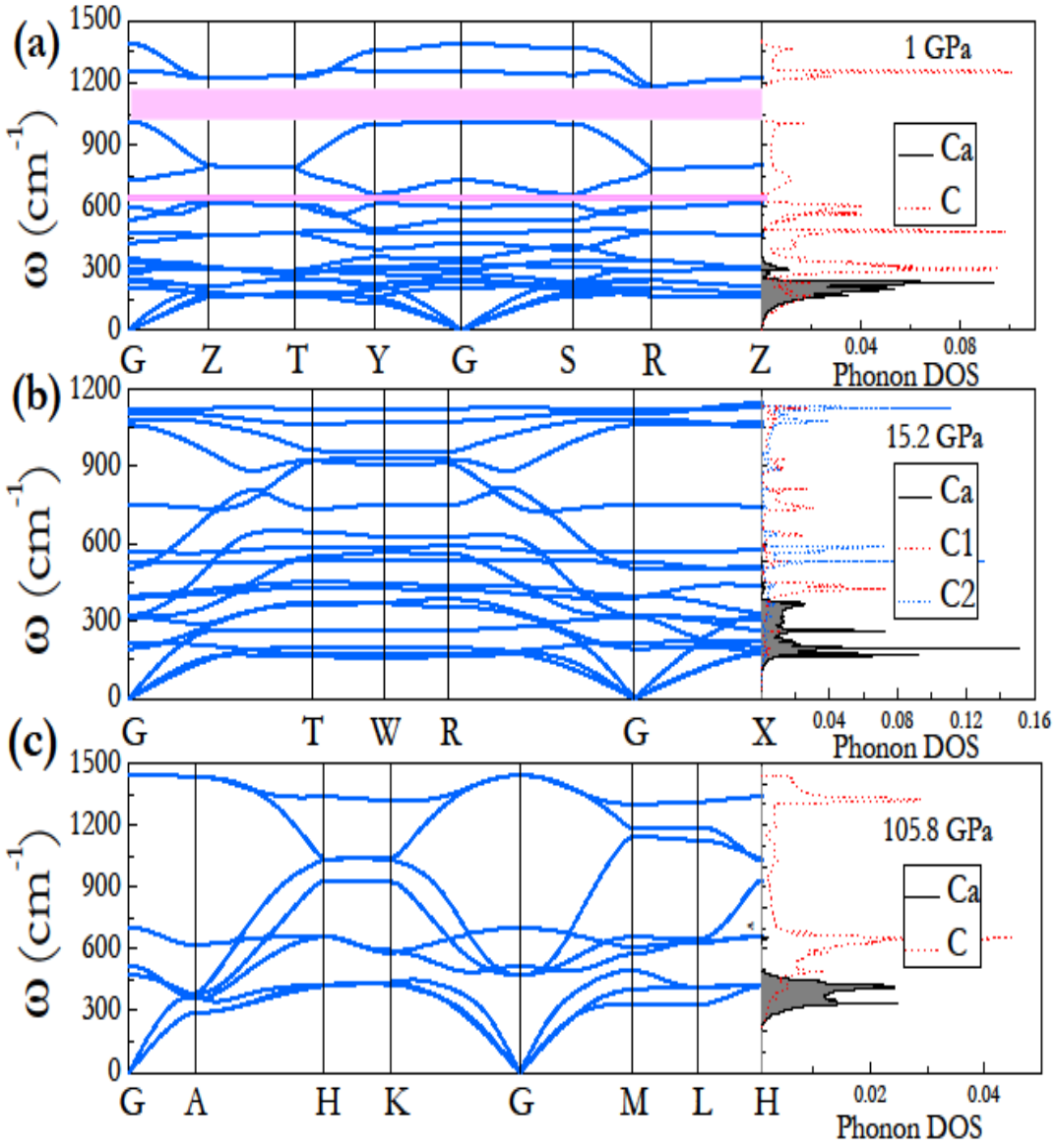


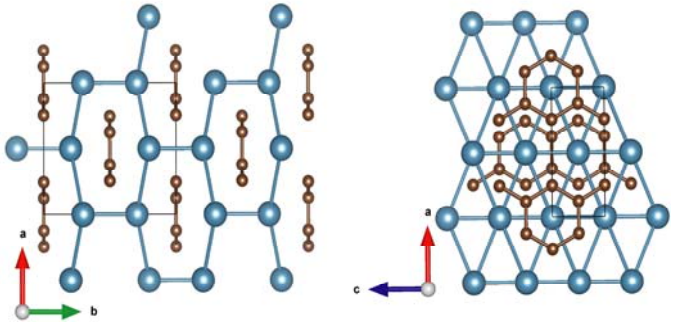


Phase III

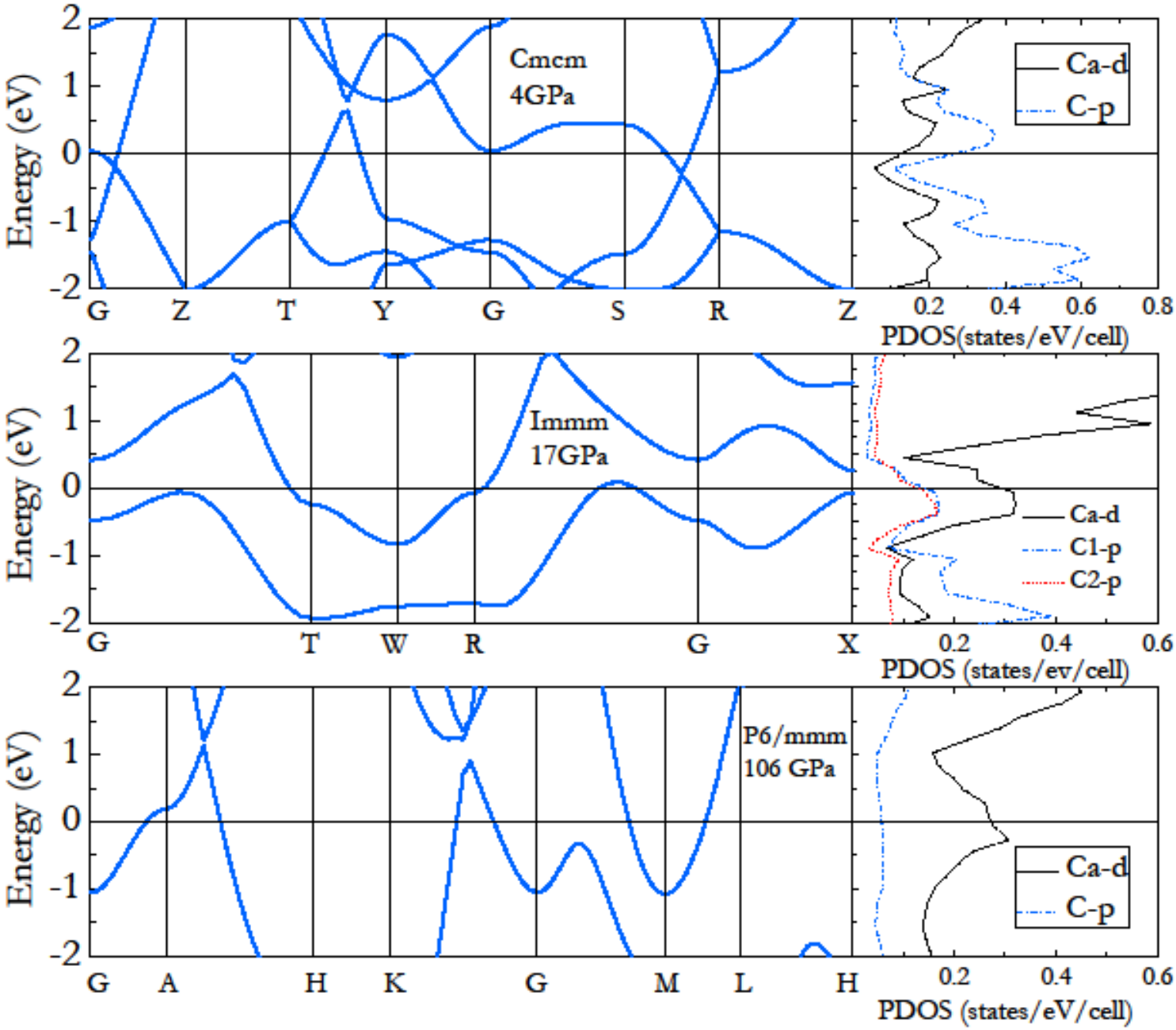

0
20
40
60
80
100
120
140
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
Δd (Å)
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
Δd(Å)
d3-d1
d2-d1
d1
d1
d2
d2
d1
d1
d3
Pressure(GPa)

