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Stochastic generation of complex crystal structures combining group and graph theory with application to carbon

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A method is introduced to stochastically generate crystal structures with defined structural characteristics. Reasonable quotient graphs for symmetric crystals are constructed using a random strategy combined with space group and graph theory. Our algorithm enables the search for large-size and complex crystal structures with a specified connectivity, such as threefold sp^2 carbons, fourfold sp^3 carbons, as well as mixed sp^2-sp^3 carbons. To demonstrate the method, we randomly construct initial structures adhering to space groups from 75 to 230 and a range of lattice constants, and we identify 281 new sp^3 carbon crystals. First-principles optimization of these structures show that most of them are dynamically and mechanically stable and are energetically comparable to those previously proposed. Some of the new structures can be considered as candidates to explain the experimental cold compression of graphite.

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I. INTRODUCTION

The prediction of crystal structures for a given composition is a central topic to the study of condensed matter [1]. Many methods have been developed, such as *ab initio* random structure searching [2,3], evolutionary approaches [4–6], particle swarm optimization methods [7,8], periodic graph theory [9,10], metadynamics [11,12], simulated annealing [13,14], and basin or minima hopping methods [15–17]. Elemental carbon can form a large number of allotropes, such as graphite, cubic diamond, hexagonal diamond, and other carbon phases with currently undetermined structures [18–23]. This is due to the propensity of carbon to sp, sp^2, and sp^3 hybridization, and it makes carbon a challenging target for crystal structure prediction. Over recent decades, many interesting aspects of elemental carbon have been explored. For example, much theoretical effort has been expended on the enumeration of hypothetical metastable carbon structures [24–35], predicting potential superhard carbon materials [36–45], searching for possible superdense carbon crystals [46–48], solving the crystalline structures of the previously synthesized carbon phases [49–59], determining the ultimate fate of carbon under extreme compression [60], as well as designing direct-band gap carbons for solar cell application [61,62]. As documented in the Samara Carbon Allotrope Database [63], there are at least 522 three-dimensional crystal structures that have been previously proposed for carbon. The number of potential carbon crystal structures increases rapidly [64–67]. In a very recent article, a large number of three-dimensional C_8 carbon crystals [68] were proposed and it was noted that there are at least 460 articles concerning carbon structures in the literature.

In this paper, we describe a method for generating crystal structures with defined structural features. It is based on a random sampling strategy combined with space group and graph theory (RG^2). We find that it efficiently yields reasonable quotient graphs for symmetric crystals with specified coordination (such as sp^2 carbons, sp^3 carbons, and mixed sp^2-sp^3 carbons) and unit cell. Using RG^2, we systematically search for crystal structures of sp^3 carbon in space groups from 75 to 230 with various lattice parameters and find 281 interesting sp^3 carbon crystal structures. Our first-principles results show that most of these new structures are dynamically and mechanically stable with comparable energetic stabilities to previously proposed carbon crystal structures. Some of them with low energy have been further found to be superhard semiconductors. These results suggest that RG^2 is a powerful tool for the generation of crystal structures with defined geometrical features.

II. METHOD

A. Relation between crystal structure and quotient graph

As discussed by Wells [69], each periodic crystal structure can be completely described by an infinite net. The translationally repeated part of the crystal structure can correspondingly represented as a finite quotient graph. Generally, each given quotient graph can be mapped back to a crystal structure through proper optimization. That is to say, we can predict crystalline structures through systematic enumeration of reasonable quotient graphs. Using such an idea, Winkler *et al.* systematically enumerated many small sp^2 carbon

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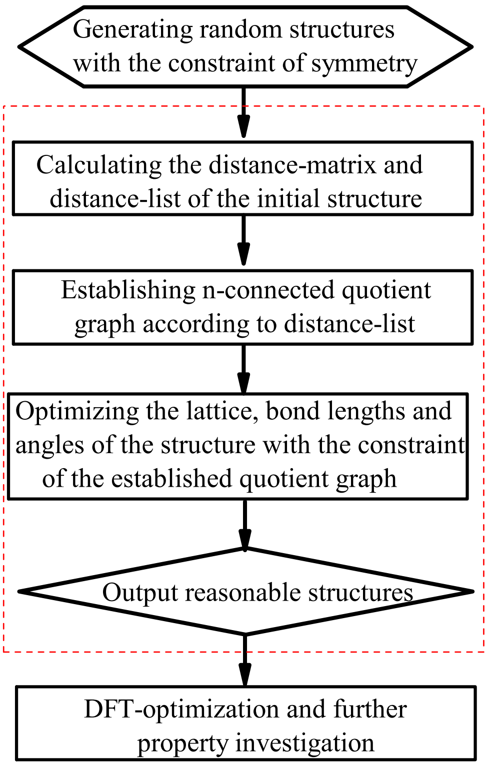

