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Systematic search for low-enthalpy \( sp^3 \) carbon allotropes using evolutionary metadynamics

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We present a systematic search for low-energy metastable superhard carbon allotropes by using the recently developed evolutionary metadynamics technique. It is known that cold compression of graphite produces a new allotrope at 15-20 GPa. Here we look for all low-enthalpy structures accessible from graphite. Starting from 2H- or 3R-graphite and applying the pressure of 20 GPa, a large variety of intermediate \( sp^3 \) carbon allotropes were observed in evolutionary metadynamics simulation. Our calculation not only found all the previous proposed candidates for ‘superhard graphite’, but also predicted two new allotropes (X-carbon and Y-carbon) showing novel ‘5+7’ and ‘4+8’ topologies. These superhard carbon allotropes can be classified into five families based on ‘6’ (diamond/lonsdaleite), ‘5+7’ (M/W-carbon), ‘5+7’ (X-carbon), ‘4+8’ (bct C\(_4\)), and ‘4+8’ (Y-carbon) topologies. This study shows evolutionary metadynamics is a powerful approach to systematically search for low-energy metastable phases reachable from given starting materials.

I. INTRODUCTION

Carbon can adopt a wide range of structures, from superhard/superdense insulating (diamond, lonsdaleite, hypothetical phases hP3, t112 and tP12\( ^{21} \)) to ultrasoft semimetallic (graphite, fullerences) and even superconducting (doped diamond\(^2\) and alkali-doped fullerences\(^3\)). The quest for carbon materials with desired properties is of great interest in both fundamental science and advanced technology. One important direction in carbon research is the discovery of carbon allotropes with advanced mechanical and electronic properties.

It is well known that graphite transforms to the thermodynamically stable diamond at high pressures (\( >12 \) GPa) and high temperatures (1900-2500 K\(^1\)). On the contrary, several experiments reported that cold compression of graphite produces a metastable superhard and transparent phase, clearly different from diamond or lonsdaleite, but the exact crystal structure could not be determined\(^8\). The difficulty to experimentally resolve the crystal structure has stimulated the 10-20
two
theoretical efforts\(^10-20\). Several structural models were found using different techniques. Physical properties of these models (M-carbon\(^10\), W-carbon\(^12\), \( \alpha \)C16 (also called Z-carbon\(^13-15\), R/P carbon\(^16\), bct C\(_4\)) have been intensely studied. The simulated X-ray diffraction patterns and band gaps of these models are mostly in good agreement with experimental data, making it even harder to decide which one is the metastable product observed in experiments. On the other hand, it is not guaranteed that there is not even a better solution for this experimental puzzle. Furthermore, it is likely that different metastable phases will be obtained by room-temperature compression of different polytypes of graphite, or under various non-hydrostatic conditions. This motivates us to do a systematic search for the low-energy metastable carbon allotropes.

So far, there are several methods to find the ground state structures of unknown materials. However, none of them are designed to search for metastable states. Our recently proposed evolutionary metadynamics method\(^22\) can focus on that task. Starting from a reasonable initial crystal structure, with this technique one can produce efficiently both the ground state and metastable states easily reachable from that initial structure. In this paper, we applied this technique to systematically search for metastable carbon allotropes easily reachable from graphite. Starting the calculation at 20 GPa from two polytypes of graphite (2H and 3R), we easily found the diamond structure (ground state) and a number of low-energy metastable structures with \( sp^3 \) hybridization which could possibly explain ‘superhard graphite’.

II. METHDOLOGY

The idea of metadynamics is to introduce a history-dependent potential term, and fill the minima in the free energy surface so that the system could cross the energy barriers and undergo phase transitions\(^23\). This technique is usually applied as an extension of molecular dynamics (MD) simulation technique\(^23\). Since it relies on MD simulation to equilibrate the system, it often leads to trapping in metastable states and amorphization rather than transition to a stable crystal structure. We recently proposed a hybrid method, basically a metadynamics-like method driven not by local MD sampling, but by efficient global optimization moves\(^10,24\).

