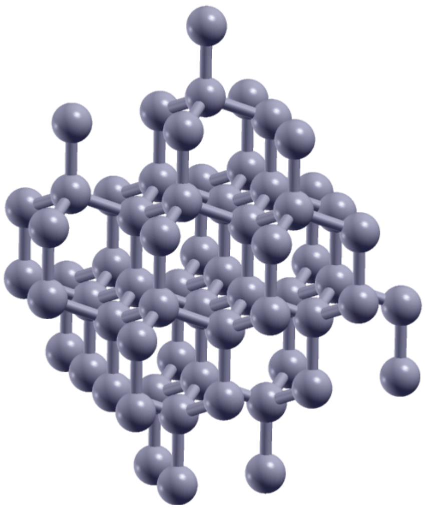
Superconductivity and Magnetism in Amorphous Carbon

Yuki Sakai

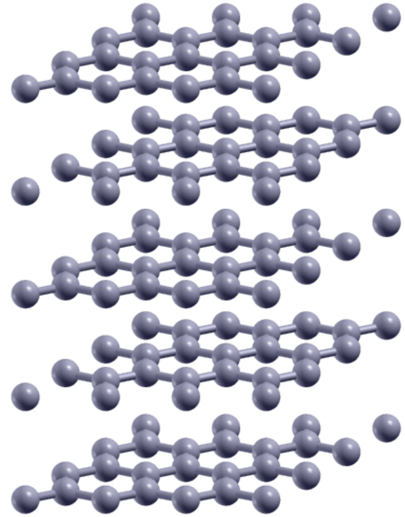
Oden Institute for Computational Engineering and Sciences,
The University of Texas at Austin

