

Predicting experimentally stable allotropes: Instability of penta-graphene

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In recent years, a plethora of theoretical carbon allotropes have been proposed, none of which has been experimentally isolated. We discuss here criteria that should be met for a new phase to be potentially experimentally viable. We take as examples Haeckelites, 2D networks of sp^2 -carbon-containing pentagons and heptagons, and “penta-graphene,” consisting of a layer of pentagons constructed from a mixture of sp^2 - and sp^3 -coordinated carbon atoms. In 2D projection appearing as the “Cairo pattern,” penta-graphene is elegant and aesthetically pleasing. However, we dispute the author’s claims of its potential stability and experimental relevance.

nanocarbon | modeling | allotropes | penta-graphene | Haeckelite

One of the joys of carbon research is the huge flexibility of carbon bonding (1–4), resulting in many varied allotropes that have already been experimentally identified. Computational modeling opens the floor to predicting many more, and tools such as graph theory (5) and evolutionary algorithms (6) allow systematic exploration of potential bonding networks. New computationally proposed phases are typically identified as metastable via positive phonon modes, and sometimes via molecular-dynamics (MD) simulations showing lattice coherence at experimental operating temperatures. However, there are common criteria beyond these two tests that link those allotropes that have been experimentally isolated.

First, they occupy deep potential wells in the surrounding energetic landscape. Additionally, the surrounding energy wells are all higher in energy, “funneling” toward the stable structural form. Finally, barriers to subsequent conversion to alternative structures are typically high. Buckminsterfullerene, I_h -C₆₀, is a good example. The disconnectivity graph for C₆₀ connecting the 1,812 isomers with pentagonal and hexagonal faces via branches whose height indicates the transformation barrier has a “willow tree pattern,” with a gentle funnel running toward the stable I_h -C₆₀ isomer (7) (Fig. 1A). The relatively high barriers are accessible during high-temperature growth and alternatively can be catalyzed via the presence of impurities or carbon interstitial atoms (8–10).

In contrast, attempts to experimentally isolate higher-order boron fullerenes have been largely unsuccessful to date. For the proposed fullerene B₈₀, this can be understood because the energy landscape was shown to feature many closely related isomers with similar (and sometimes lower) energies (11). In contrast, calculations for B₄₀, for which there are first experimental indications (12), show a single (D_{2d} , 1A1) cage isomer, energetically well separated from alternative isomers (Fig. 1B). This behavior is consistent with the rules discussed above.

We apply here a similar analysis for experimental viability to other proposed phases, starting with “penta-graphene,” a 2D carbon allotrope proposed by Zhang et al. (4). The structure can be viewed as a series of out-of-plane distorted ethylene units connected via tetrahedral sp^3 -carbon linkers. The result is a corrugated layer that in projection matches the “Cairo pattern” of distorted pentagons (Fig. 2A).

Results and Discussion

Thermodynamic Stability: Relative Energy. The first test of any new proposed structure is of its thermodynamic stability. Considering penta-graphene, although real phonon energies (positive eigenvalues from the Hessian matrix) indicate that it is at least a local structural minimum (4), its formation enthalpy shows that it is a very high-energy structure. We have performed a number of calculations on penta-graphene and structural derivatives, using density functional theory (DFT) (Methods). Penta-graphene is 0.761 eV per atom less stable than graphene. This is significantly less stable than amorphous carbons (0.16 eV) (13), most nanotubes, and I_h -C₆₀ (0.39 eV) (14), and places it in a similar energy range to experimentally unconfirmed isomers such as R3-carbon (15).

Transforming to Graphene. Second, penta-graphene is not the stable center of a “funnel” of isomeric structures, but instead forms part of an energetic funnel of structures centered on graphene. Fig. 2 shows an example sequence of bond rotations and bond breakages by which penta-graphene can be transformed directly to graphene. Each step is exothermic, but only if the unit cell vectors are allowed to geometrically relax along with all atoms. This does not appear to have been done in the original paper by Zhang et al. The unit cell area increases 19.6% from penta-graphene (25.96 Å²) to graphene (31.05 Å²). This is because the sp^3 bonding and corresponding nonplanarity in penta-graphene give it a relatively dense 2D projected basal plane compared with graphene. Constraining the unit cell dimensions to those of penta-graphene therefore energetically disadvantages planar sp^2 restructuring.

Significance

We describe criteria that should be applied when evaluating whether theoretically proposed carbon allotropes may be experimentally isolated. We discuss the importance of energetic isomeric “funnels” centered on a stable allotropic form, the role of defects in catalyzing structural transformations to lower energy isomers, and chemical stability. This is demonstrated with literature examples such as C60 and B80. We apply these criteria to a recently proposed carbon allotrope, penta-graphene, demonstrating with the aid of density functional calculations that it will not be experimentally attainable. A second example, Haeckelites, are unlikely to be experimentally achievable when neutral but may be stabilized through significant charge transfer. The principles discussed here are general and can be applied to any theoretically proposed materials.