FIG. 1. The flow chart of our algorithm to generate, n-connected crystalline network.

crystals with up to six atoms per unit cell in 2001 [30]. In 2004, Strong *et al.* applied this method to predict small sp^3 carbon crystals containing four carbon atoms per unit cell and proposed eight new sp^3 carbon crystals [10]. However, the method faces challenges in predicting large-size crystal structures. As the number of atoms per unit cell increases, the generation of possible quotient graphs and the embedding into three dimensions becomes more difficult. To the best of our knowledge, most of the previously proposed large-size carbon crystals are generated by special techniques, such as segment recombination [41,42,44] and topological analysis [70,71]. Very recently, a systematic enumeration of carbon crystals with up to eight atoms per unit cell has been achieved through the artificial-force-induced reaction method (AFIR) [68]. The work suggests the construction of other quotient graphs from known equal-sized quotient graphs, thereby generating other crystals from known crystal structures. We propose a simple way to generate a feasible quotient graph for crystal structures with defined geometric features.

B. Building the quotient graph and generating the structures

We have developed RG^2 to rapidly yield reasonable quotient graphs that will produce low-energy carbon crystal structures. As shown in Fig. 1, we first generate a random initial structure in a given or randomly chosen space group. We do not initially worry about the quality of the structure and simply select the atomic positions so that the atoms are randomly and uniformly spread through the unit cell. We then give each atom in the central cell an index i, where $(i = 1,N)$, and calculate the distances between each i atom and the other j atoms in any of the hkl cells, and so build a distance matrix for the initial structure:

$$\begin{pmatrix} & d_{11}^{hkl} & d_{12}^{hkl} & \dots & d_{1N}^{hkl} & \\ & \dots & \dots & \dots & \dots & \\ \dots & & & & & \dots \\ & \dots & \dots & d_{ij}^{hkl} & \dots & \\ & d_{N1}^{hkl} & d_{N2}^{hkl} & \dots & d_{NN}^{hkl} & \end{pmatrix}^{DM}, \tag{1}$$

where N is the number of atoms in the unit cell and d_{ij}^{hkl} is the distance between the i atom in the 000 cell and the j atom in the hkl cell. Based on the calculated distance matrix, we sort all the distances d_{ij}^{hkl}. We then build the bonds one by one by working through the unsaturated pairs, from small to large separations, until all the atoms are saturated or all the pairs have been considered. For each new bond, we record the corresponding cell index $[hkl]$ and keep track of the number of bonds for each atom. In such a way, we construct the quotient graph for the structure as

$$\begin{pmatrix} Q_{11} & Q_{12} & \dots & Q_{1N} \\ Q_{21} & Q_{22} & \dots & Q_{2N} \\ \dots & \dots & Q_{ij} & \dots \\ Q_{N1} & Q_{N2} & \dots & Q_{NN} \end{pmatrix}^{QG}, \tag{2}$$

where $Q_{ij} = [hkl]$ or zero. The zero value for Q_{ij} indicates that atom i and j are not connected and $[hkl]$ indicates that the i atom is bonded to j atom in the adjacent hkl cell. We reject those structures with unsaturated atoms and generate a new random trial. After building a saturated quotient graph, we adjust the lattice parameters and atomic positions so as to improve the bond lengths and bond angles in the initially random structure. In the current work, the ideal values are bond lengths of 1.55 Å and angles of 109.47°. The quotient graph is not updated during the optimization stage. Namely, we adjust the atomic positions according to only those distances d_{ij}^{hkl} with nonzero value of Q_{ij}. When the structure has bond lengths and angles sufficiently close to our ideal values, we recalculate the whole distance matrix of the structure and compare the values of all the nonbonding distances to the bonding distances. We reject structures which have nonbonding distances that are shorter than the bonding distances. The surviving structures are studied further through density functional theory (DFT)–based first-principles optimization (see further details in the S1 part in our Supplemental Material [72]).