2019 Electronic Structure Workshop
May 22, 2019

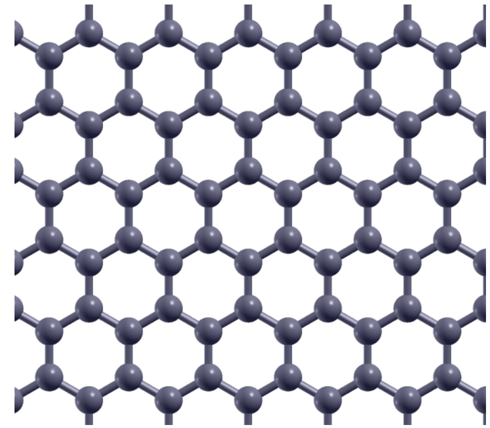
Allotropes of carbon



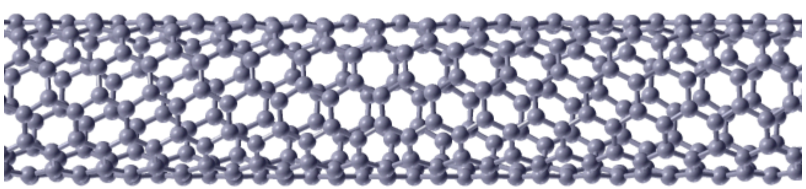
Diamond



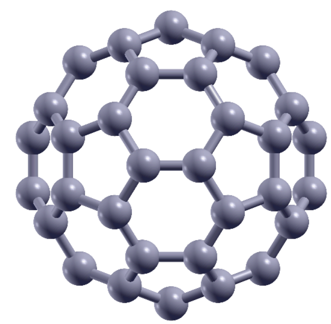
Graphite



Graphene



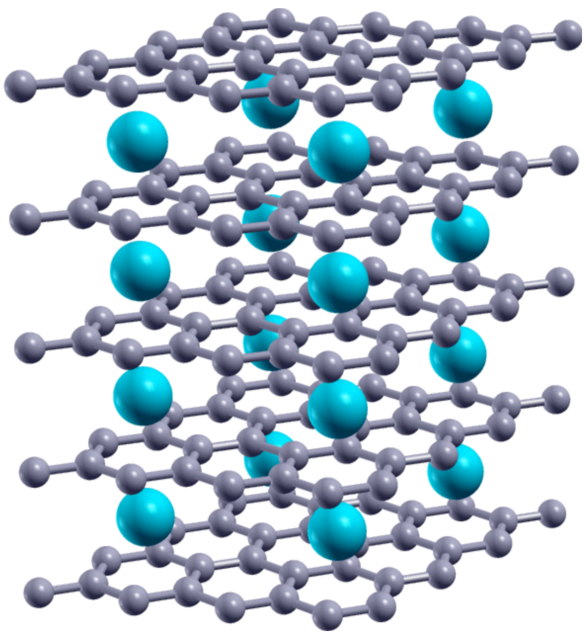
Carbon nanotubes

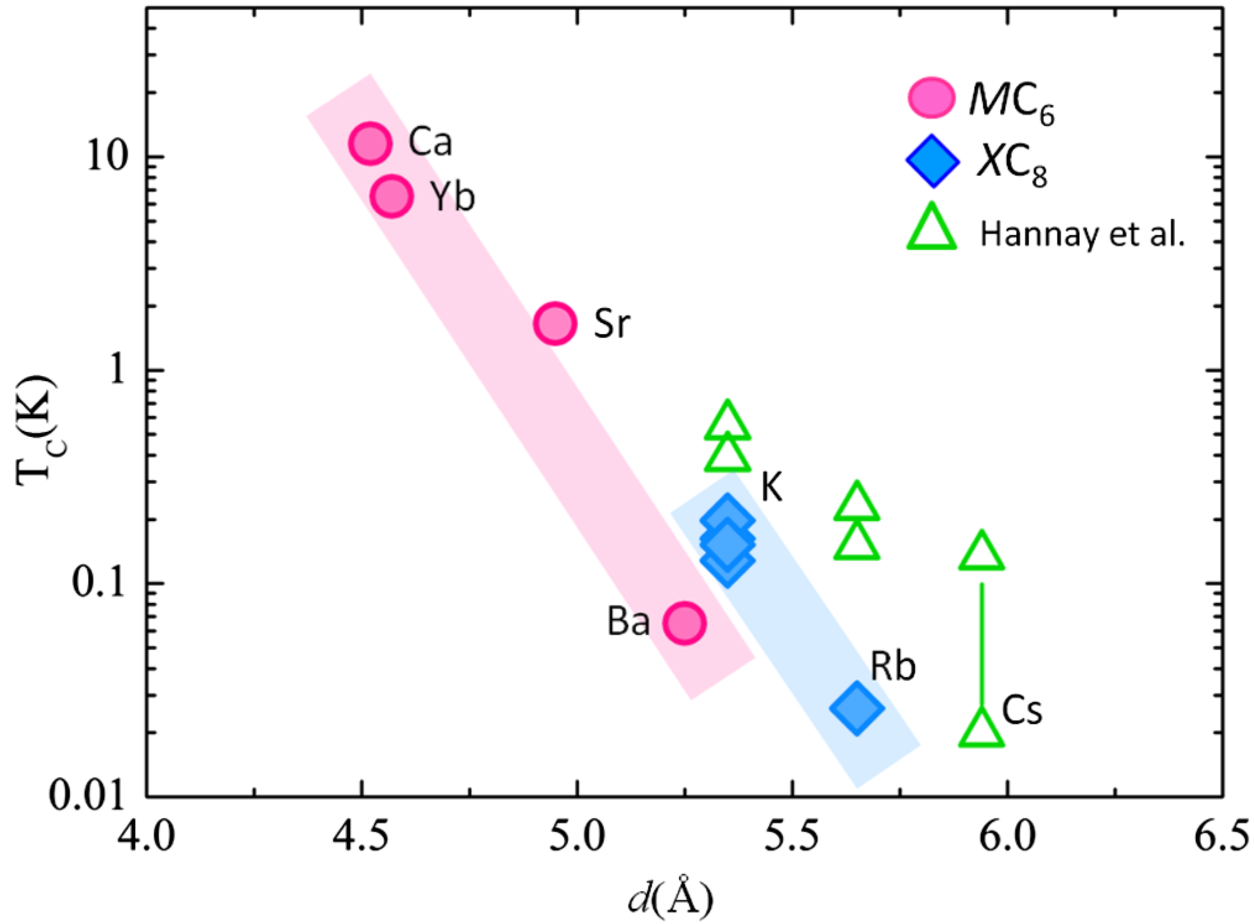


Fullerene

Various physical properties associated with various structures

Superconductivity in carbon materials

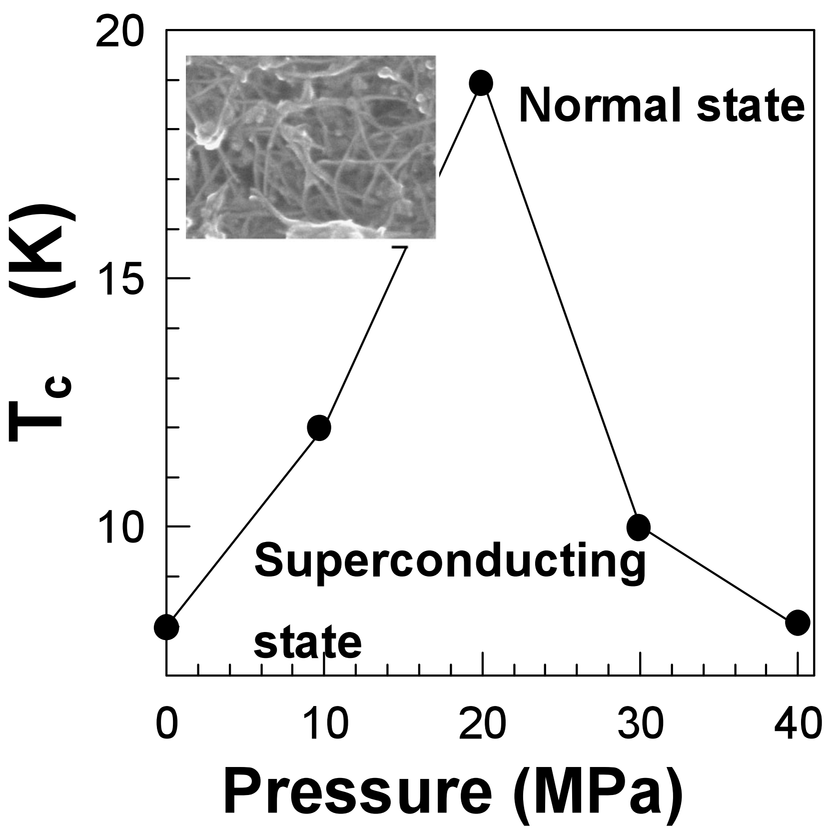




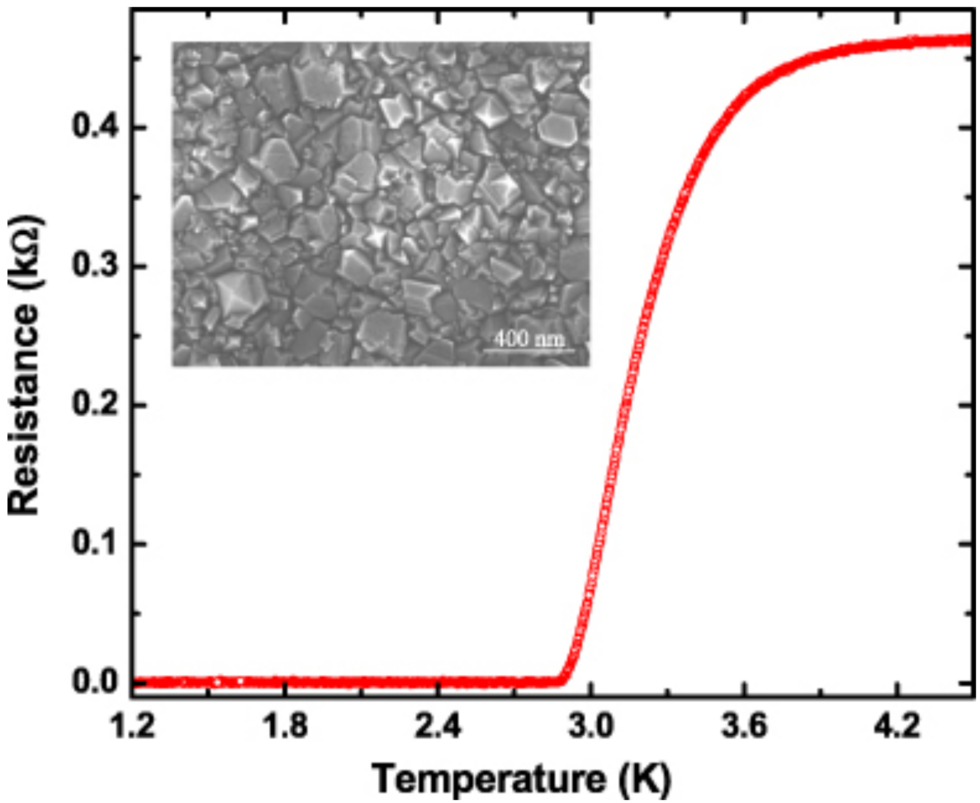
Graphite Intercalation Compounds
(Electron doping from intercalants)