In this approach\(^24\), we start from one known initial structure at a given external pressure \( P \). Following Martonak et al., we used the cell vectors matrix \( h_{ij} \) (also representable as a 6-dimensional vector \( h \)) as a collective variable to distinguish the change of state of the system\(^23\). For a given system with volume \( V \) under external pressure \( P \), the derivative of the free energy \( G \) with respect to \( h \) is

\[
- \frac{\partial G}{\partial h_{ij}} = V[h^{-1}(P - p)]_{ji}
\]

At each generation (or metastep), many structures are produced and relaxed at fixed \( h \), and we select the lowest energy structure and compute it internal tensor \( p \). The technique used here generates many structures at each metastep, while in
traditional metadynamics\[23\], only one structure is produced at each metastep. The cell shape is then updated with a stepping parameter \( \delta h \)

\[
h_{im}(t + 1) = h_{im}(t) + \frac{\delta h}{|f|^2} S_{ijkl} f_{kl} h_{jm}(t) \tag{2}
\]

where \( S \) is the elastic compliance tensor corresponding to an elastically isotropic medium with Poisson ratio 0.26, which corresponds to the border between brittle and ductile materials\[25\] and is a good average value to describe both metals and insulators. The driving force \( f = -\frac{\partial G}{\partial h} \) in Eq. (2) comes from a history-dependent Gibbs potential \( G(t) \) where a Gaussian has been added to \( G(h) \) at every point \( h(t') \) already visited in order to discourage it from being visited again,

\[
G(t) = G^0 + \sum W e^{-\frac{(h - h(t'))^2}{2\delta h^2}} \tag{3}
\]

where \( W \) is the Gaussian height. Then we compute the vibrational modes for the selected structure according to the dynamical matrix constructed from bond hardness coefficients,

\[
D_{\alpha\beta}(a, b) = \sum_{m} \frac{\partial^2}{\partial a_{\alpha} \partial b_{\beta}} \left( \frac{1}{2} \sum_{i,j,l,n} H_{ij}^{l,n} \left( (x_i^n - x_j^n)^2 + (y_i^n - y_j^n)^2 + (z_i^n - z_j^n)^2 \right) \right) \tag{4}
\]

Here coefficients \( \alpha, \beta \) denote coordinates \((x, y, z)\); \( a, b, i, j \) describe the atom in the unit cell; \( l, m, n \) denote the unit cell number. Therefore \( x_i^n \) is the \( x \)-coordinate of atom \( i \) in the unit cell \( l \). \( H_{ij}^{l,n} \) is the hardness coefficients for a bond between the atom \( i \) in the unit cell \( l \) and atom \( j \) in the unit cell \( n \). The bond hardness coefficients are computed from bond distances, covalent radii and electronegativities of the atoms\[24\]. Note that the dynamical matrix corresponds to zero wavevector (extension to non-zero wavevectors is straightforward) and unit masses.

The simulated vibrational modes are used to produce new generation (typically 20–40 softmutated structures). To perform softmutation\[21,24\], we move the atoms along the eigenvector of the softest calculated mode. One structure can be softmutated many times using different non-degenerate modes and displacements. The magnitude of the displacement \( (d_{\text{max}}) \) along the mode eigenvector is an input parameter: with relatively small \( d_{\text{max}} \) and displacements represented by a random linear mixture of all mode eigenvectors, it is similar to MD-metadynamics in crossing energy barriers and equilibrating the system. With large \( d_{\text{max}} \) along the softest mode eigenvectors, we obtain the softmutation operator\[24\], capable of efficiently finding the global energy minimum.

A new generation of softmutated structures are produced and relaxed in the new cell. Repeated for a number of generations, this computational scheme leads to a series of structural transitions and is stopped when the maximum number of generations is reached.

In this work, structure relaxations were done using density functional theory (DFT) within the generalized gradient approximation (GGA)\[26\] in the framework of the all-electron projector augmented wave (PAW)\[27\] method as implemented in the VASP\[28,29\] code. We used the plane wave kinetic energy cutoff of 550 eV for the plane-wave basis set and the Brillouin zone sampling resolution of \( 2\pi \times 0.08 \text{ Å}^{-1} \), which showed excellent convergences of the energy differences, stress tensors and structural parameters.

III. RESULTS AND DISCUSSIONS

In a compression experiment at low temperatures (low enough to preclude transition to the stable state), the product depends on the nature of the starting materials, and on the energy landscape (in particular, energy barriers). To fully investigate the possible candidate materials, we performed simulations starting from two different graphite polytypes (graphite-2H and 3R), which differ in the stacking of graphene layers.