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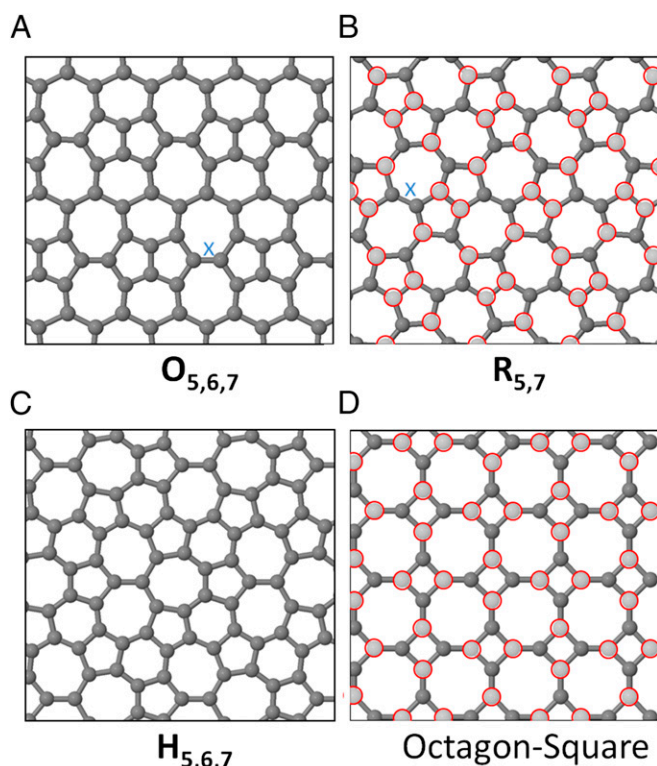


Fig. 3. Three Haeckelite structures. (A) Oblique $O_{5,6,7}$, (B) a rectangular $R_{5,7}$, and (C) hexagonal $H_{5,6,7}$ (nomenclature from ref. 2), and (D) octagon-square structure. In MC_2B_2 borocarbides, lighter carbon atoms marked with red circles are replaced with boron in (B) $M = Sc$ and (D) $M = Ce, Y, Ca, Ln$ (metal ions located above the center of heptagons and octagons, respectively). Bonds marked "x," when rotated, convert a 5–7–7–5 patch into four hexagons.

Chemical Stability and Oxidation. Although chemical stability is not strictly a criterion for experimental viability, it is nonetheless an important indicator. To examine potential environmental stability of penta-graphene, we calculated its reaction with O_2 . In the triplet state, O_2 oxidation of the surface is highly exothermic, releasing 2.24 eV per O_2 molecule, with a barrier to chemisorption of only 0.16 eV. Accounting for spin conversion to an eventual singlet state (surface crossing) releases a further 2.34 eV. Oxygen forms epoxides at the distorted localized surface $C=C$ bonds. Thus, penta-graphene would undergo highly exothermic spontaneous oxidation on the slightest exposure to air.

Haeckelites and Related sp^2 -Layered Structures. Our next example is the Haeckelites (1–3), a family of layered sp^2 -carbon structures constructed from pentagons, heptagons, and optionally hexagons. Despite extensive theoretical investigation since their first proposition nearly 20 y ago (1), these structures have never been unambiguously experimentally isolated.

Fig. 3 A–C shows three Haeckelite structures. In terms of thermodynamic stability, all three are less stable than graphene, oblique $O_{5,6,7}$ by 0.377 eV/C (Fig. 3A), rectangular $R_{5,7}$ by 0.244 eV/C (Fig. 3B), and hexagonal $H_{5,6,7}$ by 0.251 eV/C (Fig. 3C), although the energies relative to graphene are significantly lower than that of penta-graphene. Structures in Fig. 3A and Fig. 3B can both be converted to graphene via 90° bond rotations of the bonds labeled "X" in Fig. 3, and hence lie on the thermodynamic funnel terminating at graphene. As discussed previously, the bond rotation barrier can also be lowered through the presence of defects. The structure in Fig. 3C cannot reconstruct via bond rotations to graphene but, if produced through a sequential edge growth process, could still be replaced by thermodynamically preferable graphene.

Thus, from the arguments above, we would not expect these structures to be experimentally viable.

If the system is charged, however, the thermodynamic picture changes. Fig. 4 shows the energy of Haeckelite- $H_{5,6,7}$ and penta-graphene relative to graphene at different charge states. Although penta-graphene becomes increasingly unstable with charging, the Haeckelites become increasingly stable, and for high charge accumulation, Haeckelite- $H_{5,6,7}$ becomes more stable than graphene. The effect is even more marked for the octahedral-square structure (Fig. 3D), which shifts from 0.57 eV/C less stable than neutral graphene, to comparable energy when charged 0.25e/C.

