# Phase stability of carbon clathrates at high pressure

Jian-Tao Wang,<sup>1,a)</sup> Changfeng Chen,<sup>2</sup> Ding-Sheng Wang,<sup>1</sup> H. Mizuseki,<sup>3</sup> and Y. Kawazoe<sup>3</sup> <sup>1</sup>Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China <sup>2</sup>Department of Physics and HiPSEC, University of Nevada, Las Vegas, Nevada 89154, USA

<sup>3</sup>Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

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Group-IV element clathrates have attracted considerable interest in recent years. Here, we report an *ab initio* study on the structural stability of carbon clathrates at high pressure and identify fcc-C<sub>136</sub> clathrate as the third most stable carbon phase after cubic diamond and hexagonal graphite. A pressure-induced phase transition is predicted to occur around 17 GPa from hexagonal graphite to fcc-C<sub>136</sub>, which is more stable than other carbon clathrates such as hex-C<sub>40</sub> and sc-C<sub>46</sub>, and the recently predicted metastable *M*-carbon up to 26 GPa. Phonon dispersion calculations confirm the dynamic stability of fcc-C<sub>136</sub> as well as diamond. © *2010 American Institute of Physics*. [doi:10.1063/1.3359682]

## **I. INTRODUCTION**

Carbon has long been known to crystallize in cubic diamond and hexagonal graphite structures. Recent studies have identified a rich variety of other carbon structures including fullerenes,<sup>1,2</sup> carbon nanotubes,<sup>3</sup> and the two-dimensional polymerized C<sub>60</sub> phase.<sup>4</sup> Another class of interesting carbon structures is the so-called clathrates formed by regular arrays of  $I_h$ -C<sub>20</sub>,  $D_{6d}$ -C<sub>24</sub>,  $D_{3h}$ -C<sub>26</sub>, or  $T_d$ -C<sub>28</sub> cages. Under the topological restriction that only fourfold coordination  $(sp^3$ -bonding) is allowed and that only five- or sixfold rings may occur, Benedek et al.<sup>5</sup> proposed three basic series of periodic lattices of carbon clathrates (see Fig. 1). The facecentered cubic (fcc) lattices are generated by four  $C_{20}$  and two C<sub>28</sub> cages, belonging to the space group  $Fd\overline{3}m$  with 34 atoms per unit cell (or 136 atoms per supercell); the hexagonal (hex) lattices are generated by three C<sub>20</sub>, two C<sub>24</sub>, and two  $C_{26}$  cages, belonging to the space group P6/mmm with 40 atoms per unit cell; and the simple cubic (sc) lattices are generated by two C<sub>20</sub> and six C<sub>24</sub> cages, belonging to the space group  $Pm\overline{3}n$  with 46 atoms per unit cell. Experimentally, group-IV element clathrates have been synthesized in pure or guest-atom modified Si and Ge structures.<sup>6-12</sup> In contrast, similarly structured carbon clathrates are much less understood. Some pioneer works on the structural and electronic properties of  $C_{46} \mbox{ or } C_{136} \mbox{ phases have been reported in }$ detail with density functional theory calculations.<sup>12–17</sup> The key questions on the relative phase stability and structural transitions at high pressure for carbon clathrates remain to be further investigated.

The present work aims to explore the energetics and dynamic stabilities of the proposed carbon clathrates at high pressure. Our *ab initio* calculations show that fcc-C<sub>136</sub> (or C<sub>34</sub>) clathrate is a metastable phase that has the third lowest energy after cubic diamond and hexagonal graphite. A pressure-induced structural transition is predicted to occur around 17 GPa from hexagonal graphite to fcc-C<sub>136</sub>, which is always more stable than hex- $C_{40}$  and sc- $C_{46}$  clathrates and is also more stable than the recently predicted *M*-carbon<sup>18</sup> up to 26 GPa. Phonon dispersion calculations confirm the dynamic stability of fcc- $C_{136}$ .

## **II. CALCULATIONAL METHOD**

The calculations were performed using the Vienna *ab initio* simulation package (VASP)<sup>19,20</sup> with the projector augmented wave (PAW) method<sup>21</sup> and generalized gradient approximation-Perdew-Burke-Ernzerhof.<sup>22</sup> The energy minimization is done over the atomic and electronic degrees of freedom using the conjugate gradient iterative technique with an energy cutoff of 800 eV for the plane-wave basis set, and  $4 \times 4 \times 4$ ,  $8 \times 8 \times 8$ , and  $8 \times 8 \times 8$  *k*-meshes, for fcc-C<sub>136</sub>, sc-C<sub>46</sub>, and hex-C<sub>40</sub>, respectively, in the Brillouin zone. Forces on the ions are calculated through the Hellmann– Feynman theorem allowing a full geometry optimization. The search for the pressure effect are considered with a wide pressure range of 0–40 GPa. Phonon calculations are performed using the package FROPHO (Ref. 23) with the forces calculated from VASP.