S. Heguri et al., Phys. Rev. Lett. **114**, 247201 (2015)

Superconductivity in B-doped carbon



B-doped carbon nanotubes

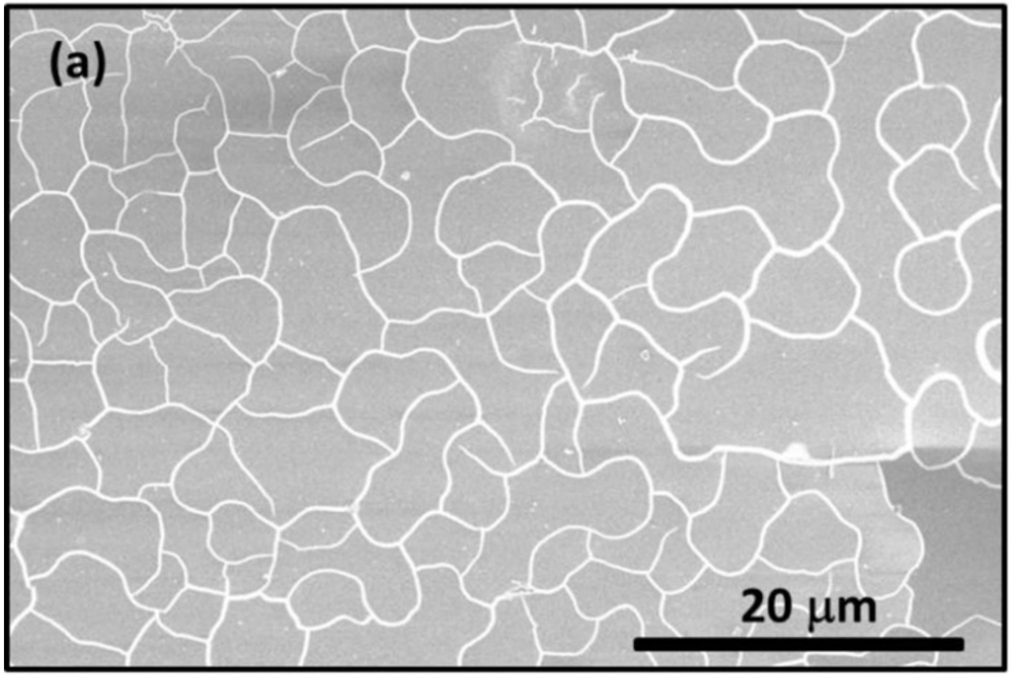


B-doped diamond

Can be superconductors when substitutionally boron doped

J. Haruyama et al., J. Supercond. Nov. Magn. **24**, 111 (2011)
S. Mandal et al., Nanotechnology **21**, 195303 (2010)

New amorphous carbon: Q-carbon

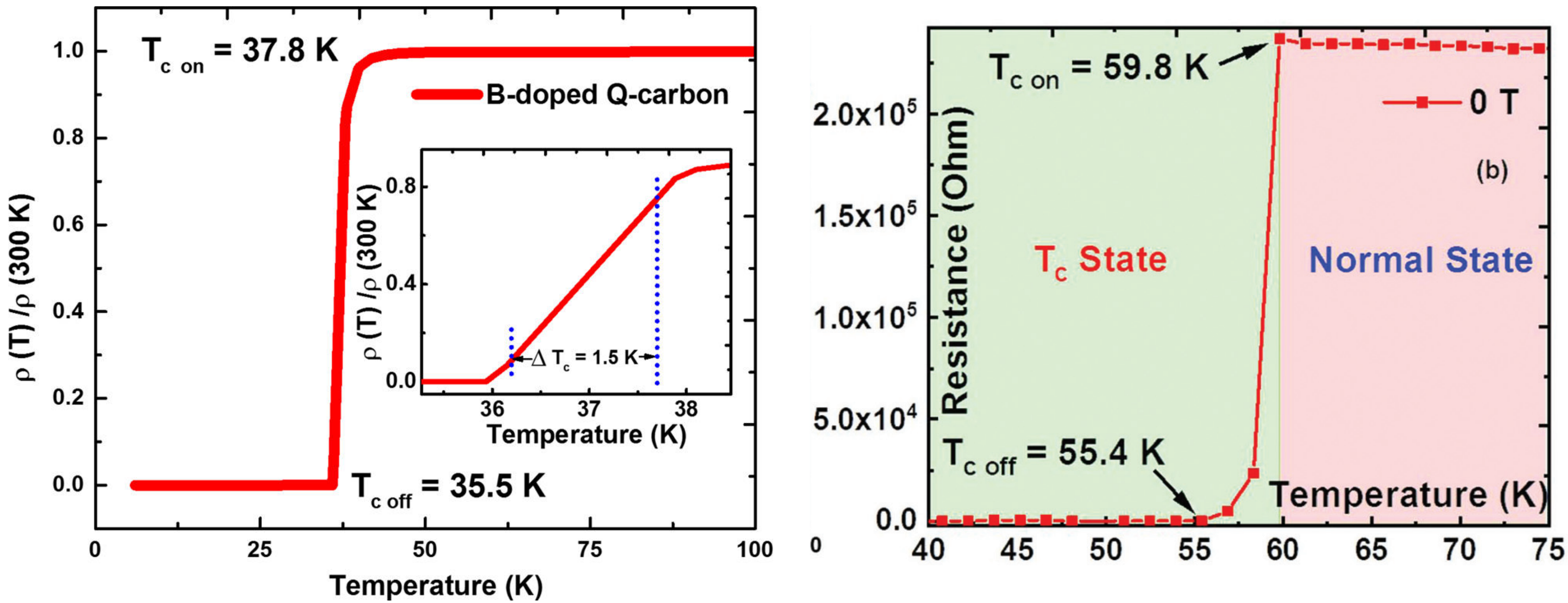


Scanning electron microscopy image

New form of amorphous carbon with 75-85 % of *sp*^{3}-hybridized carbon atoms

J. Narayan and A. Bhaumik, J. Appl. Phys. **118**, 215303 (2015)

Superconductivity in B-doped Q-carbon

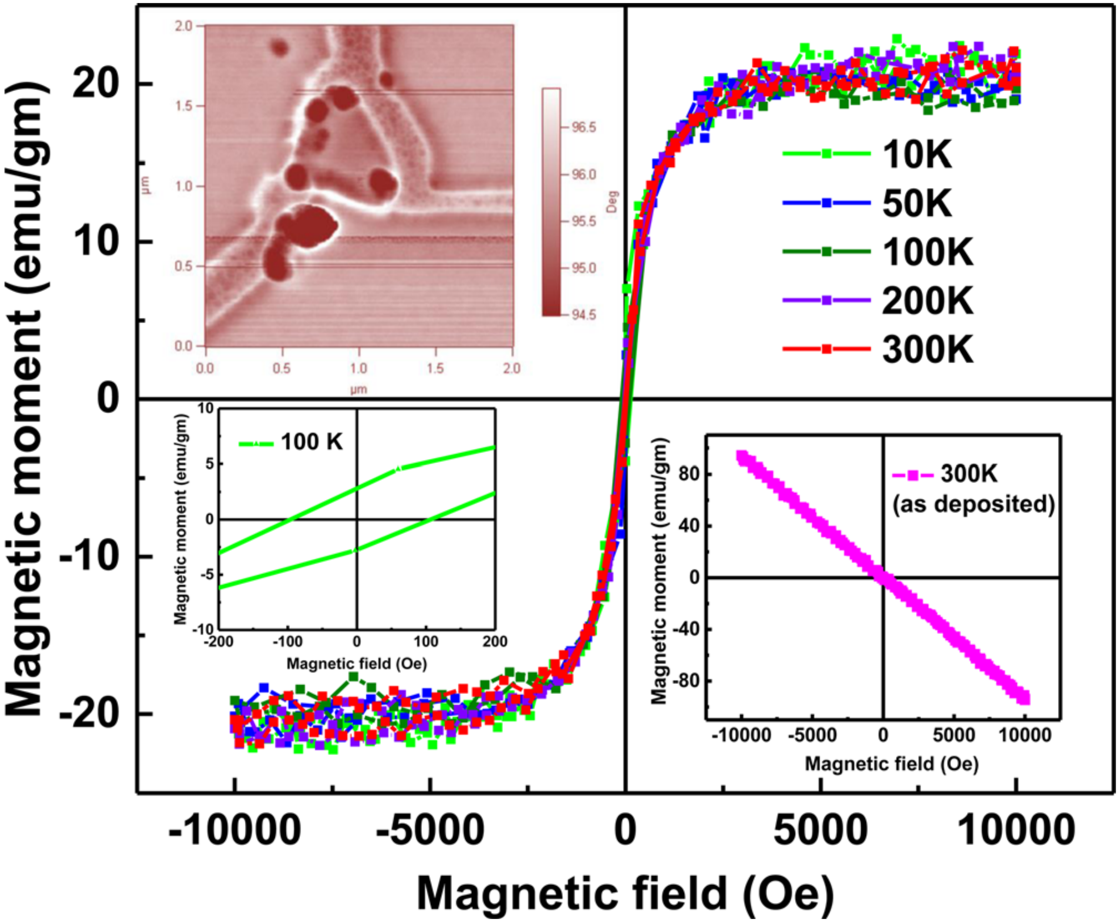


Temperature dependence of resistivity

- T_c of 36 (55) K when 17 (27) % boron doped
- Higher than T_c of B-doped diamond (11 K) or nanotubes (19 K)
- Highest T_c in carbon materials

A. Bhaumik, et al., ACS Nano **11**, 5351 (2017).
A. Bhaumik and J. Narayan, Nanoscale (2019)

Magnetic properties of Q-carbon



Ferromagnetism (0.4 μ_B/atom) at room temperature unusual in carbon materials

J. Narayan and A. Bhaumik, J. Appl. Phys. **118**, 215303 (2015)

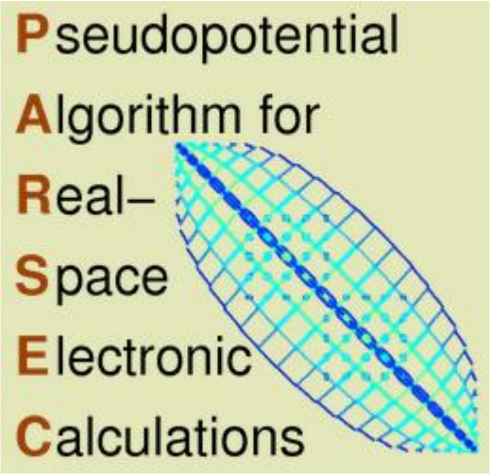
Purpose of research

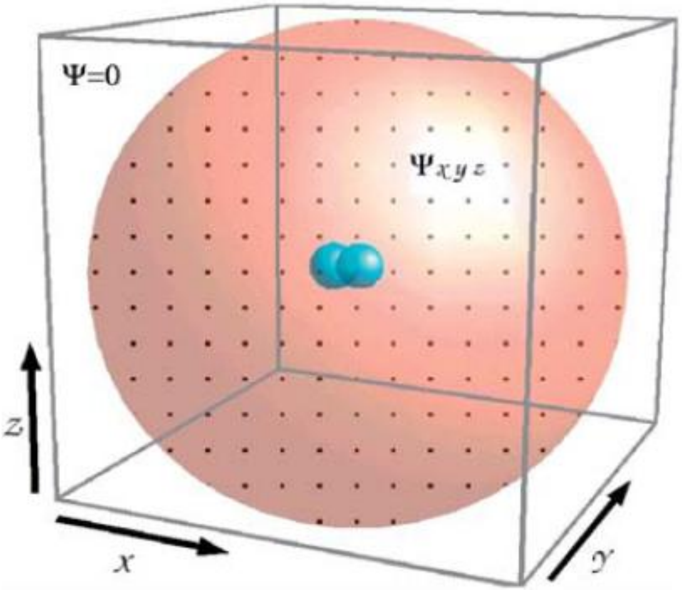
Investigate magnetism and
superconductivity in amorphous carbon

⬇

Understand interesting physical properties of Q-carbon
(with unknown amorphous structure)

Realspace pseudopotential DFT code PARSEC

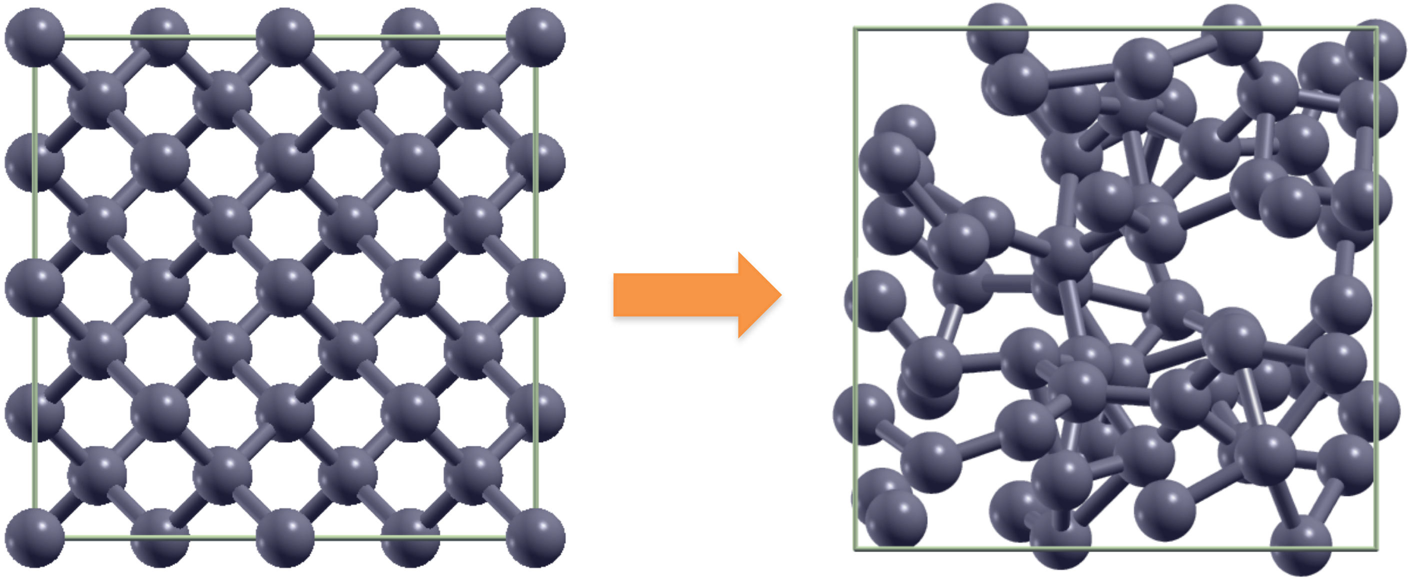




- Solve Kohn-Sham equations on realspace grid points without explicit basis function
  - Grid spacing as a convergence parameter
- Less global communication
- Applied to systems with ~20k atoms

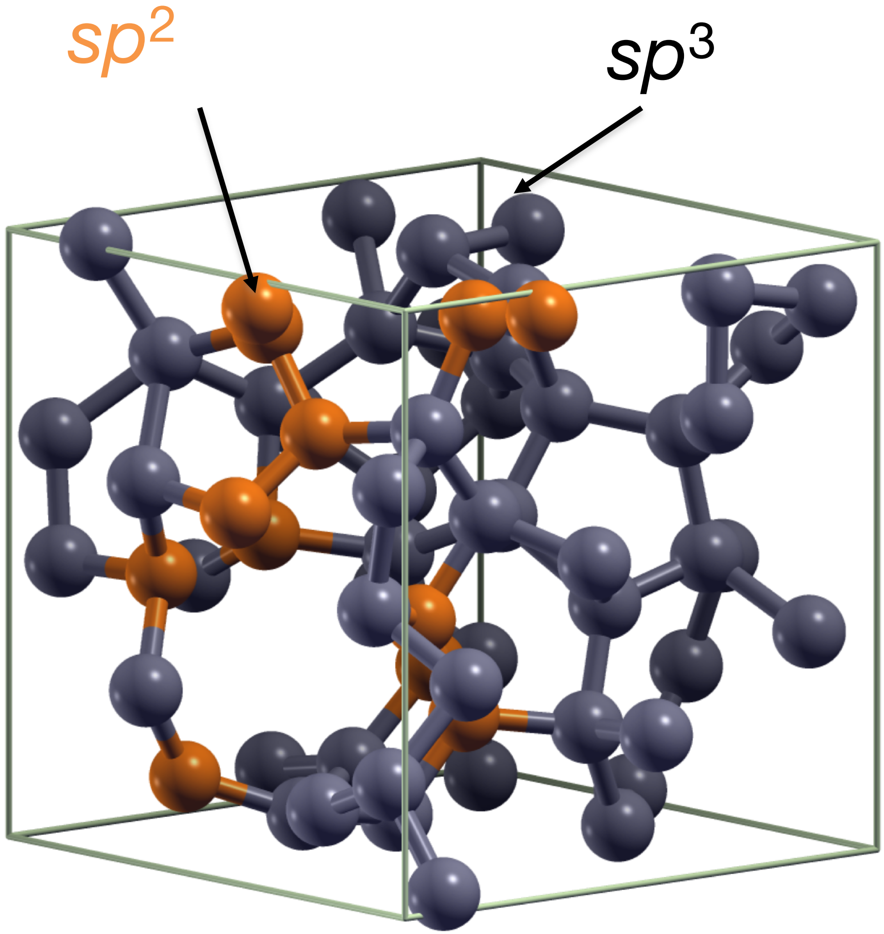
Zhou, Saad, Tiago, and Chelikowsky, PRE **74**, 066704 (2006)