Structural analogs that have indeed been experimentally isolated are metal borocarbides MB_2C_2 , where $M = Mg, Sc, Ce, Ca, Y, La,$ and Lu (17, 18). These are layered B_2C_2 structures intercalated with metal ions (Fig. 3). Hexagon, pentagon-heptagon (Fig. 3B), and octagon-square lattices (Fig. 3D) have been experimentally identified depending on the metal cation (18). Among these phases, MgB_2C_2 exhibits a stable hexagonal graphene-like lattice. This can be understood because the Mg^{2+} cation donates sufficient electrons to compensate the electron deficiency of boron with respect to carbon, i.e., two electrons for each B_2C_2 motif. In contrast, M^{3+} cations ($La^{3+}, Ce^{3+}, Y^{3+}, Sc^{3+}, Lu^{3+}$) donate one extra electron compared with Mg^{2+} , leading to an extra charge of $0.25e$ per lattice atom. These cations form nonhexagonal borocarbide lattices, in agreement with our analysis of thermal stability vs. charge state for carbon sheets, where at $0.25e$ per carbon atom Haeckelite and octahedron-square lattices become thermodynamically competitive with graphene. [The exception is Ca^{2+} , which also favors a square-octahedral lattice; however, this is because of additional effects (ionic radius).]

Thus, although the calculations suggest that isolated Haeckelites are unlikely to be formed experimentally, in situations of heavy doping, such as metal-ion intercalation in layered crystals, or ion overlayers on surfaces, experimental isolation of Haeckelites may be possible.

Conclusions

The calculations presented here strongly suggest that penta-graphene will not be an experimentally achievable allotrope of carbon. Not only would penta-graphene be difficult to isolate from the plethora of alternative isomers with similar energies, it should rapidly restructure toward graphene in the presence of even a few catalytic impurities. Even were it to form, it would not

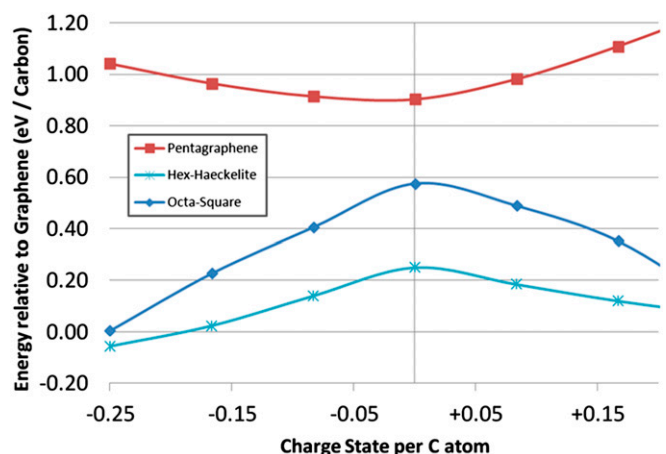


Fig. 4. Relative stability of penta-graphene (Fig. 2A) and hex-Haeckelite (Fig. 3A) compared with graphene, as a function of charge state per C atom. Although penta-graphene is increasingly unstable with charging, Haeckelites and square-octahedral structures are increasingly stabilized, becoming comparable with graphene or even thermodynamically favored at 0.25e per carbon.

be environmentally stable. Haeckelites, although unlikely to be experimentally attainable in isolation, may still be experimentally achievable in the presence of charge transfer ions.

In general, when determining the experimental feasibility of synthesizing new carbon phases, it is not sufficient to establish the pristine material as a metastable minimum on a local energy surface. We have highlighted here the importance that the structure lie at the apex of a disconnectivity graph of related isomers, occupying a unique energetically isolated position. Chemical and kinetic stability, notably in the presence of catalytic defects (both intrinsic and extrinsic) are also critical. This analysis could easily be extended to other proposed carbon allotropes, such as the various graphyne phases (19), and indeed is general beyond its simple application to carbon.

Methods

DFT calculations under the local density approximation were performed using the AIMPRO code (20), with a basis set containing 22 independent

Gaussian-based functions per carbon atom and 40 per oxygen atom. Hartwigsen–Goedecker–Hutter relativistic pseudopotentials were used (21). Finite temperature smearing was used for the electronic state population with temperature $kT = 0.01$ eV. Lattice vectors were relaxed simultaneously with atom positions and lattice symmetry broken. For penta-graphene and related 12-atom unit cells, a 4×4 Monkhorst–Pack (22) k -point grid was used; for the 2×2 48-atom cell, a 2×2 k -point grid was used. Saddle points were determined using the climbing nudged elastic band algorithm (23). Orthorhombic octahedron-square cells contained 4 atoms, $8 \times 8 \times 1$ k -points; hexagonal H_{567} cells had 16 atoms, $4 \times 4 \times 1$ k -points; $R_{5,7}$ cells contained 48 atoms, $2 \times 2 \times 1$ k -point grid; and $O_{5,6,7}$ cells had 12 atoms, $4 \times 4 \times 1$ k -point grid.

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