III. RESULTS AND DISCUSSION

As summarized in SACADA [63], there are at least 522 carbon crystals, including pure sp^2, pure sp^3, and mixed sp^2-sp^3 carbon crystals, that have been previously proposed. In our present work, the 95 sp^3 with tetragonal, hexagonal, and cubic symmetry are considered as reference systems. The newly developed RG^2 is applied to systematically search for sp^3 carbon crystals in space groups from 75 to 230 (tetragonal, hexagonal, and cubic). The results show that most of the previously proposed sp^3 carbon crystals can be generated except for those large-size carbons structures constructed using specialized methods [41,42,44,70,71]. Otherwise, our approach generates 281 sp^3 carbon crystals which are different from those in SACADA. About 129 of

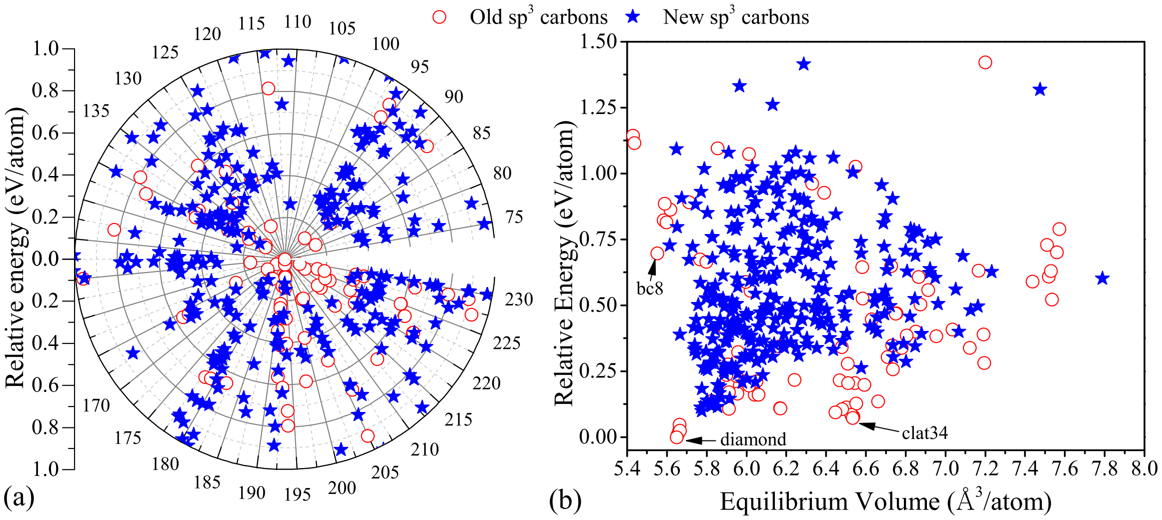

FIG. 2. The total energies per atom of the sp^3 carbon crystals belonging to space groups from 75 to 230 relative to diamond (a). The total energies are mapped as radius and the space group numbers are mapped as degrees. The red circles and blue solid five-point stars denote the sp^3 carbon crystals discovered in previous work and those newly discovered in our present work, respectively. The scatter plot of the relative average energy (eV/atom) against equilibrium volume (Å^3/atom) for sp^3 carbons with tetragonal, hexagonal, and cubic symmetry (b).

these sp^3 carbons contain atom numbers per primitive cell larger than 40 (35 of them contain more than 100 atoms per primitive cell and 5 of them contain more than 200 atoms).

The results (before DFT calculations) are obtained in just a few days, running on a single CPU. We then optimize all of these 281 sp^3 carbon crystals directly using the VASP code, which takes a few weeks on a cluster (100 CPUs). After that, some of these sp^3 carbons, with relatively lower energy or with special structural characteristics, are further investigated for their dynamical stabilities and electronic and mechanical properties. In Figs. 2(a) and 2(b), the average energies and the scatter plot of the average energies against equilibrium volume of these sp^3 carbon crystals relative to diamond are plotted. The crystalline information files (CIF) of these 281 sp^3 carbons are provided as Supplemental Material and key data are listed [72], including their names, space groups, Hermann-Mauguin symbols, atom numbers, total energies, total volumes, average volumes, and average energies relative to diamond. We have shown that RG^2 can quickly generate many sp^3 carbon crystals with energies around 100 to 1000 meV higher than diamond. Many of these structures have very large unit cells. Details of these results will be discussed below according to their crystal systems.

