Project Title:

Theoretical prediction of new graphene allotropes

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1. Background and purpose of the project, relationship of the project with other projects

The experimental realization of graphene has stimulated tremendous research activities on this fascinating 2D material. This one-atom-thick carbon network exhibits extraordinary mechanical and physical properties and promises great application potentials in many areas such as energy store, nanoelectronics, electrodes material and functional membranes. Therefore, graphene is considered as a revolutionary material to future industry. These various applications, however, require versatile and controllable properties. Thus, many graphene allotropes (GAs) have been proposed to expand the family of 2D carbon-based material and to enlarge the range of their Applications.

The current project aims to theoretically explore new GAs by first-principles calculations. Then we will investigate their thermal and electronic properties. This research will certainly enlarge the known family of GAs and explore some new features. These new GAs are expected to be useful for future industry.

2. Specific usage status of the system and calculation method

I got my RICC account on Jan. 20th, 2014. During this period nearly 5000 CPU hours has been used.

First-principles calculations are performed using Vienna Ab-initio Simulation Package and Quantum Espresso codes. We also employ phonopy code for studying thermal properties of GAs.

3. Result

We have calculated the Helmholtz free energy as a function of temperature T for all interested GAs[*]. In the range from 0K to around 830K, our calculation confirm that graphene is the most stable one. But when the temperature goes above 830K, a supergraphene structure (2-30) has the lowest energy. Further when temperature goes above 1500K, another structure (graphdiyne) has the lowest energy. This may indicate thermal phase transitions from graphene to supergraphene and graphdiyne at high temperature.

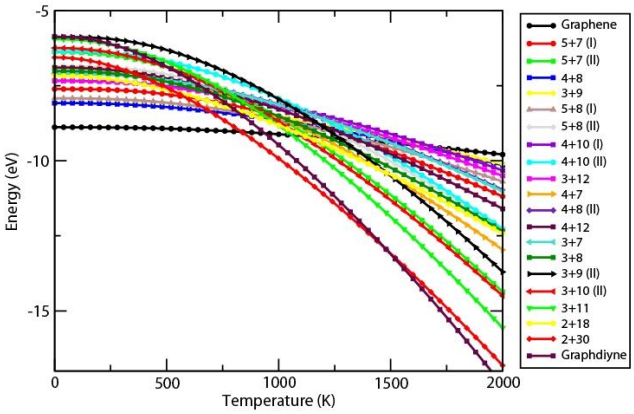

Fig 1. Helmholtz free energy as a function of temperature for GAs.

One hexagonal structure composed of 3+11 membered rings are of particular interests. Its electronic band structure display a linear dispersion at K point which mimics the case in pristine graphene. This means the low energy quasiparticles are Dirac Fermions described by Dirac equation. The fermi velocity is estimated to be around 3×10^5 m/s, which is about 1/3 of that of graphene .

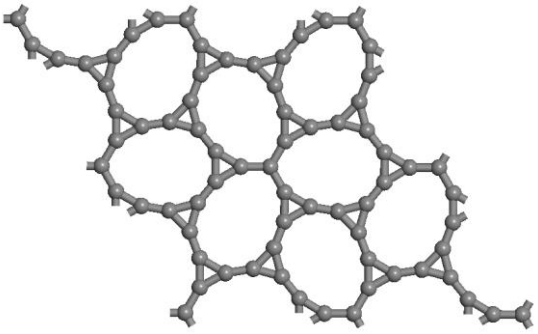

Fig 2. One GA structure composed of 3+11 membered rings.

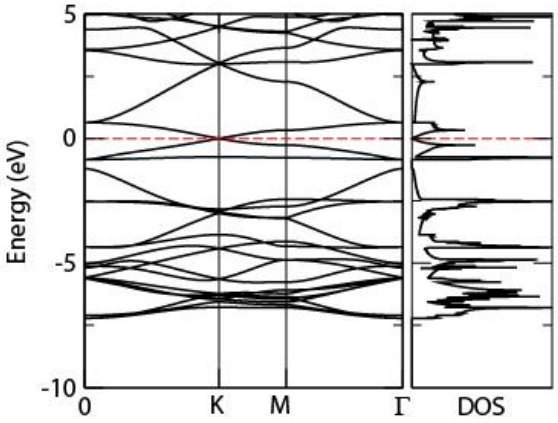

Fig 3. The electronic band structure and DOS for 3+11 membered rings.

The phonon and Raman spectra of this new structure is also calculated. The absent of imaginary mode on the phonon spectra confirm its dynamical stability and the Ramam spectra provides evidence for further experimental synthesis.

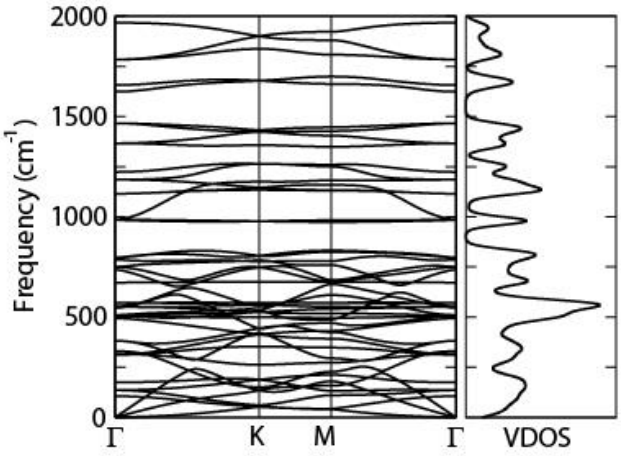

Fig 4. The phonon spectra and vibrational DOS for 3+11 membered rings.

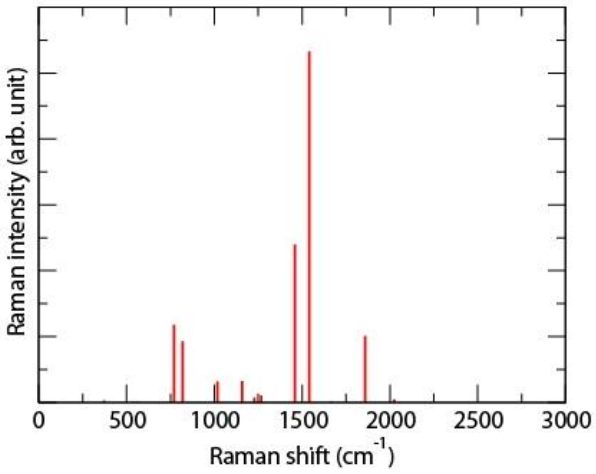

Fig 5. The Raman shift for 3+11 membered rings.

4. Conclusion

We have constructed a series of GAs from pristine graphene based on two general schemes. The structural and intrinsic properties of these structures have also been investigated.

Our study demonstrate the power of these simple schemes and dig a tiny hole to peep the infinite set of GAs. Our rule to construct GAs is keeping the geometries simple, which can be realized from two aspects: the least cycle species and the least atom number in the cell. However, this is not an energetically favored route. A preferable route would be constructing geometries with hexagons. In that cases, amount of GAs with intriguing properties could be theoretically expected.

5. Schedule and prospect for the future

Among all the constructed structures, some pieces of the puzzle are missing. For example, we have GAs composed of 5+7, 4+8, 3+9, 5+8, 4+10, 3+12, 5+7, membered rings and many others. But come combination such as 4+9, 4+11 are missing. Finding them would complete this subset of GAs. Also, in previous research, we considered only the

geometrically simple structures, which turn out to be energetically unfavorable. More structures with hexagons to lower the formation energies could also be expected.

[*] Partial results are obtained by using RICC.