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Ab initio prediction of superdense tetragonal and monoclinic polymorphs of carbon

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The design and synthesis of three-dimensional denser carbons are one of the hot issues in condensed matter physics because of their fascinating properties. Here we identify by *ab initio* calculations several tetragonal and monoclinic polymorphs of carbon that adopt the $t32$, $t32^*$, $m32$, and $m32^*$ structures in $P\bar{4}2_1c$, $P4_32_12$, $P2_1/c$, and $C2$ symmetry, respectively. These carbon polymorphs have large 32-atom unit cells in all-sp^3 bonding networks comprising five- and six-membered rings that are dynamically stable, as verified by a phonon mode analysis. Electronic band structure calculations show that they are insulators with band gaps in the range of 5.19–5.41 eV, close to the calculated band gap of 5.34 eV for diamond. Remarkably, these carbon phases possess an extremely high atom number density exceeding that of diamond. The present results establish different types of carbon phases and offer insights into their outstanding structural and electronic properties.

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I. INTRODUCTION

The synthesis and characterization of novel carbon phases of fullerenes [1], nanotubes [2], and graphene [3] are prominent milestones in materials research. The tremendous success of these materials has invigorated the search for additional carbon polymorphs that may also exhibit extraordinary properties [4]. Under high static pressure and high temperature conditions, graphite can be converted to cubic diamond or twinned cubic diamond with $\{111\}$ hexagonal-diamond-like stacking faults [5]. Recent advances include the transformation of the cold-compressed graphite [6] into superhard carbon phases [7–12] with a strength superior to diamond [13], and the synthesis of new carbon phases with unusual bonding configurations by heating carbon soot or shock compressing polycrystalline graphite [14–17], which led to a body-centered-cubic BC12 carbon phase [18]. Although diamond is the densest known three-dimensional carbon allotrope in a wide range of pressures, theoretical studies proposed $hP3$ and $tI12$ carbon structures [19] to be denser than diamond, as BC8 carbon [20–22]. Searching for different superdense carbon allotropes should provide an excellent account for the modification of the structural and electronic properties of carbon.

Carbon crystals share many structural similarities with silicon and germanium because of their common s^2p^2 valence electron configuration [23,24], and thus it is instructive to compare the structural form and relation among various polymorphs of these elements. Silicon and germanium crystallize in a cubic diamond structure at ambient conditions; they transform to the β-Sn phase at high pressure and turn into the BC8 and $R8$ Si and ST12 Ge phases upon decompression [25–27]. The BC8 structure is adopted by a high-pressure carbon phase at ~1100 GPa [20–22], and this structure is also present in diamondlike carbon thin films [28]. Most recently an ultrafast laser-induced confined microexplosion experiment [29] produced several new Si phases, including previously predicted ST12 and BT8 Si [30,31], and two new tetragonal $t32$ and $t32^*$ Si [29]. In addition, two monoclinic structures $m32$ and $m32^*$ are identified as dense metastable Si phases based on a search of the *ab initio* random structure [29]. These structures may be adopted by carbon phases under appropriate conditions, and this insight offers an avenue for exploring carbon allotropes produced in various dynamic and catalyzed synthesis processes.

In this paper, we report on an *ab initio* study of tetragonal and monoclinic polymorphs of carbon that adopt the $t32$, $t32^*$, $m32$, and $m32^*$ structures in $P\bar{4}2_1c$, $P4_32_12$, $P2_1/c$, and $C2$ symmetry, respectively. These structures have large 32-atom conventional cells in all-sp^3 bonding networks comprising five- and six-membered rings, and they are more favorable than the cubic BC12 carbon structure [18] in energy. Phonon calculations confirm that these superdense carbon polymorphs are dynamically stable, and electronic band structure calculations show that they are insulators with band gaps in the range of 5.19–5.41 eV, close to 5.34 eV for diamond. These carbon phases possess an extremely high atom number density exceeding that of diamond, making them superdense carbon polymorphs. Simulated x-ray diffraction patterns of these carbon polymorphs match well the distinct diffraction peak around 50.8° found in experiments relative to the so-called n-diamond [32–37].