To conveniently manage and discuss such large numbers of structures generated by RG^2, we require a naming strategy. The carbon structures are named according to key structural information including the space group number (No), the number of inequivalent atoms (Ne), the lattice constants (abc) of the corresponding crystalline cell, the hybridization type (h), and an additional index number (i), as "No-Ne-abc-h-i." The value of "No" can be 1 to 230 and the value of "Ne" can be any nonzero integers. The hybridization type "h" can be, for example, 3, 4, and 34, which means pure sp^2, pure sp^3, and mixed sp^2-sp^3 carbon structures, respectively. We project the lattice parameters a, b, and c of the conventional cell onto the 26 letters (a–z and A–Z) in the following way:

$$\begin{pmatrix} [0.5,1) & [1,1.5) & [1.5,2) & [2,2.5) & \dots & [25.5,26) & [26,\infty) \\ \downarrow & \downarrow & \downarrow & \downarrow & \dots & \downarrow & \downarrow \\ a & A & b & B & \dots & z & Z \end{pmatrix} \tag{3}$$

Further information is provided in the Supplemental Material [72].

A. Cubic sp^3 carbons

The literature records that various cubic carbons [21,73–77] can be synthesized under high-pressure conditions and some of them are still structurally unresolved. Much theoretical effort has been expended on predicting cubic carbon crystals over the past decades [56–58,78–80]. According to SACADA [63], there about 38 sp^3 carbons belonging to the cubic system, including diamond, BC8 [47,81], T-carbon [29], fcc-C34 [82], and sc-C46 [82]. In our present work, we can generate most of these previously proposed cubic carbons, excepting those containing very large numbers of atoms per cell (such as KXI, KVI, clathrates I-100, clathrates I-280, clathrates II-100, clathrates II-280, clathrates II+Iva, and clathrates I+II) [70,71,83]. As listed in the Supplemental Material [72], we find 65 sp^3 cubic carbon crystals.

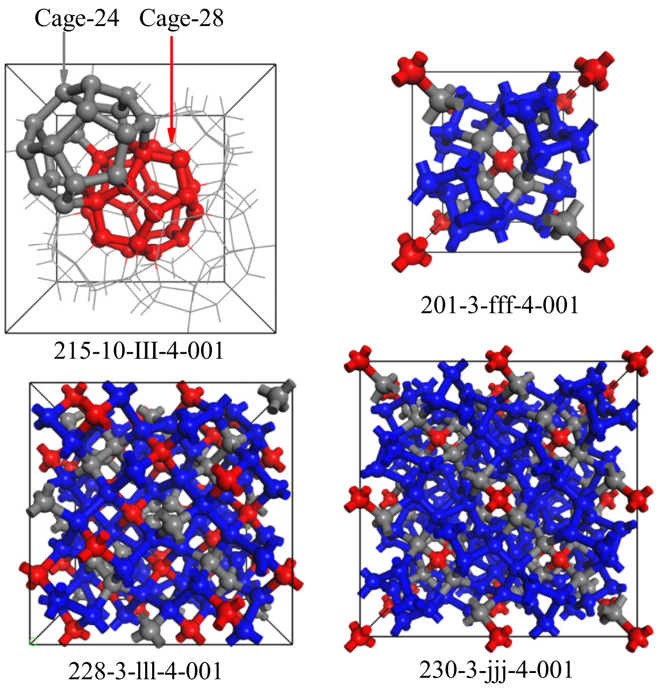

FIG. 3. The perspective crystalline views of the clathrate-like 215-10-III-4-001 and the diamond-like 201-3-fff-4-001, 228-3-lll-4-001, and 230-3-jjj-4-001 with only six-member rings.

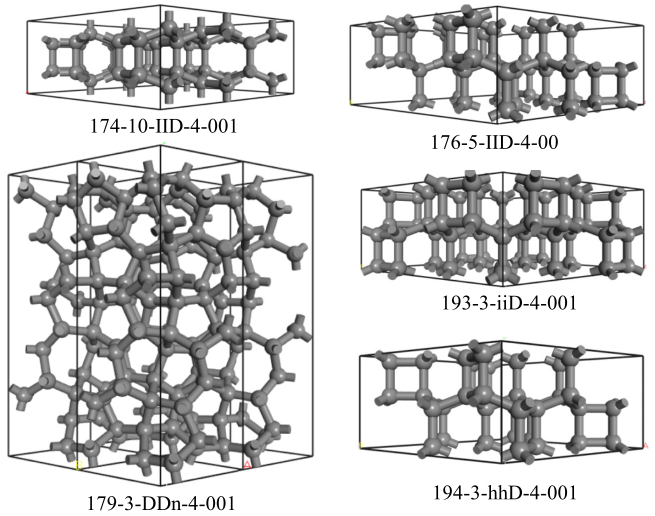

FIG. 4. The perspective crystalline views of 174-10-IID-4-001, 179-3-DDn-4-001, 176-5-IID-4-001, 193-3-iiD-4-001, and 194-3-hhD-4-001 can be structurally translated from graphite.