FIG. 1. (Color online) Cell representation of (a) fcc- $C_{136}$ , (b) sc- $C_{46}$ , and (c) hex- $C_{40}$  carbon clathrates following variable cell optimization.

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<sup>&</sup>lt;sup>a)</sup>Electronic mail: wjt@aphy.iphy.ac.cn.



FIG. 2. (Color online) Total energy as a function of the volume for structures  $fcc-C_{136}$ ,  $sc-C_{46}$ ,  $hex-C_{40}$ ,  $C_{60}$  polymer (Ref. 4), and *M*-carbon (Ref. 18) in comparison with diamond and graphite.

#### **III. RESULTS AND DISCUSSION**

We first examine the ground state structural stability at 0 K and 0 GPa conditions. Figure 2 shows the calculated total

energy as a function of the volume for fcc-C<sub>136</sub>, hex-C<sub>40</sub>, sc-C<sub>46</sub>, 2D-C<sub>60</sub> polymer,<sup>4</sup> and M-carbon<sup>18</sup> in comparison with graphite and diamond. The relative stability order is hexagonal graphite>diamond>fcc- $C_{136}$ >sc- $C_{46}$ >hex- $C_{40}$ >M-carbon $>C_{60}$  with energy differences of 0.133, 0.207, 0.239, 0.260, 0.295, and 0.387 eV per atom, respectively, relative to graphite. The fcc- $C_{136}$  as the third most stable phase locates at a considerable volume range of 6.35–7.4 Å<sup>3</sup> per atom between graphite and diamond phases. The fcc- $C_{136}$  is more stable than sc- $C_{46}$ , hex- $C_{40}$ , C<sub>60</sub>, and *M*-carbon energetically, but less stable than the diamond phase with an energy loss of 0.075 eV per atom. Similar behavior is also found for Si clathrates. The fcc-Si<sub>136</sub> is more stable than sc-Si<sub>46</sub> and hex-Si<sub>40</sub>, while less stable than diamond-structured Si with an energy loss of 0.062 eV per Si atom, in good agreement with the value of 0.08 eV reported by San-Miguel et al.<sup>12</sup> This relative structural stability is attributed to the small angle distortions of the  $sp^3$  bonds in clathrates.<sup>24</sup> By fitting the energy versus volume data to the Birch–Murnagham form, we get the equilibrium volume  $V_0$ =6.60 Å<sup>3</sup>, lattice parameter  $a_0$ =9.65 Å, and bulk modulus  $B_0$ =3.68 Mbars for carbon clathrate C<sub>136</sub>. The bulk modulus is practically the same for all the three clathrates and about 15% less than that of diamond. The same results are also obtained by the DMOL<sup>3</sup> method.<sup>25</sup> The calculated lattice parameters, cohesive energy with available experimental data,<sup>26,27</sup> and calculated data<sup>12,15</sup> are listed in Table I. The other possible zeolite-type structures<sup>24</sup> such as tetragonal C<sub>172</sub> (P4<sub>2</sub>/mnm) and hex-C<sub>34</sub> (P6/mmm) are all less stable in energy and are omitted here.

We now consider the pressure effect on structural stabil-

TABLE I. Calculated equilibrium volume ( $V_0$  in Å<sup>3</sup>/atom), lattice parameters ( $a_0$ ,  $c_0$  in Å), cohesive energy (eV/atom), and bulk modulus ( $B_0$  in Mbar) for fcc-C<sub>136</sub>, sc-C<sub>46</sub>, hex-C<sub>40</sub>, diamond, and graphite at zero pressure, compared to available experimental data (Refs. 26 and 27) for diamond and graphite and calculated data (Refs. 12 and 15) for C<sub>46</sub> and C<sub>136</sub>.

Structure	Method	V <sub>0</sub> (Å <sup>3</sup> )	$\stackrel{a_0}{({ m \AA})}$	с <sub>0</sub> (Å)	$E_{\rm coh}$ (eV)	B <sub>0</sub> (Mbar)
fcc-C <sub>136</sub>	VASP	6.601	9.647		-7.709	3.680
	DMOL <sup>3</sup>	6.688	9.689		-7.263	3.637
	DFT <sup>a</sup>					3.98
sc-C <sub>46</sub>	VASP	6.543	6.702		-7.677	3.637
	DMOL <sup>3</sup>	6.604	6.722		-7.235	3.586
	VASP <sup>b</sup>	6.526	6.696			3.71
hex-C <sub>40</sub>	VASP	6.609	6.695	6.809	-7.656	3.601
	DMOL <sup>3</sup>	6.697	6.725	6.839	-7.213	3.505
Diamond	VASP	5.705	3.574		-7.783	4.291
	DMOL <sup>3</sup>	5.787	3.591		-7.350	4.405
	Expt. <sup>c,d</sup>	5.673	3.567		-7.20	4.43
Graphite	VASP	8.878	2.470	6.721	-7.916	2.757
	DMOL <sup>3</sup>	8.983	2.479	6.747	-7.516	2.629
	Expt. <sup>c,d</sup>	8.803	2.462	6.708	-7.40	2.86

<sup>a</sup>Reference 12.