II. COMPUTATIONAL METHOD

The calculations were carried out using the density functional theory as implemented in the Vienna *ab initio* simulation package (VASP) [38]. Both the local density approximation (LDA) in the form of Ceperley-Alder [39] and generalized gradient approximation (GGA) developed by Perdew, Burke, and Ernzerhof [40] are used for the exchange-correlation energy functional. The all-electron projector augmented wave (PAW) [41] method is adopted with $2s^22p^2$ treated as valence electrons. We used a plane-wave basis set with an energy cutoff of 800 eV. The structural geometries are optimized with symmetry constraints until the remaining atomic forces are less than 10^{-4} eV/Å and the energy convergence criterion

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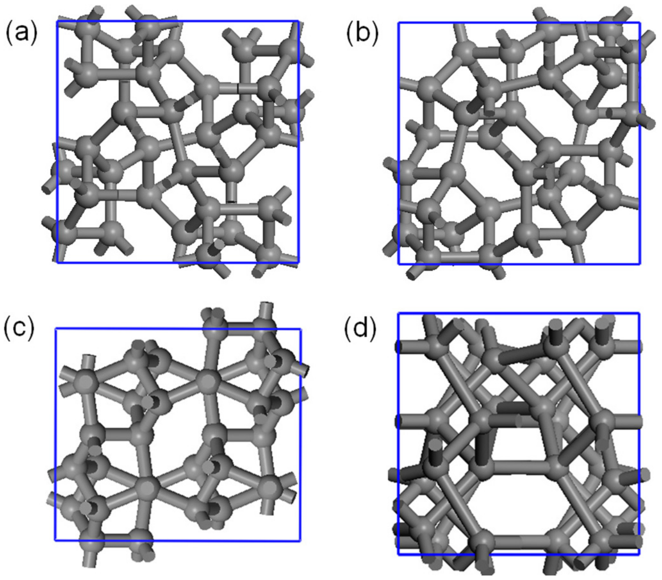

FIG. 1. Crystalline structures of (a) $t32$, (b) $t32^*$, (c) $m32$, and (d) $m32^*$ carbon polymorphs in $P\bar{4}2_1c$, $P4_32_12$, $P2_1/c$, and $C2$ symmetry, respectively.

is set at 10^{-6} eV. Electronic band structures are calculated using the Heyd-Scuseria-Ernzerhof hybrid functional (HSE06) [42] under GGA. Phonon calculations are performed using the PHONOPY package [43,44] with the forces calculated from VASP.

III. RESULTS AND DISCUSSION

We first characterize the four carbon structures shown in Fig. 1, which all have a 32-atom conventional cell in all-sp^3 bonding networks comprising five- and six-membered rings. The $t32$ structure has four $8e$ Wyckoff positions: $C1$ (0.5296, 0.3763, 0.7723), $C2$ (0.3778, 0.2777, 0.0308), $C3$ (0.0276, 0.3767, 0.2792), and $C4$ (0.2802, 0.8746, 0.0283) in $P\bar{4}2_1c$ symmetry with equilibrium lattice parameters $a = 6.282$ Å and $c = 4.423$ Å. The $t32^*$ structure has four $8b$ Wyckoff positions: $C1$ (0.3745, 0.5279, 0.0927), $C2$ (0.2806, 0.6220, 0.6004), $C3$ (0.8742, 0.2763, 0.8478), and $C4$ (0.5304, 0.1233, 0.8485) in $P4_32_12$ symmetry with equilibrium lattice parameters $a = 6.281$ Å and $c = 4.426$ Å. The $m32$ structure has eight $4e$ Wyckoff positions: $C1$ (0.6563, 0.4989, 0.3482), $C2$ (0.1702, 0.6521, 0.1714), $C3$ (0.9301, 0.2476, 0.6250), $C4$ (0.6692, 0.6515, 0.6745), $C5$ (0.0741, 0.6539, 0.5736), $C6$ (0.1568, 0.9991, 0.3463), $C7$ (0.3174, 0.2515, 0.1227), and $C8$ (0.4305, 0.1526, 0.4219) in $P2_1/c$ symmetry with equilibrium lattice parameters $a = 3.847$ Å, $b = 6.273$ Å, $c = 7.352$ Å, and $\beta = 80.035°$. The $m32^*$ structure has eight $4c$ Wyckoff positions: $C1$ (0.8448, 0.3616, 0.1252), $C2$ (0.0980, 0.1044, 0.6246), $C3$ (0.6519, 0.0482, 0.0278), $C4$ (0.3436, 0.0534, 0.4691), $C5$ (0.3991, 0.8024, 0.6223), $C6$ (0.6543, 0.5536, 0.1237), $C7$ (0.6548, 0.3588, 0.7816), and $C8$ (0.8460, 0.8624, 0.7237) in $C2$ symmetry with equilibrium lattice parameters $a = 6.275$ Å, $b = 4.432$ Å, $c = 8.879$ Å, and $\beta = 135.063°$. Remarkably, these carbon phases are 1.1%–1.2% denser than diamond (see Table I), making them superdense carbon polymorphs.