The relative energies of our cubic sp^3 carbons are shown in Figs. 2 and S1(a). Nearly all of these sp^3 cubic carbons possess relative energies higher than that of diamond, exceeding 300 meV/atom (excep 205-6-iii-4-002 and 215-10-III-4-001). Our present work indentifies some large-size carbon crystals. For example, our 230-7-OOO-4-001, 224-10-KKK-4-00, 224-10-kkk-4-001, 230-5-nnn-4-001, 230-5-MMM-4-001, 227-9-PPP-4-001, 221-7-JJJ-4-001, 230-4-LLL-4-002, and 230-4-LLL-4-001 contain 304, 226, 220, 208, 208, 170, 160, 156, and 156 atoms per cell, respectively. Some of these sp^3 cubic carbons (those name containing “nnn”, “NNN”, “ooo,” and “OOO”) possess lattice constants of nearly 14.7 Å. These results show that the method RG^2 possesses the ability to explore large-size carbon crystals, such as the one experimentally discovered in natural Posigai impact crater [21]. Unfortunately the simulated X-ray diffraction pattern (XRD) (Fig. S3) of these large-size cubic carbons do not explain the superlarge cubic carbon discovered in the Posigai impact crater.

Some of our sp^3 cubic carbons are structural intriguing and topologically interesting, for example, the clathrate-like 215-10-III-4-001 (it had been topologically predicted as odg [84] but not been investigated as a carbon phase) belonging to space group no. 215. The calculated total energy of 215-10-III-4-001 is of about 296 meV/atom higher than that of diamond. It is more stable than the previously predicted T-carbon [29], BC8 [47,81], and BC12 [46]. As shown in Fig. 3(a), 215-10-III-4-001 can be constructed from cage-24 and cage-28, similar to fcc-C34, hex-C40, and sc-C46 [82]. Both the dynamical and mechanical stabilities of 215-10-III-4-001 are confirmed through its vibrational spectra and elastic constants as discussed in the Supplemental Material [72]. As shown in Table S1 and Fig. S5, our results also indicate that it is a superhard semiconductor. In Figs. 3(b)–3(f), we show three sp^3 cubic carbons with only six-member carbon rings similar to diamond, BC8 [47,81], and BC12 [46]. They are 201-3-fff-4-001, 228-3-lll-4-001, and 230-3-jjj-4-001, which possess total energies about 1264, 931, and 414 meV/atom higher than that of diamond, respectively.

B. Hexagonal sp^3 carbons

A well-known hexagonal carbon crystal is hexagonal diamond. In the past decades, many hypothetical hexagonal carbons, such as 4H-diamond, 12R-diamond [85], CFSs [26], and hex-C40 [82], have been proposed. As collected in SACADA, there are at least 35 sp^3 hexagonal carbon allotropes that have been previously proposed. Our present work rediscovered most of these hexagonal sp^3 carbons and generates 92 other hexagonal sp^3 carbons. As shown in Fig. S1(b), we can see that the most stable sp^3 hexagonal carbons are hexagonal diamond and their modifications in space groups 166, 191, and 194. Some of our sp^3 hexagonal carbons possess a relatively low energy in comparison with most of the previously proposed ones. For example, 174-10-IID-4-001, 176-5-IID-4-001, 179-3-DDn-4-001, 193-3-iiD-4-001, and 194-3-hhD-4-001 (see in Fig. 4) are structurally translated to graphite. Their energies are just 166, 125, 196, 114, and 145 meV/atom higher than that of diamond, respectively. That is to say, they are energetically comparable to those previously proposed candidates (such as M-carbon [4,55], W-carbon [49], Z-carbon [50–52] and S-carbon [53]) for the superhard carbons cold compressed from graphite [22].