Generating amorphous structure

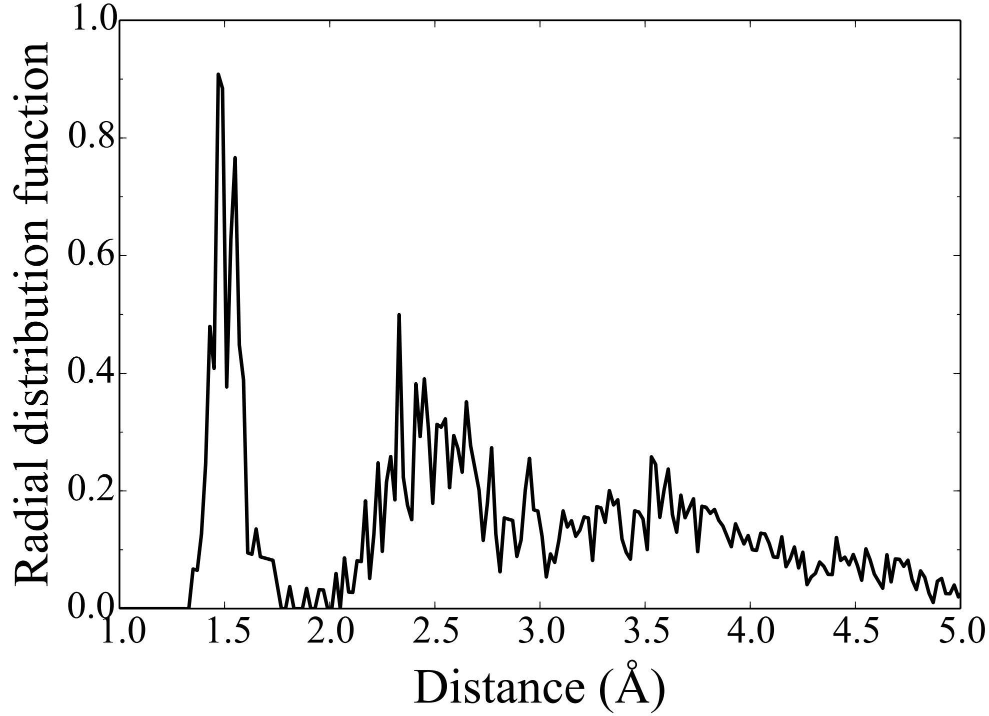


- Molecular dynamics simulation using PARSEC
  - Simulating melting process
- NVT ensemble molecular dynamics
  - Langevin thermostat
  - Obtain randomized (liquid-like) atomic coordinates
- Relax (quench) the structure

Undoped amorphous carbon



Structure (3.4 g/cm^3)



Radial distribution function

Outline

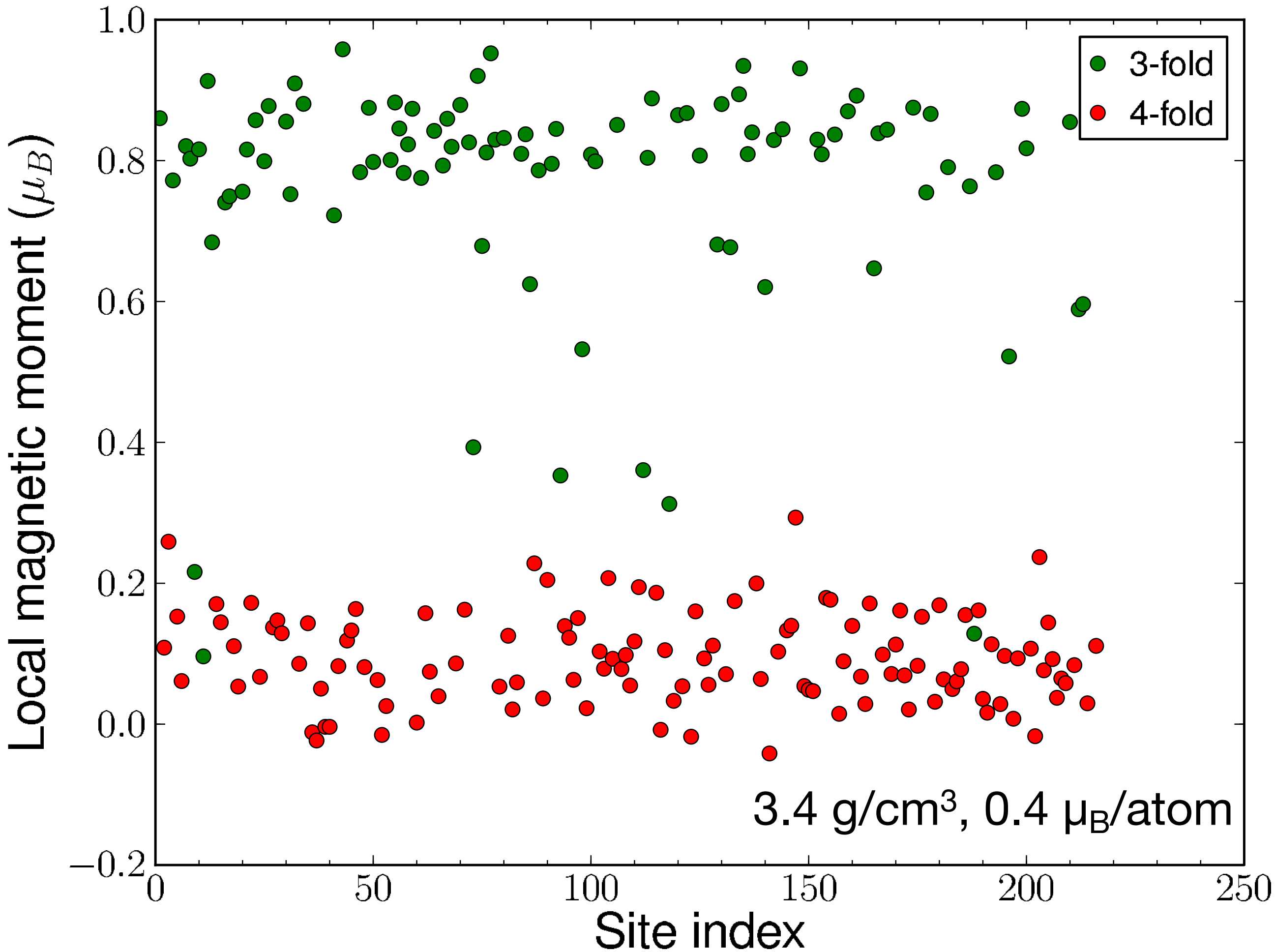
- Magnetism in amorphous carbon
- Superconductivity in B-doped amorphous carbon

Computational method (magnetism)

- 216-atoms supercell
- Different mass densities from 2.6 to 3.4 g/cm^3
- Optimize structure under fixed magnetization for the study of magnetism
  - Imposing two different Fermi energies for two orientations of electron spins
  - 0 to 0.4 μ_B/atom (experimental value)

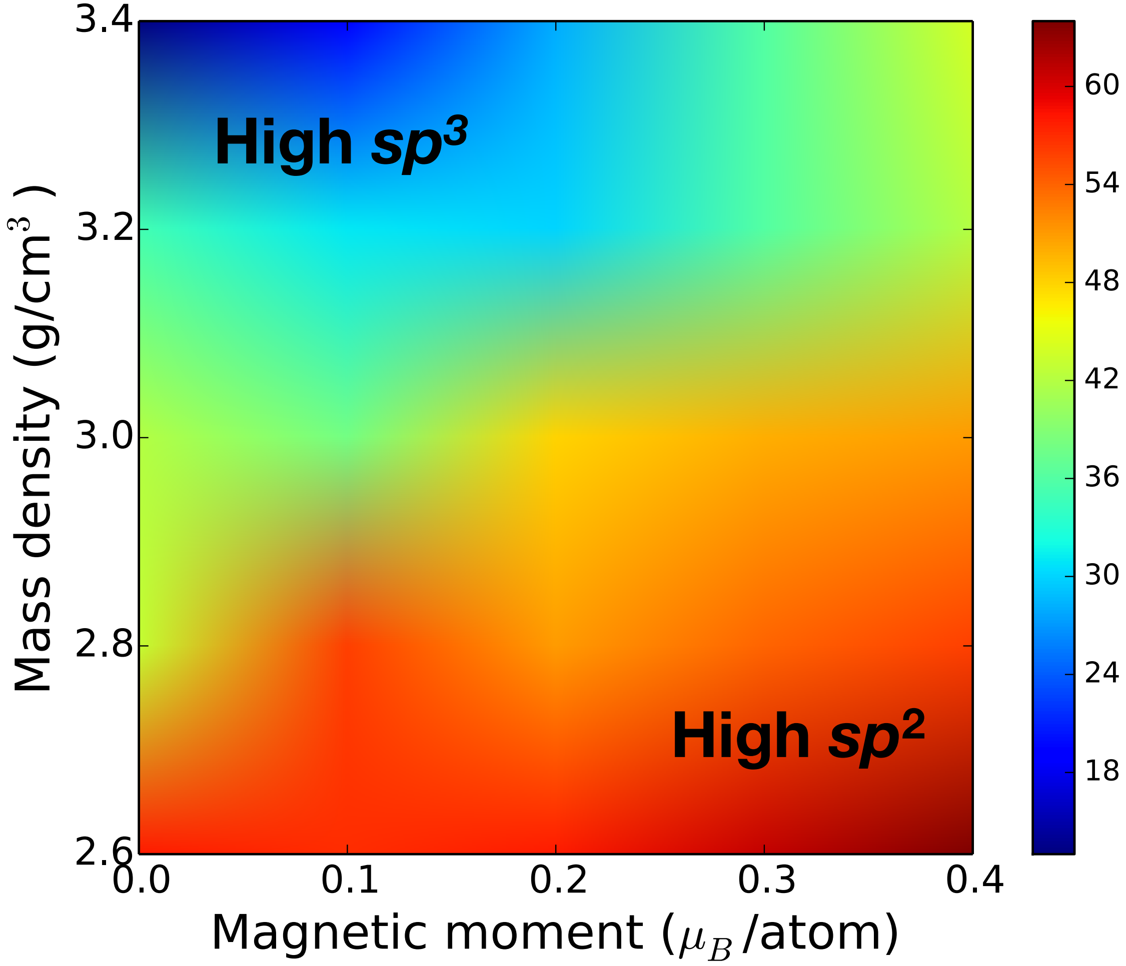
Study structural and energetic properties as a function of mass density and fixed magnetization