TABLE I. Calculated equilibrium structural parameters (volume per atom V_0, density ρ), total energy per atom E_{tot}, and bulk modulus B_0 for diamond, $R8$, BT8, BC8, ST12, bct4, $t32$, $t32^*$, $m32$, and $m32^*$ carbon, compared to available experimental data for diamond [47].

Carbon	Method	V_0 (Å^3)	ρ (g/cm^3)	E_{tot} (eV)	B_0 (GPa)
Diamond	LDA	5.52	3.616	−10.134	452
	GGA	5.70	3.502	−9.094	418
	Expt. [47]	5.67	3.520		442
$R8$	LDA	5.46	3.660	−9.323	384
	GGA	5.65	3.532	−8.277	348
BT8	LDA	5.70	3.637	−9.281	370
	GGA	5.94	3.508	−8.237	333
BC8	LDA	5.41	3.684	−9.447	409
	GGA	5.61	3.556	−8.399	372
ST12	LDA	5.47	3.657	−9.248	417
	GGA	5.66	3.536	−8.205	379
bct4	LDA	5.83	3.423	−9.914	421
	GGA	6.02	3.315	−8.900	390
BC12	LDA	5.58	3.576	−9.235	428
	GGA	5.76	3.461	−8.205	393
$t32$	LDA	5.47	3.657	−9.326	390
	GGA	5.66	3.530	−8.280	352
$t32^*$	LDA	5.47	3.655	−9.327	388
	GGA	5.67	3.528	−8.281	351
$m32$	LDA	5.47	3.652	−9.304	381
	GGA	5.67	3.524	−8.259	345
$m32^*$	LDA	5.46	3.659	−9.347	389
	GGA	5.66	3.531	−8.301	353

Figure 2(a) shows the total energy as a function of volume for $t32$, $t32^*$, $m32$, and $m32^*$ carbon compared to the results for several known carbon structures that are in all-sp^3 bonding form, including BC12, BC8, BT8, $R8$, ST12, and bct4 [8] carbon. Our calculated energetic data establish the stability sequence: BC12 $<$ ST12 $<$ BT8 $<$ $m32$ $<$ $R8$ $<$ $t32 \simeq t32^*$ $<$ $m32^*$ $<$ BC8 $<$ bct4 $<$ diamond. We can see that the four identified carbon structures are energetically less stable than BC8, but more stable than BC12 carbon [18] as found in recent shock-compressed experiments [15]. From the Murnaghan fit [45] of the total-energy curves, the bulk modulus (B_0) of $t32$, $t32^*$, $m32$, and $m32^*$ carbon are obtained as 390, 388, 381, and 389 GPa, respectively. These values are lower than that for diamond (452 GPa), but very closed to the value for c-BN (396 GPa) [46], suggesting that they belong to the superhard material family.