As shown in the Supplemental Material [72] in Table S1 and Fig. S2, 174-10-IID-4-001, 176-5-IID-4-001, 179-3-DDn-4-001, 193-3-iiD-4-001, and 194-3-hhD-4-001 are dynamically stable. Their electronic and mechanical properties are shown in Table S1 and Fig. S5. We can see that they are carbon structures with semiconducting and superhard properties. Our present search generates 14 hexagonal sp^3 carbon crystals which can

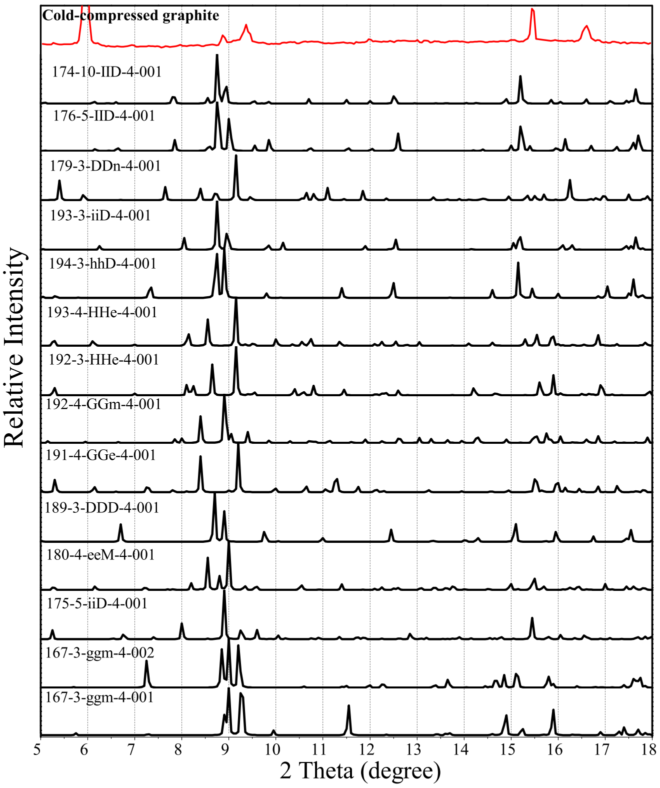

FIG. 5. The simulated XRDs of our sp^3 hexagonal carbons, which can be considered as good candidates for explaining the superhard carbon crystals synthesized by cold-compressing graphite.

be structurally obtained from graphite. The simulated XRDs of these 14 hexagonal sp^3 carbons are plotted in Fig. 5. We can see that most of them can be considered as good candidates for explaining the superhard carbons synthesized in cold-compressing graphite [22].

We find some intriguing hexagonal carbons with chiral framework structures (CFS) similar to the previously proposed CFSs [26]. These CFSs mainly distribute in chiral space groups 152 (154), 169 (170), 178 (179), and 180 (181). Shown in Fig. S4 are two typical pairs of CFSs, namely the previously proposed P6122 (P6522) and our 169-4-FFe-4-001 (170-4-FFe-4-001). Our present work also shows some large-size sp^3 hexagonal carbons with lattice constants very similar to those of the experimentally discovered chaoite ($a = 8.948$ Å, $c = 14.078$ Å) [18–20]. Examples are 193-6-IIm-4-001 and 172-26-iiM-4-001 with lattice constants of $a = 9.47$ Å, $c = 12.84$ Å and $a = 8.95$ Å, $c = 13.27$ Å, respectively. The relative energies of 193-6-IIm-4-001 and 172-26-iiM-4-001 are 637 and 362 meV/atom, respectively. We find that 172-26-iiM-4-001 can also be structurally constructed based on the precursor (graphite) used to synthesize chaoite [19,20]. The simulated XRDs of these two new large-size sp^3 hexagonal carbons cannot, however, explain the experimental XRD of chaoite.

C. Tetragonal sp^3 carbons

A tetragonal carbon structure had been reported experimentally. It has been named as P-diamond [86] and has lattice constants of $a = 3.68$ Å and $c = 3.47$ Å. The detailed structure of such a simple tetragonal carbon phase is still an open question. On the other hand, there is experimental evidence that element silicon can form tetragonal crystals [87,88]. Most of these experimentally reported silicon phases are still structural unsolved. The prediction of a range of tetragonal carbon structures can provide candidates for explaining experimentally synthesized tetragonal silicon crystals and potential tetragonal carbon crystals which may be synthesized in future.