A. Starting from graphite-2H

We did a preliminary test at 20 GPa starting from the graphite-2H structure, and successfully found diamond as the ground state, \( M \)-carbon and bct \( C_4 \) as metastable states\[21\]. In the calculation we set \( d_{\text{max}} = 2.5 \text{ Å}, W = 4000 \text{ kbar·Å}^3 \) and \( \delta h = 0.6 \text{ Å} \).
structures shows a larger diversity. In some of these structures, intermediate between these two structures. The ‘5+7’ class of there is no surprise that its thermodynamic properties are in- 5-membered rings form pairs, while in others these they are topology. The observed many low-energy structures based on ‘5+7’ or ‘4+8’ single. The difference of the 5-membered ring pairs’ orienta- Z-graphite. Since C, recently suggested as a candidate for superhard 16 inherits layers of bct-C \( \times 4 \)-carbon and diamond, \( \times 4 \)-carbon structures containing 5+7 membered rings (Fig. structure with a ‘5+7’ topology, which is in Fig. 3g. The pro- 3 shows the results. Since the initial model has 3 graphene layers, it could form a large variety of \( M+D \) and \( B+D \) struc- 5-membered rings; (d) Z-carbon (belonging to \( B+D \) type); (e) M-carbon with 5+7 membered rings; (f) W-carbon with 5+7 membered rings; (g) \( M+D \) type carbon. Polygons are highlighted by different colors (quadrangle: turquoise; pentagon: green; hexagon: blue). tion leads to two allotropes: \( M \)-carbon (Fig. 2b) and W-carbon (Fig. 2f). Some structures can be thought of as combinations of layers of the \( M \)-carbon and diamond structures (\( M+D \) car- tion.

B. Starting from graphite-3R

Starting the calculation at 20 GPa from another polytype, graphite-3R, which contains 3 layers per lattice period, we again easily found the diamond structure and a number of low-energy metastable structures with \( sp^3 \) hybridization. Fig. 3 shows the results. Since the initial model has 3 graphene layers, it could form a large variety of \( M+D \) and \( B+D \) structures based on ‘4+6+8’ or ‘5+6+7’ topologies. For instance, we observed a \( B+D \) structure containing 2 \( \times 4+8 \) layers and 1 \( \times 6 \) layer (Fig. 3a); or 1 \( \times 4+8 \) layers and 1 \( \times 6 \) layer (Fig. 3b); and \( M+D \) structure containing 2 \( \times 5+7 \) layers and 1 \( \times 6 \) layer (Fig. 3e,f). Most strikingly, we also observed another structure with a ‘5+7’ topology, which is in Fig. 3g. The projections of pentagons and heptagons along the \( c \) axis could not be separated as in \( M \)-carbon, but overlap each other. We extracted the ‘5+7’ part from the complex structure, and obtained a new configuration with pure ‘5+7’ topology. This crystal structure (which we call \( X \)-carbon, and the hybrid structure from \( X \)-carbon and diamond is referred to as \( X+D \) type) is shown in Fig. 4. It is a monoclinic structure with \( C2/c \) symmetry, and contains 32 atoms in the conventional cell. We also found a new unexpected ‘4+8’ topology in an allotrope that we call Y-carbon with unique ‘4+8’ membered-rings from another separate metadynamics run. It is an orthorhombic structure with \( Cmca \) symmetry, containing 16 atoms in the conventional cell. The simulated X-ray diffraction patterns of all these structures are in good agreement with experimental data (as shown in Fig. 5), suggesting that both \( X,Y \) carbon can explain the experiments on cold compressed graphite. Al- thought all these structures show a satisfactory agreement with experimental X-ray data, our recent transition path sampling calculation suggest \( M \)-carbon to be kinetically the likeliest product of cold compression of graphite-2H. Using other polytypes of graphite, or different conditions (non-hydrostatic or dynamical compression), one might produce alternative allotropes found here. Synthesis of these allotropes would be desirable in view of their physical properties.

C. Properties

From evolutionary metadynamics simulations, five families of \( sp^3 \)-hybridized structures made by stacking corrugated graphene layers and having competitive enthalpies were discovered: ‘6’ (diamond and lonsdaleite), two classes of ‘5+7’ topologies (one - \( M/W \)-carbon; the other - \( X \)-carbon), and two classes of ‘4+8’ (one - \( B+D \); the other - \( Y \)-carbon). The enthalpies of different carbon phases as a function of pressure are presented in Fig. 5. Apart from the prototypes, we also included hybrid structures (lowest enthalpy \( B+D, M+D \) and \( X+D \) carbon, see crystallographic data in Supplementary.
FIG. 3. (Color online) Structures observed during compression of graphite-3R at 20 GPa. (a) graphite-3R (2 × 2 × 2 supercell of the calculation model); (b) diamond; (c,d) B+D type structures; (e,f) M+D type structures; (g) X+D type structures. Polygons are highlighted by different colors (squares: turquoise; pentagons: green; hexagons: blue).