The calculated equilibrium volume per atom V_0, bulk density ρ, total energy per atom E_{tot}, bulk modulus B_0 for diamond, $R8$, BT8, BC8, ST12, bct4, BC12, $t32$, $t32^*$, $m32$, and $m32^*$ carbon are listed in Table I. Note that in dense covalent systems the bulk modulus strongly correlates with the average interatomic distance and approximatively meets the Cohen's relation $B = 1972d^{-3.5}$ (B in GPa and d in Å) [48]. For diamond, the C-C bond length is 1.53 Å, and the corresponding bulk modulus is 445 GPa using the formula, while for $t32$, $t32^*$, $m32$, and $m32^*$ carbon, the average C-C bond length is about 1.57 Å, which results in a smaller bulk modulus of 406 GPa. Thus the very similar bulk moduli (between 381 and 390 GPa) for the four carbon phases are

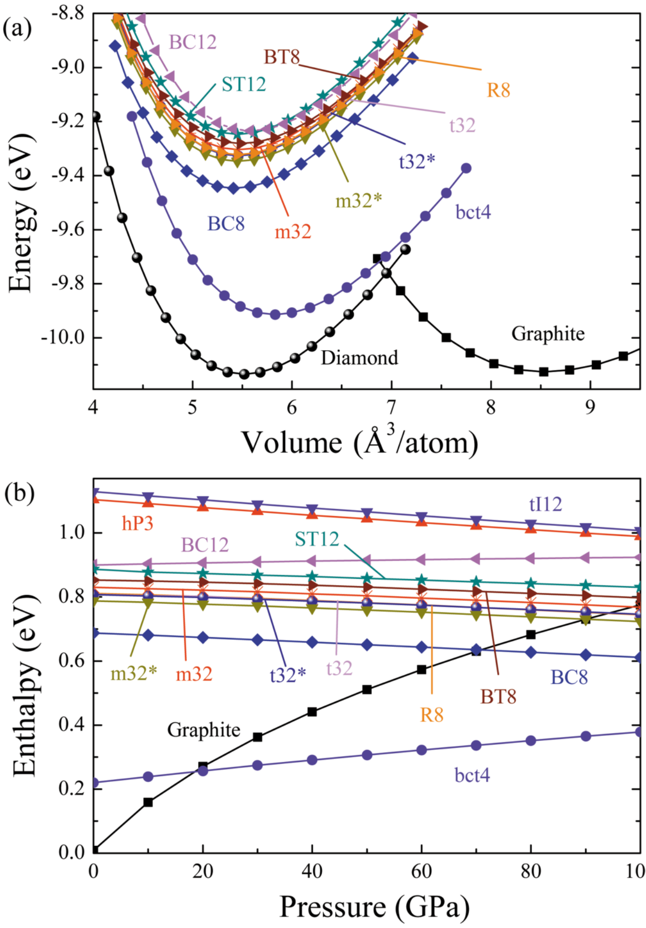

FIG. 2. (a) The energy-volume and (b) the enthalpy-pressure relations for $t32$, $t32^*$, $m32$, and $m32^*$ carbon compared to BC12, BC8, BT8, $R8$, ST12, bct4, diamond, and graphite. The enthalpy is measured relative to the value for cubic diamond.

significantly smaller than 452 GPa for the diamond structure, which can be explained by the differences in the average C-C interatomic distances.

Figure 2(b) shows the enthalpy as a function of pressure for the various carbon phases studied here. The results show that all the superdense tetragonal and monoclinic carbon polymorphs are energetically competitive compared to the previously identified all-sp^3 carbon phases in a wide range of pressure. In particular, the $m32^*$ structure is more favorable throughout the pressure range than the previously predicted metastable $R8$, BT8, and ST12 carbon phases. We also examined the enthalpy of recently proposed $hP3$ and $tI12$ superdense carbon structures [19], and the results show that both structures have much higher enthalpy in the entire pressure range and, therefore, are energetically less favorable than our $t32$, $t32^*$, $m32$, and $m32^*$ carbon phases.

To provide more information and characters for possible experimental observation, we have simulated the x-ray diffraction (XRD) spectra at 0 GPa with an x-ray wavelength of 1.5406 Å. We plot in Fig. 3(a) the simulated XRD patterns for $t32$, $t32^*$, $m32$, and $m32^*$ carbon compared to graphite, diamond, bct4, $R8$, BT8, BC8, and ST12 carbon. It shows a high intensity and sharp peak at 50.8° for $t32$, $t32^*$, $m32$, and $m32^*$ carbon, and this peak matches well with the main peaks of $R8$, BT8, and BC8 carbon. Meanwhile, the other peaks are negligibly small for $t32$, $t32^*$, $m32$, and $m32^*$ carbon, while there is a sharp second diffraction peak around 28.5° for $R8$ and BT8 and 40.8° for BC8 carbon. These results suggest that the $m32$, $t32$, $t32^*$, and $m32^*$ phases are likely candidates for the superdense polymorphs of carbon as well as BC8 carbon, among which the $m32^*$ phase is the most energetically favorable (see Fig. 2) and, therefore, the dominant phase.