Distribution of magnetic moments



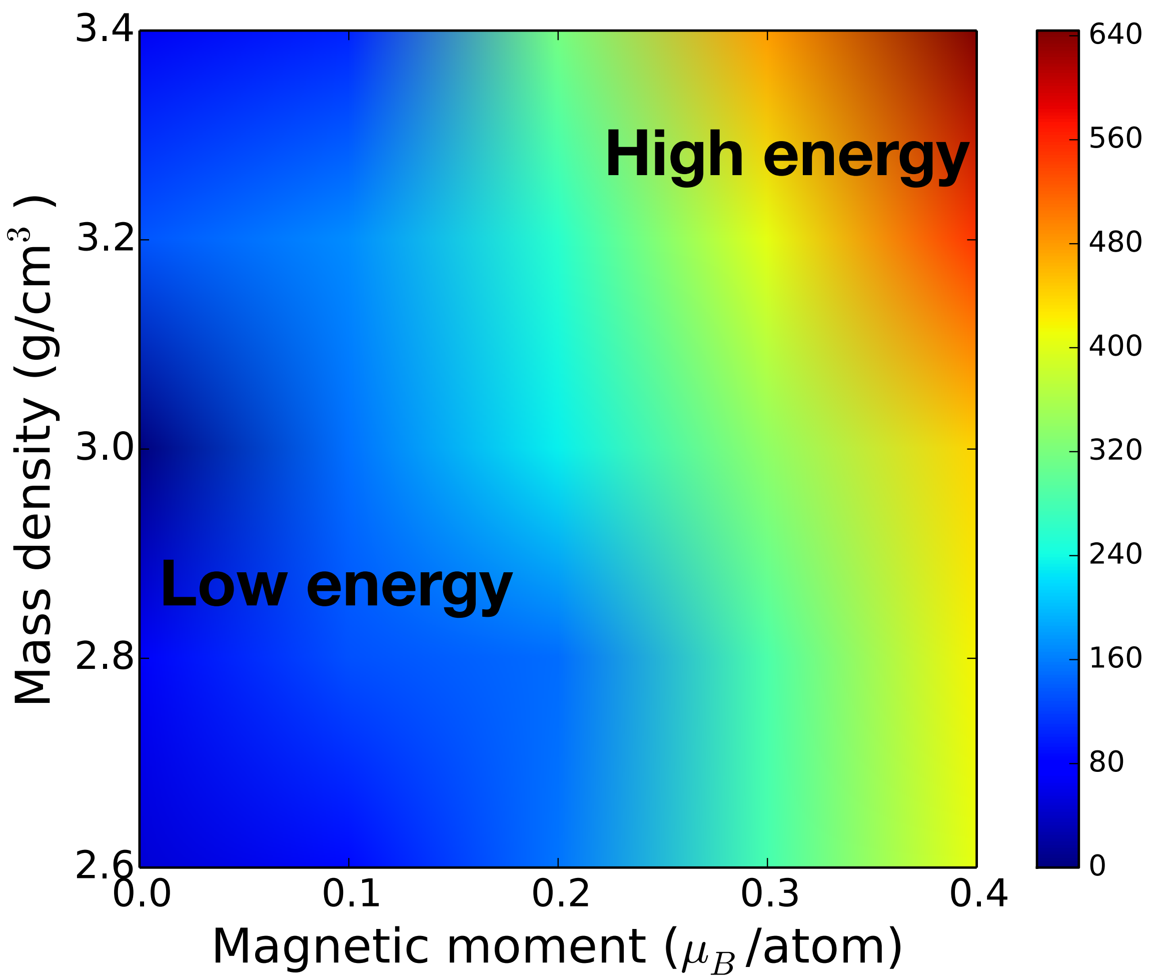
- Magnetic moments are mostly at *sp*^{2} hybridized (3-fold coordinated) carbon sites
- Unpaired electrons from *sp*^{2} hybridized atoms

Proportion of *sp*^{2} hybridized atoms



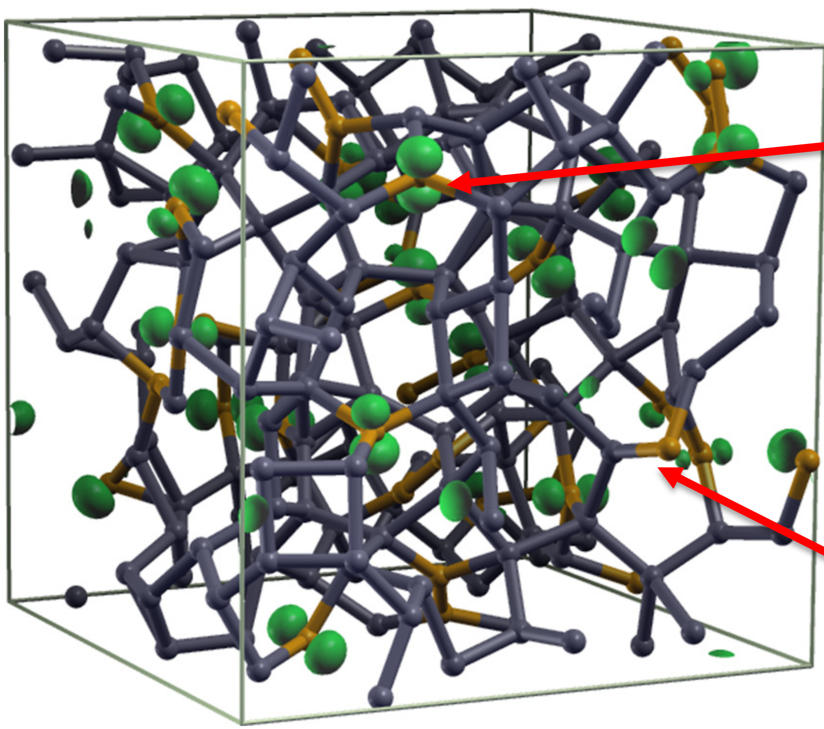
- High *sp*^{3} proportion in high density cases
- High *sp*^{2} ratio is necessary for high magnetization

Total energy (meV/atom)

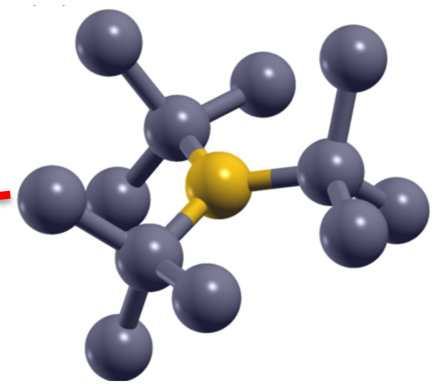


- High energy in structure with high magnetic moment
- Experimental magnetization (0.4 μ_B/atom) yields high energy more than 400 meV/atom

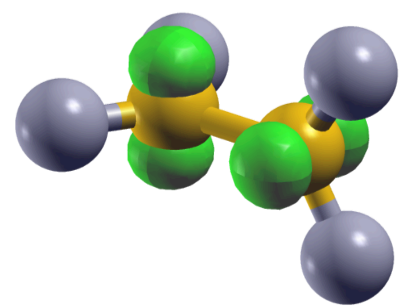
Two typical local geometries



Spin charge density
(3.4 g/cm^3, 0.1 μ_B/atom)