FIG. 4. (Color online) (a) New allotropes with ‘5+7’ topology, X-carbon, space group C2/c, a=5.559 Å, b=7.960 Å, c=4.752 Å, β=114.65°. This structure has five non-equivalent Wyckoff positions: C1(0.250, 0.083, 0.949), C2(0.489, 0.809, 0.982), C3(0.000, 0.200, 0.250), C4(0.247, 0.913, 0.801), C5(0.000, 0.816, 0.250). (b) New allotrope with ‘4+8’ topology, Y-carbon, space group Cmca, a=4.364 Å, b=5.057 Å, c=4.374 Å. This structure has one Wyckoff position: C(0.681, 0.635, 0.410). Polygons are highlighted in different colors to show the ‘5+7’ and ‘4+8’ topology.

Materials). At elevated pressures, all these allotropes become more stable than graphite. For the prototypes, M/W-carbon is energetically more favorable than bct- and X-carbon. Lower enthalpies are obtained by combining layers of these structures with layers of diamond. For the models under consideration (up to 4 graphene layers), B+D (1 × ‘4+8’ + 2 × ‘6’ layers, Fig. 3d) tends to have the lowest enthalpy, while M+D (2 × ‘5+7’ + 2 × ‘6’ layers, Fig. 3h) is quite competitive (only 8 meV/atom higher than B+D). X+D (Fig. 3b) is 50 meV/atom higher than B+D, indicating that X-carbon has poorest possibility to interface with diamond.

We also computed the mechanical and optical properties (see Supplementary Materials). Similar to previous theoretical investigations\textsuperscript{14-16,18,19}, all of these candidate allotropes exhibit high hardnesses\textsuperscript{31} and bulk moduli, which are comparable with those of diamond. Fig. 4 shows the calculated total and partial electronic densities of states in both systems. It can be clearly seen that 2p states exhibit a larger overlap with 2s states in diamond, which makes diamond the most stable allotrope among sp\textsuperscript{3} forms of carbon. The magnitude of overlap determines the order of stability: M-carbon > X-carbon > bct C\textsubscript{4} > Y-carbon. The DFT band gaps of M-carbon, X-carbon, bct C\textsubscript{4}, and Y-carbon are 3.6, 3.8, 2.7 and 2.9 eV, and we should bear in mind that DFT always underestimate the band gaps - so the real gaps are larger, and all of these sp\textsuperscript{3}-allotropes should be transparent colorless insulators.

IV. CONCLUSIONS

In summary, we performed a systematic search for metastable allotropes of carbon that can be synthesized by cold compression of graphite by using the recently developed evolutionary metadynamics technique\textsuperscript{21}. Starting from 2H- or 3R-graphite, at 20 GPa we easily found diamond as the ground state and observed a large variety of low-energy metastable sp\textsuperscript{3} carbon allotropes accessible from graphite. Apart from
diamond, lonsdaleite and their polytypes, we summarize four new families of low-enthalpy carbon allotropes which can be obtained by cold compression of graphite, (i) ‘5+7’ topology (M/W-carbon); (ii) ‘5+7’ topology (X-carbon); (iii) ‘4+8’ topology (bct C$_2$); (iv) ‘4+8’ topology (Y-carbon). All of these structures are consistent with experimental data on ‘superhard graphite’, and are predicted to have excellent mechanical properties, but transition path sampling calculations unequivocally show M-carbon to be the likeliest product of cold compression of graphite. Yet, the new allotropes predicted here could be synthesized in a different experiment protocol and starting from different materials (graphite-3R, turbostratic graphites, fullerenes, or nanotubes, etc). We find it particularly encouraging that all the previously proposed structures and 2 new ones (X- and Y-carbon) were found in a systematic way, using just one calculation per starting material (graphite-2H or 3R). Our work show that evolutionary metadynamics is a powerful method for efficiently finding not only stable but also low-energy metastable structures.

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Figure 1
Experiment

Y–carbon

W–carbon

X–carbon

BCT $C_4$

M–carbon

Graphite

18.4 GPa

2$\theta$ (degree)