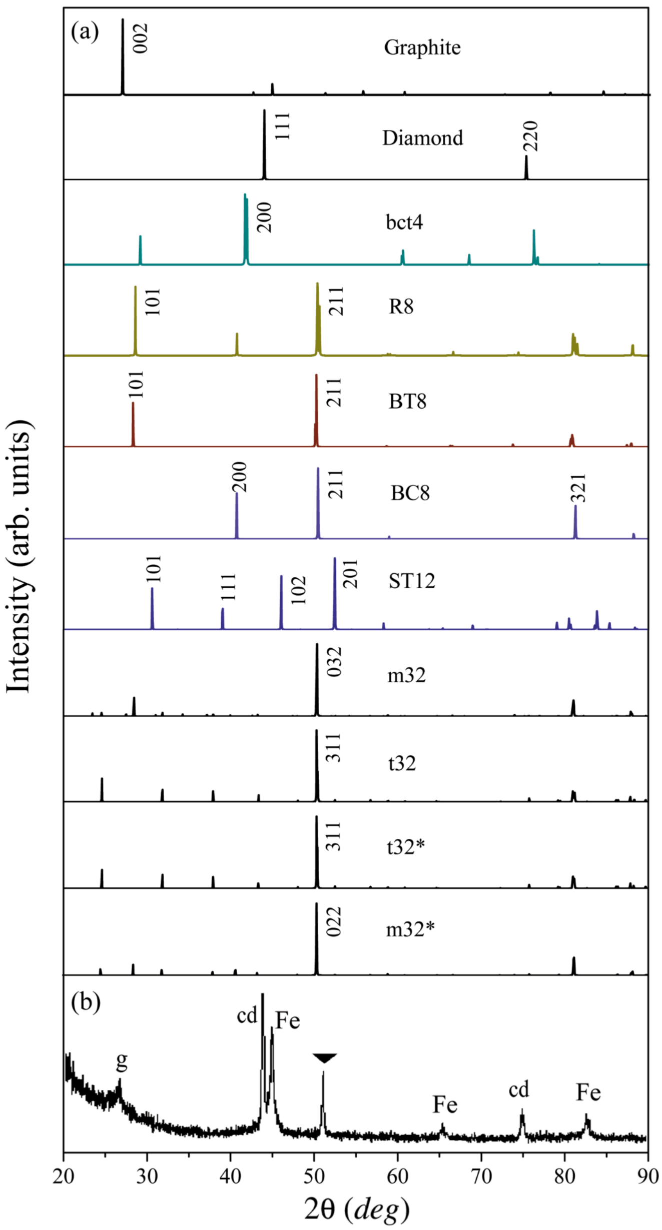

FIG. 3. (a) Simulated XRD patterns for $t32$, $t32^*$, $m32$, and $m32^*$ carbon compared to graphite, diamond, bct4, $R8$, BT8, BC8, and ST12 carbon at 0 GPa. An x-ray wavelength of 1.5406 Å is used with a copper source. (b) Experimental XRD patterns for Fe-catalyzed carbon black heat treatment at 1400 °C [35]. Symbols: g = graphite, cd = cubic diamond, ▼ denotes the peak for n-diamond.