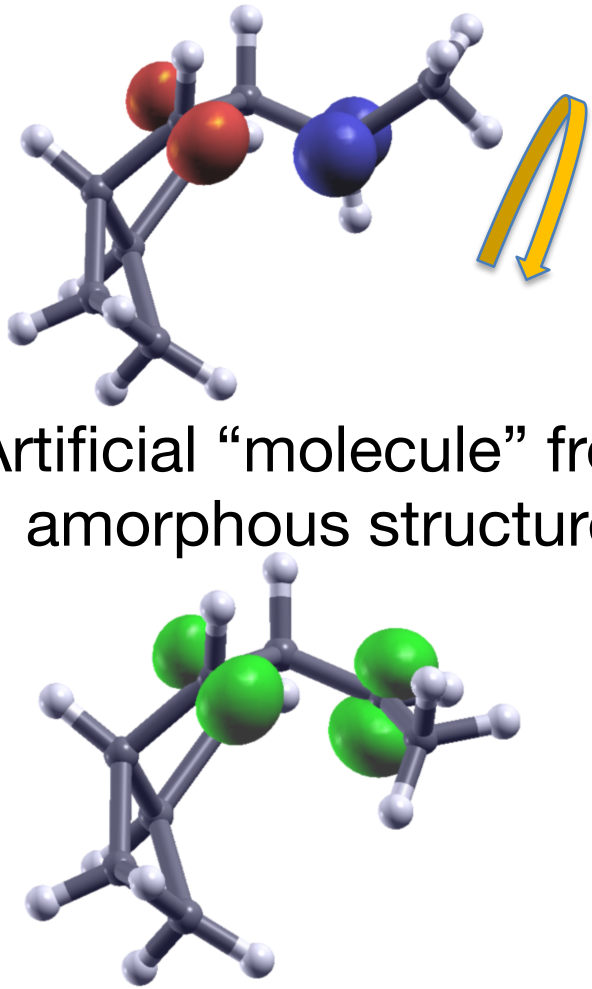
sp^2 atom surrounded by *sp*^{3} atoms



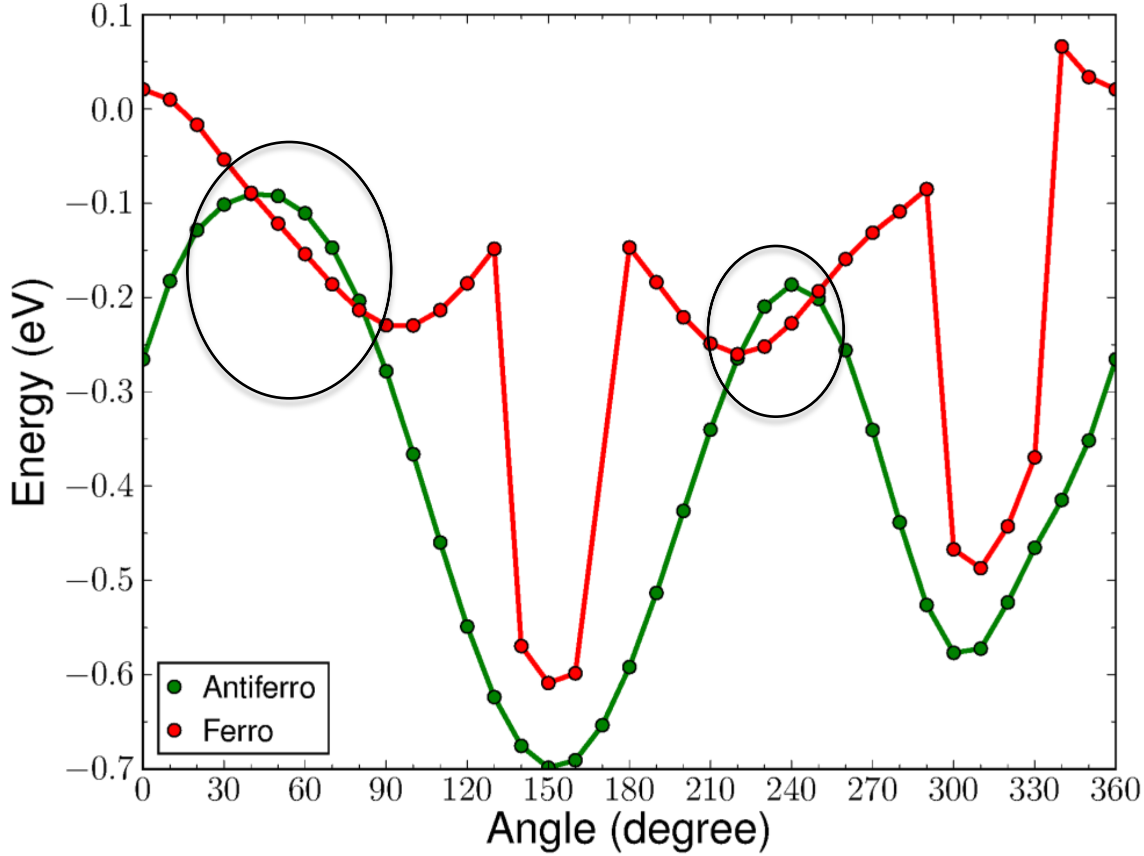
Two *sp*^{2} atoms bonded but rotated by 90°

- 0.05 μ_B/atom remains after releasing constraint
- Magnetization is possible but smaller than experimental value

Energy comparison in “molecule”



Artificial “molecule” from amorphous structure



- Total energy depends on the relative angle of *p* orbital
- Lower energy in the spin-parallel case

Summary

- Magnetism in amorphous carbon
  - Importance of *sp*^{2}-hybridized atoms
  - High energy in experimental magnetization
  - Small magnetization is possible
- Superconductivity in B-doped amorphous carbon

Y. Sakai, J. R. Chelikowsky, and M. L. Cohen, Phys. Rev. Mater. **2**, 074403 (2018)

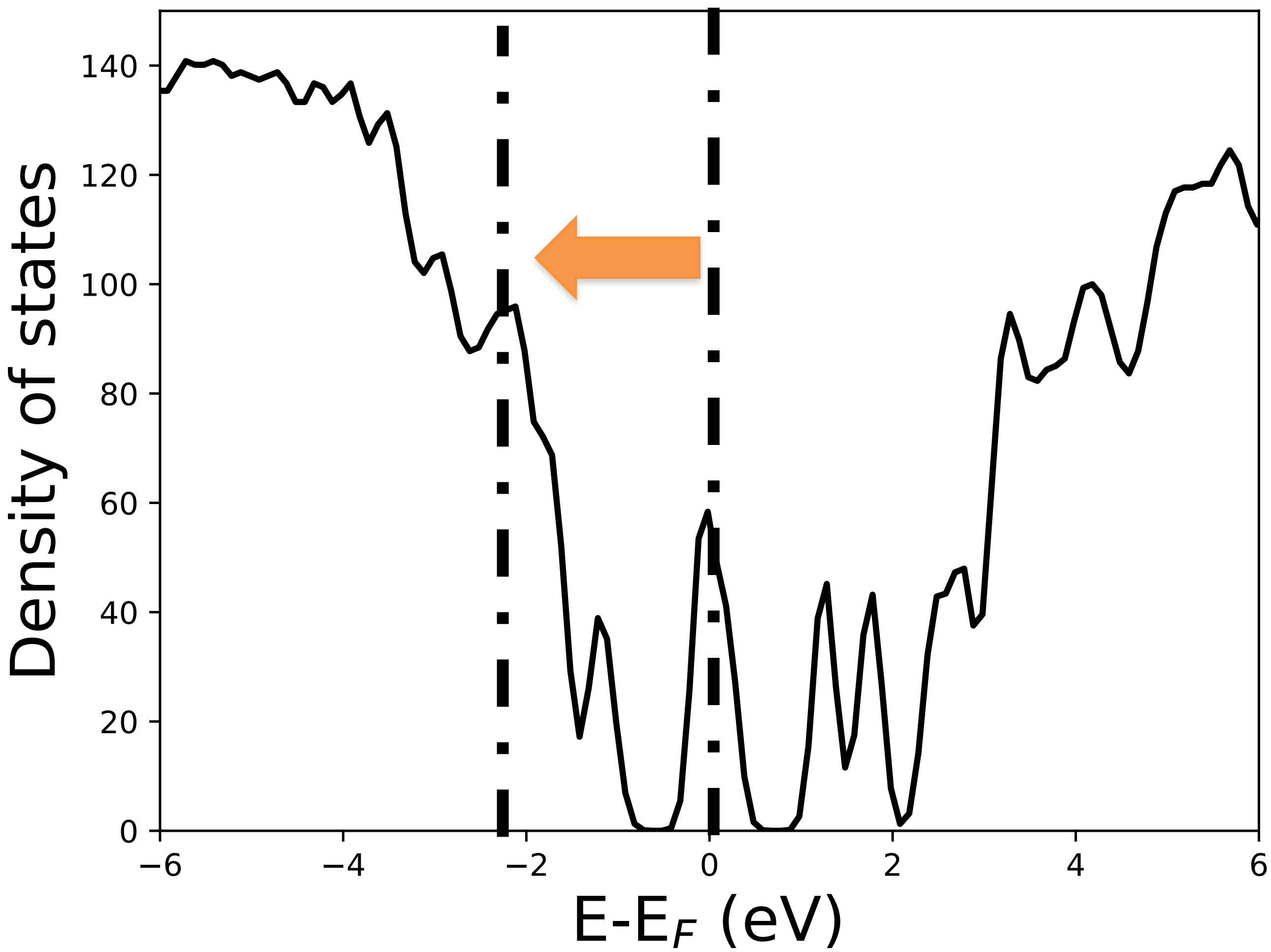
Computational method (superconductivity)

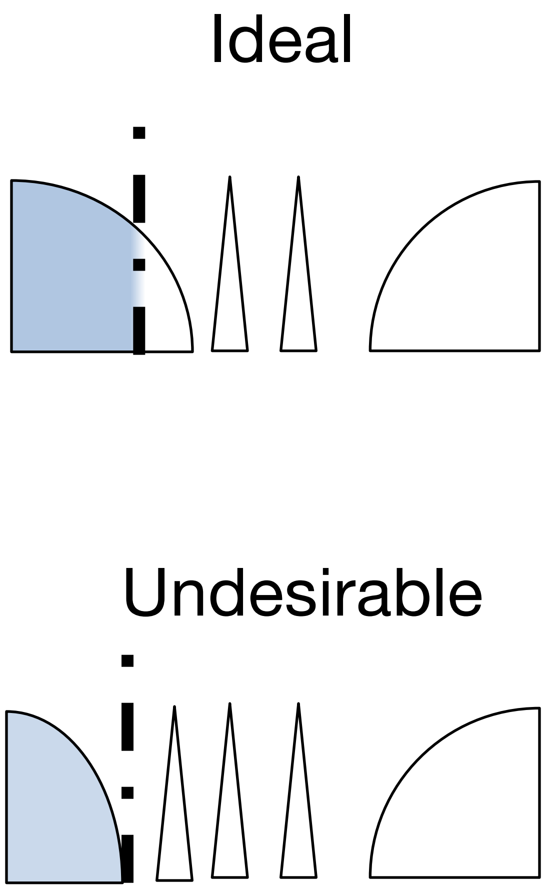
- 64-atoms supercell
- Up to 12.5 % boron doping (8 of 64 atoms)
- Substitutional B doping one by one
- Density functional perturbation theory for phonon modes and electron-phonon coupling constant
- Allen-Dynes equation for T_c estimation (μ^* of 0.12)