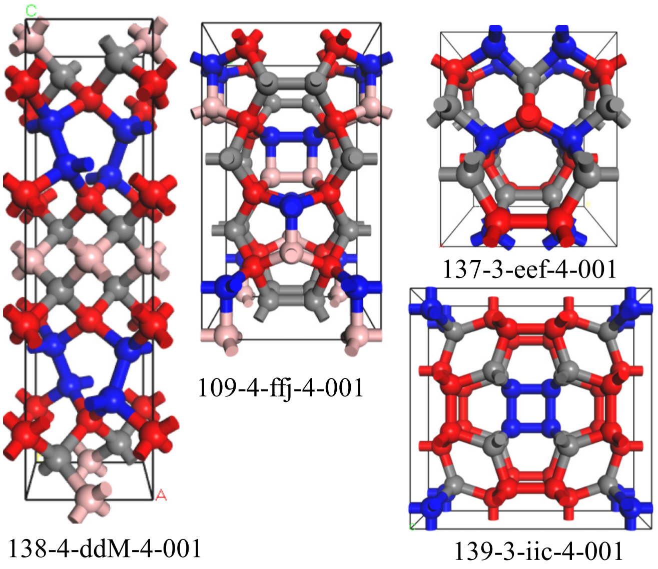

FIG. 6. The perspective crystalline views of the most stable four new tetragonal sp^3 carbon allotropes discovered by RG^2. They are 137-3-eef-4-001, 109-4-ffj-4-001, 139-3-iic-4-001, and 138-4-ddM-4-001.

There are at least 28 theoretical sp^3 tetragonal carbons which have been previously proposed, including the well-known bct-C4 [10,37–39,59], T12 [89], and clathrates III [90], as well as the recently proposed P41212 [91]. Among these sp^3 tetragonal carbons, T12 (108 meV/atom), clathrates III (113 meV/atom), P41212 (132 meV/atom), and I-4-carbon (161 meV/atom) are the most stable. In our present search, we find most of the previously proposed tetragonal sp^3 carbons. Furthermore, we uncover 124 other sp^3 tetragonal carbon structures. Some of them possess favorable energetic stability, for example, 138-4-ddM-4-001 (139 meV/atom), 137-3-eef-4-001 (207 meV/atom), 109-4-ffj-4-001 (261 meV/atom), and 139-3-iic-4-001 (264 meV/atom) as shown in Fig. 6. We investigate their vibrational, mechanical, and electronic properties using VASP. As shown in Fig. S2 and Table S1, we can see that they are dynamically and mechanically stable carbon structures. Table S1 and Fig. S4 show that they are superhard carbon semiconductors.

We also find some intriguing structures in the chiral tetragonal space groups 92 and 96. Shown in Fig. S6 are 92-6-HHC-4-001 (96-6-HHC-4-001) and 92-4-ggD-4-001 (96-4-ggD-4-001). Their relative energies are 318 and 391 meV/atom, which are slightly less stable than the recently proposed P41212 (P43212) structures which have three inequivalent atoms. Other low-energy tetragonal chiral sp^3 carbons, such as 92-4-eei-4-001 (303 meV/atom), 96-3-eeE-4-001 (685 meV/atom), and 96-2-CCi-4-001 (338 meV/atom), can be found in the Supplemental Material [72].

IV. CONCLUSION

In this study, we present a simple approach to generate crystal structures with defined geometrical features. Based on this approach, we systematically search for crystal structures of sp^3 carbon in space groups ranging from 75 to 230. We generate several hundred sp^3 carbon structures, including most of the previously proposed ones and 281 other ones. The first-principles results show that most of these 281 sp^3 carbons are dynamically and mechanically stable. These sp^3 carbon crystals include some with very large cubic or hexagonal unit cells, some chiral framework structures, and some low-energy superhard carbon structures. Some of them can be considered as candidates for explaining previous experimental results. These results suggest that RG^2 is an effective approach for the generation of crystal structures with defined geometrical features. This approach to the generation of structures can be straightforwardly extended to some other crystalline structures with defined geometrical features, such as the three-connected crystal structures for sp^2 carbon and high-pressure nitrogen (sp^3), four-connected crystal structures for sp^3 silicon and germanium, as well as the crystal structures for mixed sp^2-sp^3 carbon, C_3N_4 and Si_3N_4, by neglecting their chemical natures.

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