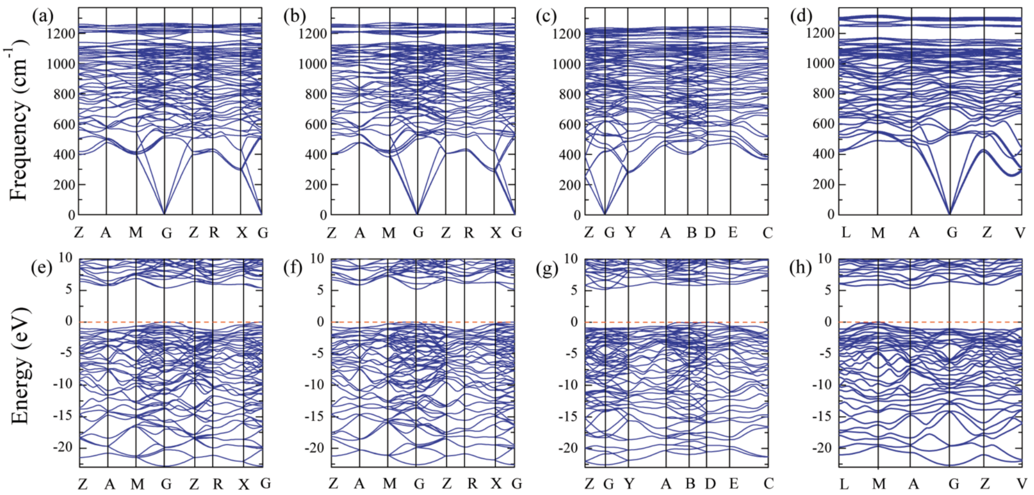

FIG. 4. Calculated phonon band structures (a)–(d) and electronic band structures (e)–(h) for $t32$, $t32^*$, $m32$, and $m32^*$ carbon at 0 GPa.

It is worth noting that an allotrope of carbon, so-called n-diamond [32–37], exhibits a distinct diffraction peak around 50.8° that is very close to the main peak of these carbon polymorphs. For comparison, typical experimental XRD spectra found in Fe-catalyzed carbon black heat treatment at 1400 °C [35] are shown in Fig. 3(b). It is suggested that the proposed superdense carbon phases may be related to the n-diamond.

Finally, we discuss the phonon and electronic band structures of the superdense tetragonal and monoclinic carbon polymorphs. The obtained phonon dispersion curves [see Figs. 4(a)–4(d)] show no imaginary frequencies throughout the Brillouin zone, thus confirming their dynamical stability. The highest phonon frequencies for $t32$, $t32^*$, $m32$, and $m32^*$ carbon are 1265, 1269, 1244, and 1320 cm^{-1}, respectively, which are slightly lower than 1350 cm^{-1} for perfectly sp^3 bonded diamond [49]. These results, together with other details on the phonon spectra, offer useful guidance in characterizing these carbon polymorphs in the synthesized specimen. Meanwhile, the calculated HSE06 band gap (5.34 eV) for diamond is very close to the experimental data (5.47 eV) [47], validating the HSE06 level calculations in predicting the band gaps for diamond and similar sp^3 bonded carbon structures. Our calculations reveal the insulating characters of $t32$, $t32^*$, $m32$, and $m32^*$ carbon with band gaps of 5.41, 5.23, 5.19, and 5.34 eV, respectively, as shown in Figs. 4(e)–4(h), which are close to the value (5.34 eV) for diamond. Interestingly, both the valence band top and conduction band bottom of $t32$ carbon are at the Γ point, making it a direct band gap insulator. These carbon polymorphs are expected to possess extraordinary structural, mechanical, and optical properties, such as an extremely high atom density, superhardness, and very high refractive indices [19].

IV. SUMMARY

In summary, we have identified by *ab initio* calculations four superdense carbon polymorphs, $t32$, $t32^*$, $m32$, and $m32^*$, that possess the space group $P\bar{4}2_1c$, $P4_32_12$, $P2_1/c$, and $C2$, respectively. They each contain 32 atoms in the conventional cell and are denser than diamond in all-sp^3 bonding networks. Total-energy calculations show that they are energetically less stable than BC8, but more stable than BC12 carbon [18] as found in recent shock-compressed experiments [15]. The dynamic stability of these structures is verified by a phonon mode analysis with large bulk moduli of 381–390 GPa, close to the value for c-BN (396 GPa) [46], suggesting that they belong to the superhard material family. Electronic band calculations indicate that they are insulators with band gaps in the range 5.19–5.41 eV as well as diamond. Simulated XRD patterns suggested that the proposed superdense carbon phases may be related to the n-diamond with a distinct diffraction peak around 50.8° found in experiments [32–37].

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