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

QUANTUMESPRESSO

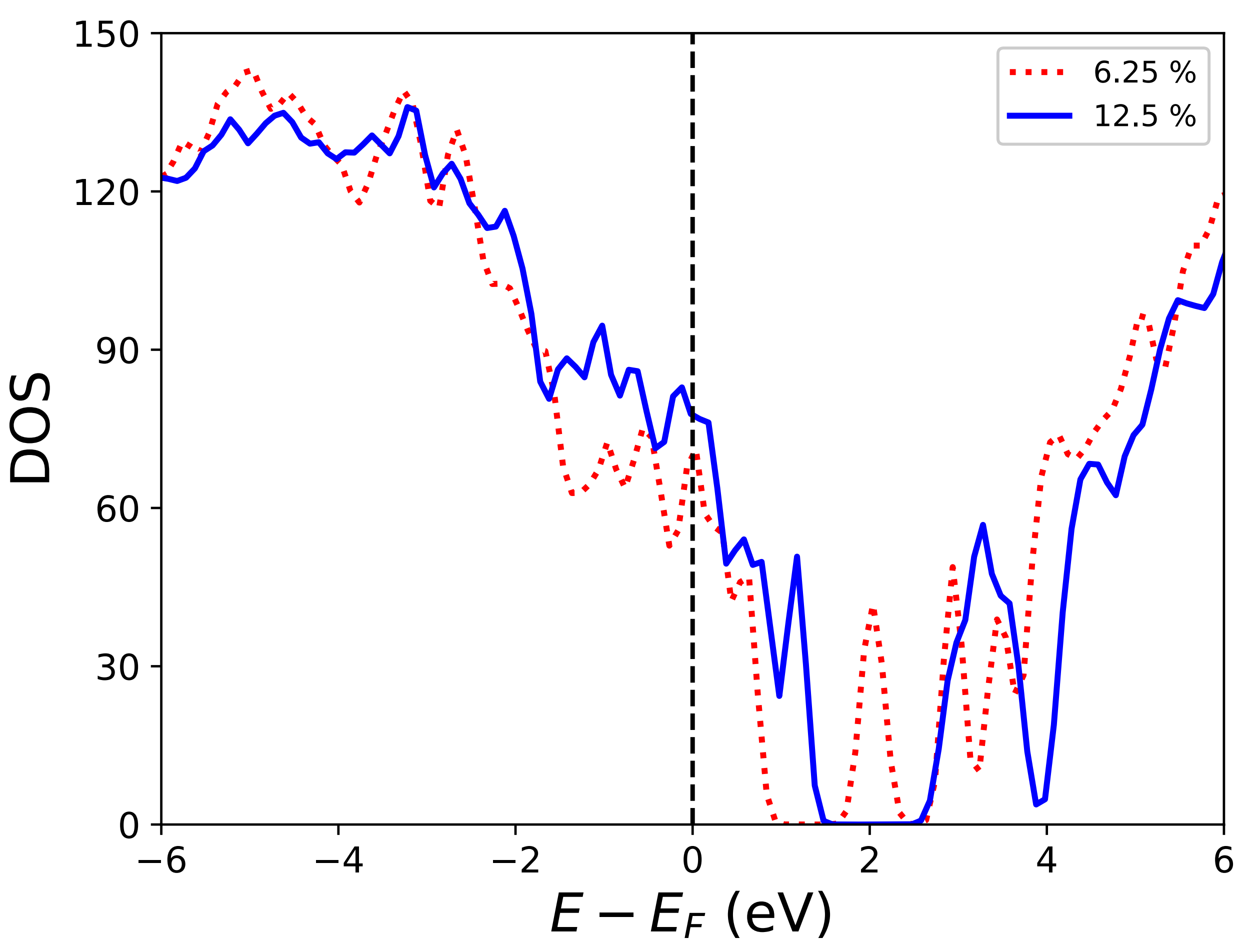
Engineering electronic density of states





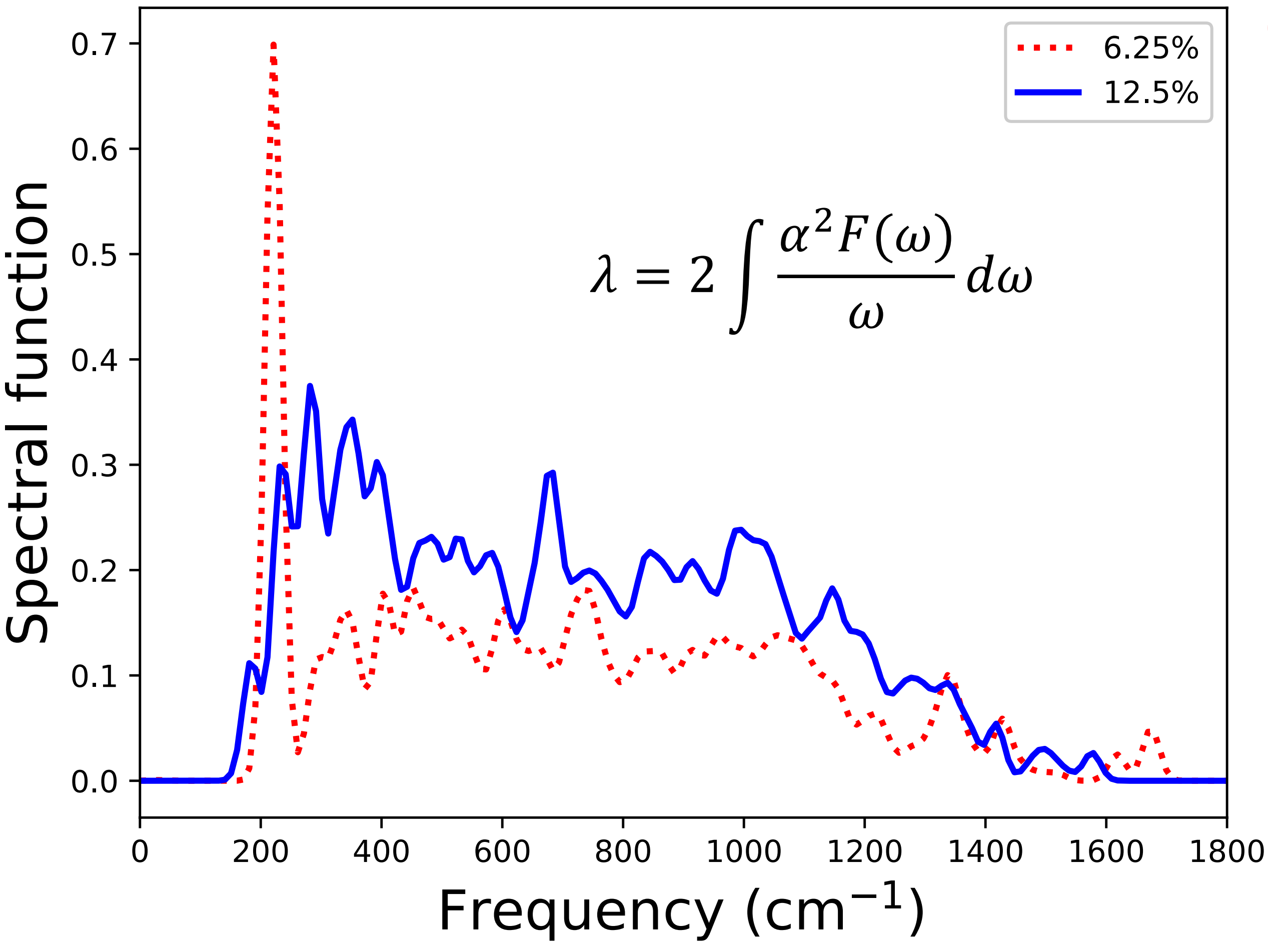
By doping boron atoms, shift the Fermi energy toward valence band without creating localized (deep) impurity states

Evolution of electronic structure



- One by one substitutional B doping to avoid creating localized defect levels
- Choose substitutional site not by low total energy, but electronic properties