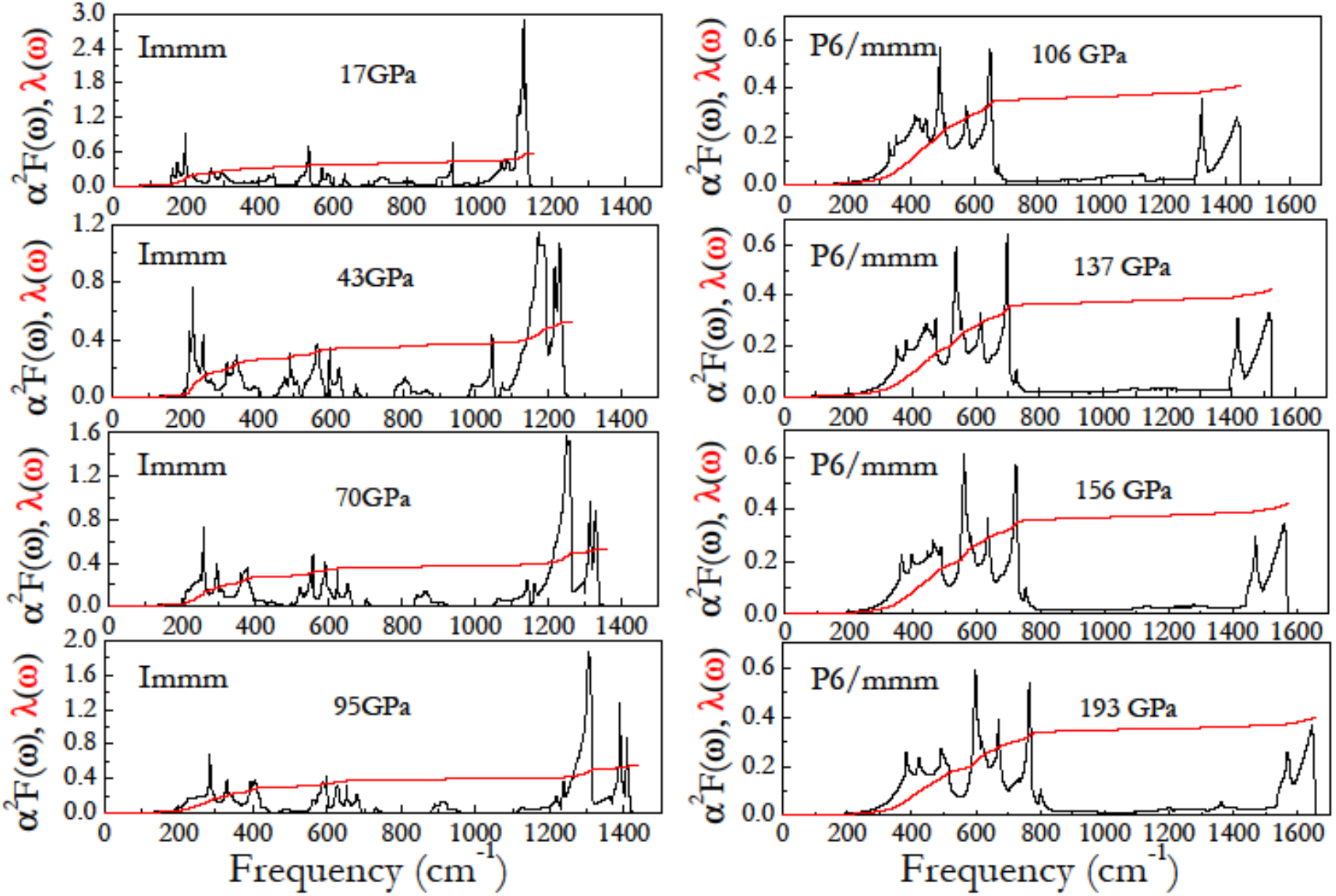
Phonon

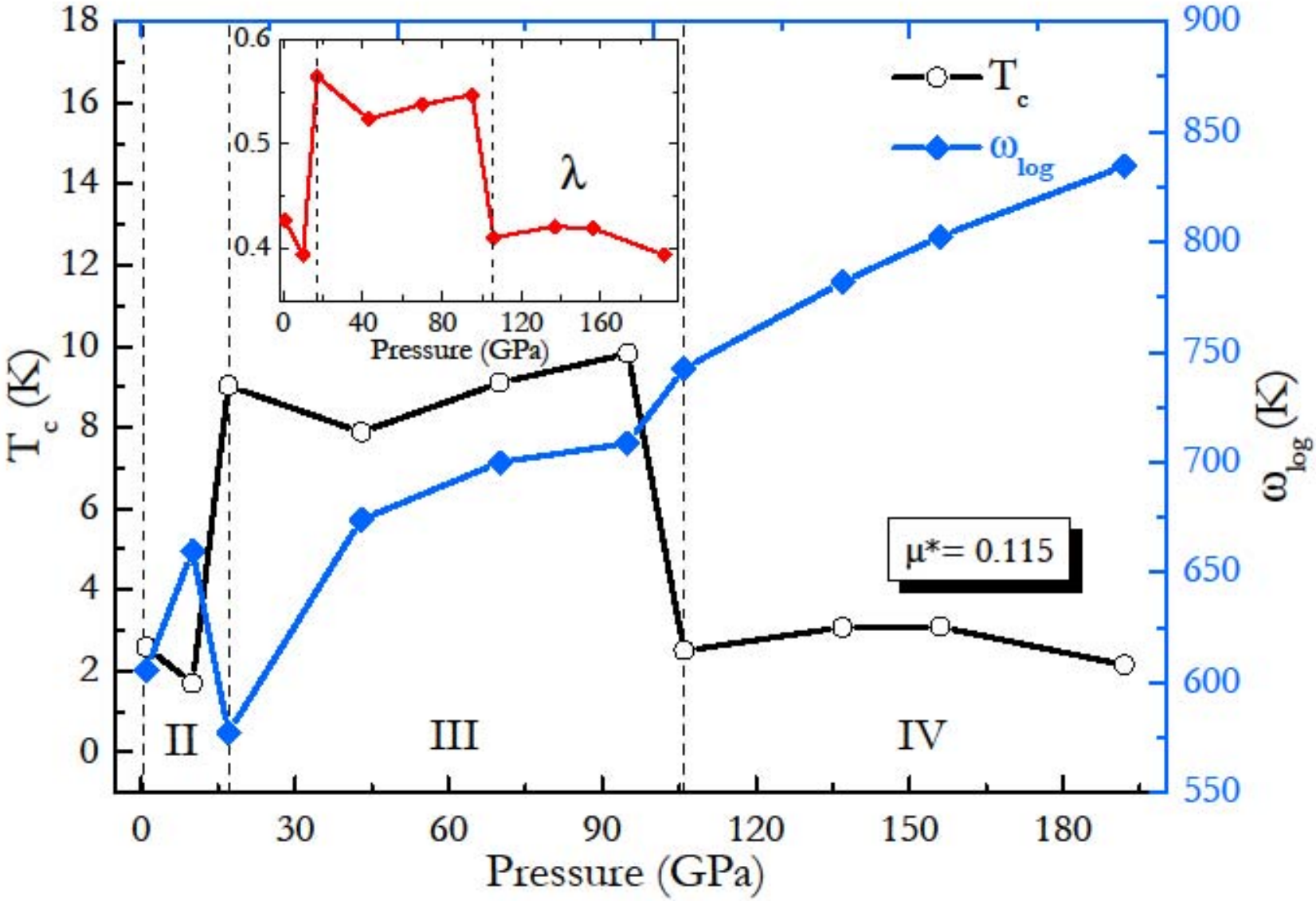




Soft modes


Energy (eV)
2
1
0
-1
-2
G
Z
T
Y
G
S
R
Z
Cmcm
4GPa
Ca-d
C-p
0.2
0.4
0.6
0.8
PDOS(states/eV/cell)
Energy (eV)
G
T
W
R
G
X
Immm
17GPa
Ca-d
C1-p
C2-p
0.2
0.4
0.6
PDOS (states/ev/cell)
Energy (eV)
G
A
H
K
G
M
L
H
P6/mmm
106 GPa
Ca-d
C-p
0.2
0.4
0.6
PDOS (states/eV/cell)


Immm
17GPa
43GPa
70GPa
95GPa
P6/mmm
106 GPa
137 GPa
156 GPa
193 GPa
α²F(ω), λ(ω)
Frequency (cm⁻¹)


T_c
ω_log
λ
μ*= 0.115
II
III
IV
T_c (K)
ω_log (K)
Pressure (GPa)
Pressure (GPa)

Conclusion

- Localized dimmer to 1D chain to quasi-1D ribbon to 2D-sheet (stability up to 1TPa).
- Metallization predicted.
- Superconductivity predicted.
- Superdonducting 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 CaC2 and BaC2,

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

2. Carbon evolution rules in AEM carbides obtained.

Acknowledgements

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Thank you for your attention.