<sup>b</sup>Reference 15.

<sup>c</sup>Reference 26.

<sup>d</sup>Reference 27.



FIG. 3. (Color online) Relative enthalpy vs pressure phase diagram for structures fcc- $C_{136}$ , sc- $C_{46}$ , hex- $C_{40}$ , diamond, and *M*-carbon. Enthalpies are measured relative to that of hexagonal graphite.

ity and transformation, which is a topic of considerable interest.<sup>28–31</sup> Neglecting temperature and zero-point motion effects, the phase with the lowest enthalpy H=E+pV is the most stable one. The relative enthalpy as a function of pressure relative to graphite is presented in Fig. 3 for fcc- $C_{136}$ , hex-C<sub>40</sub>, sc-C<sub>46</sub>, M-carbon, and diamond, respectively. Based on the calculated enthalpy data, the structural transition points are estimated to be 6.5, 17, and 21 GPa from graphite to diamond,  $C_{136}$ , or to *M*-carbon, respectively. The fcc- $C_{136}$ structure is always more stable than hex- $C_{40}$  and sc- $C_{46}$ clathrates over the entire studied pressure range, but less stable than M-carbon as the pressure exceeds 26 GPa. It suggests that the relative structural stability could be controlled by applied pressure, while the limit of each structural series is diamond to form *regular*  $sp^3$  bonds<sup>24</sup> under finite pressure. Experimentally, it has been found that the highpressure phase transformation from graphite to diamond at room temperature occurs with a starting uniaxial (along the cdirection) pressure of ~15 GPa (Refs. 28-31) via an intermediate phase such as *M*-carbon.<sup>18</sup> Our calculated results identify fcc-C136 clathrate as another metastable phase at high pressure with competitive enthalpy.

Since energetic calculations alone cannot establish the stability of a crystal structure, a thorough analysis of the elastic and dynamic stability is required.<sup>32</sup> To investigate the structural stability, phonon dispersions at ambient pressure were calculated with *ab initio* methods.<sup>23</sup> The phonon dispersion and density of states (PDOS) of fcc-C<sub>136</sub> versus diamond are presented in Fig. 4. The results show that there are no negative phonon modes, confirming that the structure is mechanically stable at ground state. The highest phonon fre-



FIG. 4. (Color online) PDOS of fcc- $C_{136}$  (a) vs diamond (b).

quency of fcc- $C_{136}$  phase is calculated to be 1256 cm<sup>-1</sup>, which is about 5% lower than the calculated highest phonon frequency of 1326 cm<sup>-1</sup> for diamond.

Finally, we discuss possible synthesis of  $fcc-C_{136}$ . The group-IV element clathrates are essentially extended fullerenes as have been demonstrated experimentally in Si and Ge clathrate structures. Even though there is so far no evidence of the existence of such a phase of fcc-C<sub>136</sub>, the reports of the synthesis of crystals made out of connected C60 (Ref. 33) and C<sub>36</sub> (Refs. 34 and 35) provide strong indications that carbon clathrates can be produced. There are at least two possible ways to synthesize fcc-C<sub>136</sub>: a direct synthesis from the reduction of a stable fullerene form such as C<sub>28</sub>H<sub>4</sub> and C<sub>20</sub>H<sub>20</sub>; or an indirect way by the aggregation of small metallofullerenes M@C28. The latter scenario is supported by experimental evidence that confirmed the presence of significant amounts of Ti@C28, Zr@C28, and Hf@C28 in the mass spectrum obtained from laser vaporization of graphite/metal-oxide composite disks.<sup>36</sup> As discussed in Ref. 11, in silicon clathrate (and the same applies for Ge clathrates), the synthesis of the Si<sub>136</sub> structure has always been obtained by emptying of guest atoms in the NarSi136 clathrate structure. Our further calculations show that the group-IV transition metals (Ti, Zr, and Hf) are maybe one of the potential guest atoms for the synthesis of the  $C_{136}$  carbon clathrates following the same path than silicon clathrates.

## **IV. CONCLUSION**

In summary, we have studied the phase stability of carbon clathrates at high pressure by *ab initio* calculations. Our results identify fcc- $C_{136}$  as the third most state carbon phase after diamond and graphite. A pressure-induced structural transition from hexagonal graphite to fcc- $C_{136}$  is predicted to occur around 17 GPa. The phonon dispersion calculations show that fcc- $C_{136}$  clathrate is dynamically stable. These results establish benchmarks for this new carbon structure and have broad implications for fundamental understanding of phase transformations and pressure effect on the fullerenes and related materials.

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