Eliashberg spectral function



6.25 % doped

λ = 0.64

T_c = 13 K

12.5 % doped

λ = 0.89

T_c = 34 K

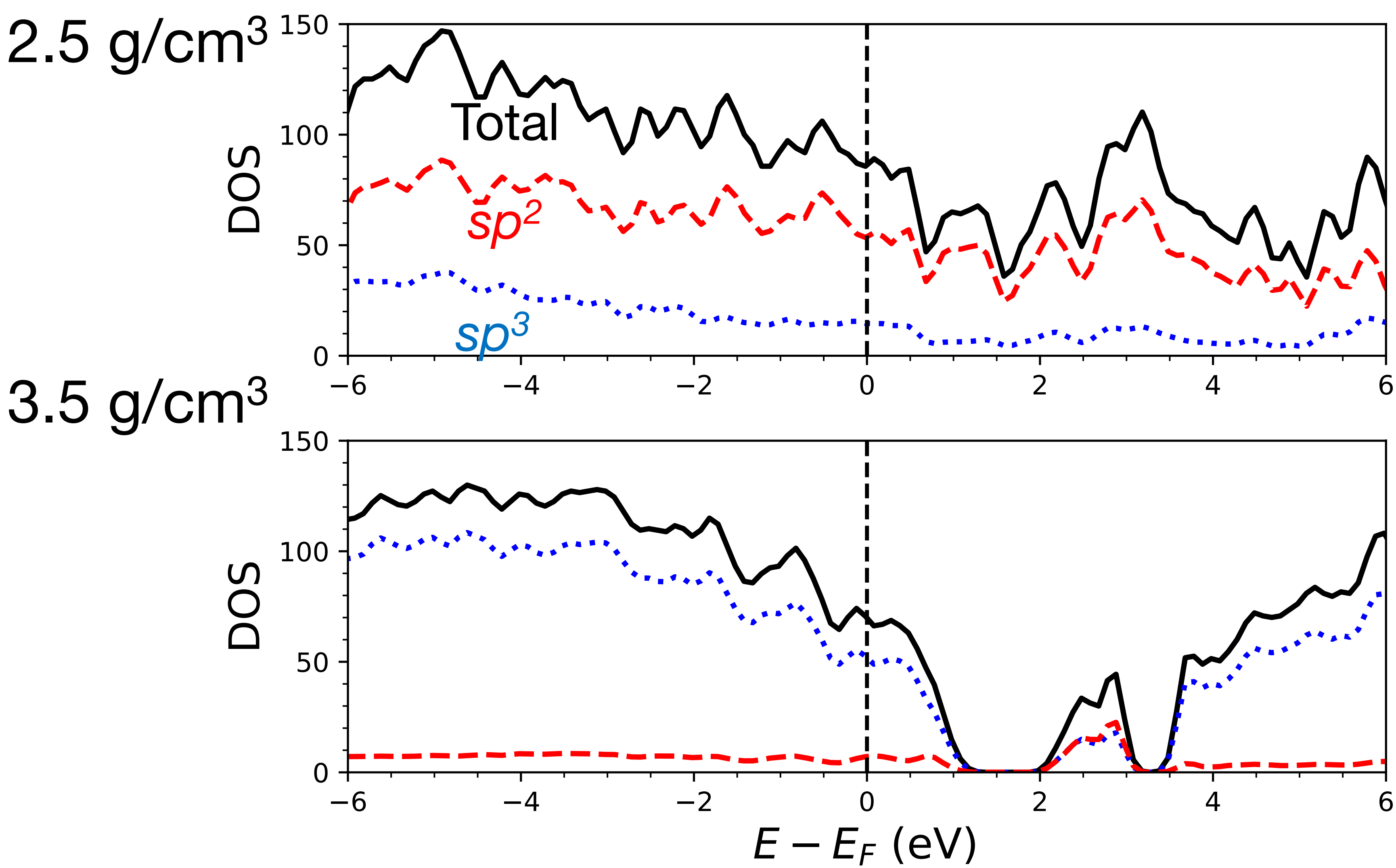
Experimental

17 % doped

T_c = 36 K

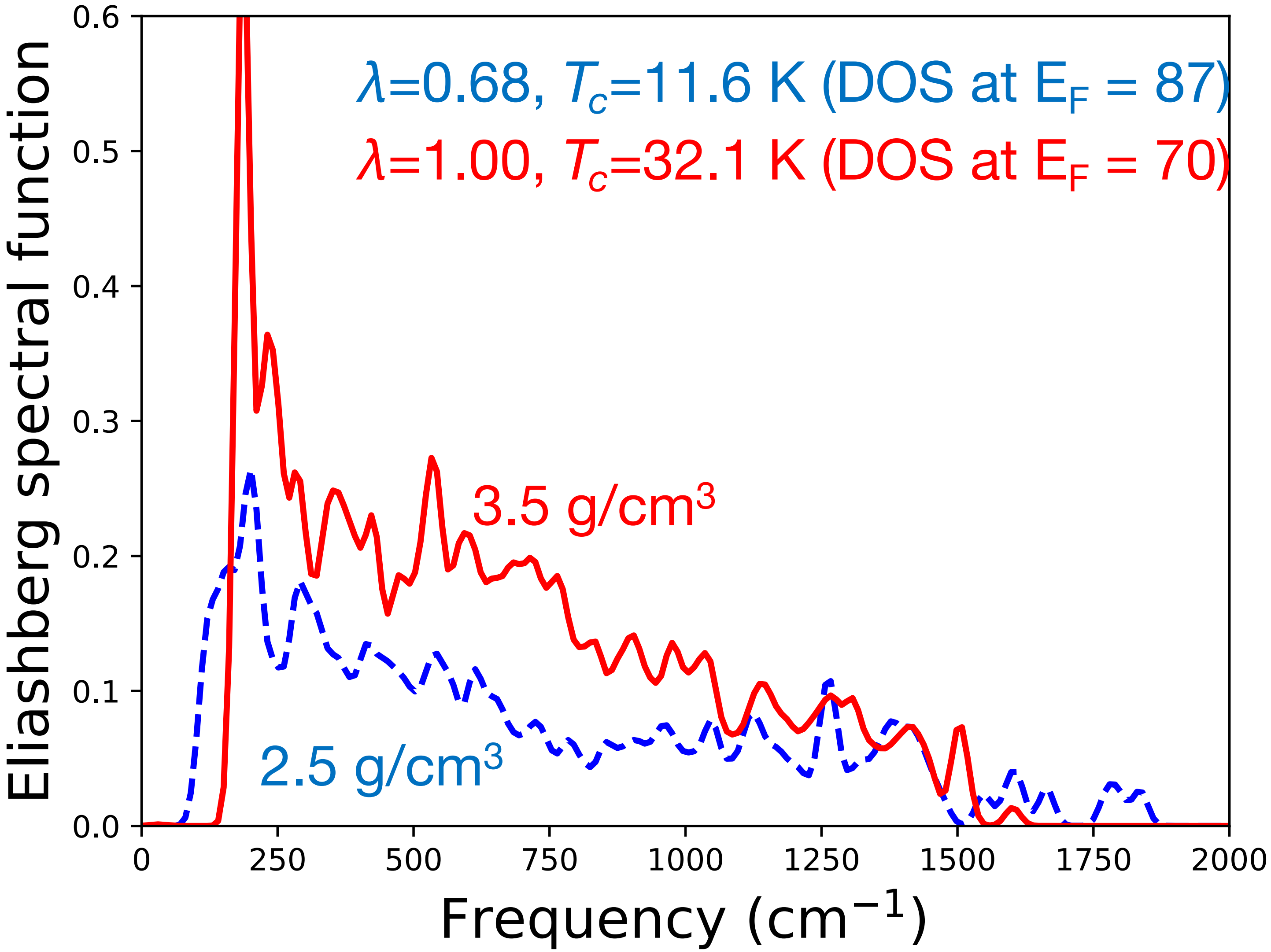
Increased electron-phonon coupling strength in entire frequency range upon B doping

Density of states in 12.5% B-doped case



DOS coming from different components depending on mass densities

Eliashberg spectral function



Importance of carrier contribution from *sp*^{3} atoms

Summary

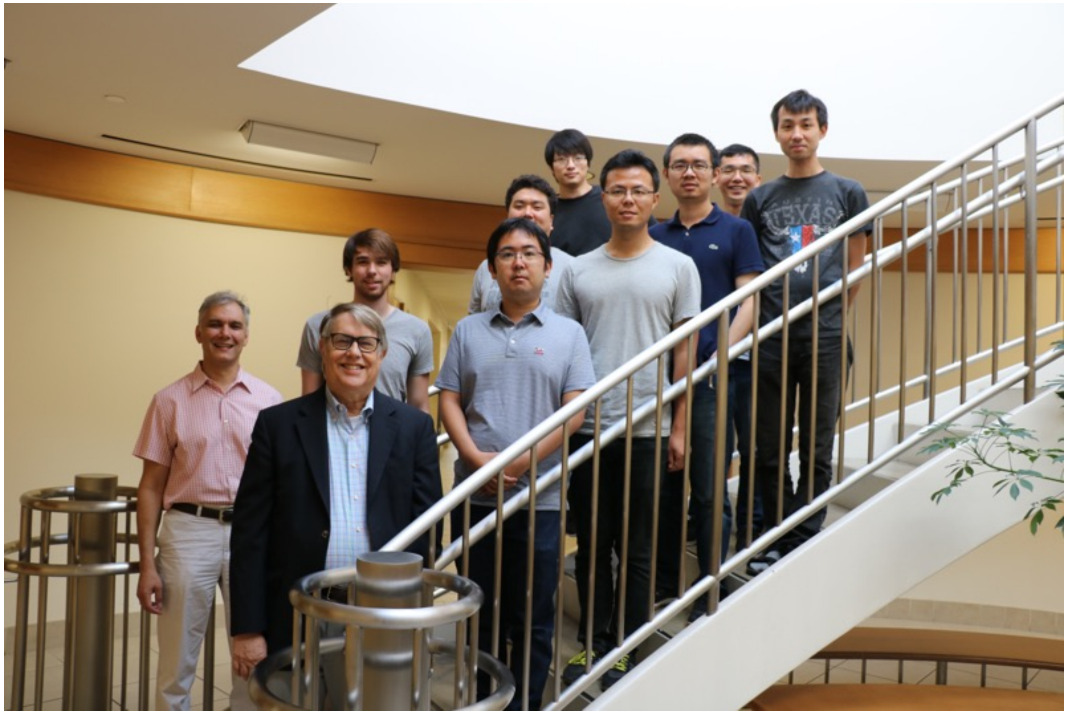
- Magnetism in amorphous carbon
  - Importance of sp^2-hybridized atoms
  - High energy in experimental magnetization
  - Small magnetization is possible
- Superconductivity in B-doped amorphous carbon
  - sp^3-hybridized atoms are more important
  - Not inconsistent with experimental studies

Atomic coordination plays an important role

Y. Sakai, J. R. Chelikowsky, and M. L. Cohen, Phys. Rev. B **97**, 054501 (2018)
Y. Sakai, J. R. Chelikowsky, and M. L. Cohen, Phys. Rev. Mater. **2**, 074403 (2018)

Acknowledgements

Professor Marvin L. Cohen
(UC Berkeley)



Professor James R. Chelikowsky
and Chelikowsky group members
(UT Austin)

Acknowledgements

NERSC
National Energy Research Scientific Computing Center

U.S. DEPARTMENT OF ENERGY | Office of Science

XSEDE
Extreme Science and Engineering Discovery Environment

TACC
TEXAS ADVANCED COMPUTING CENTER

The University of Texas at Austin
Oden Institute for Computational Engineering and Sciences