

## Hypothetical hard structures of carbon with cubic symmetry

Filipe J. Ribeiro,<sup>1,2</sup> Paul Tangney,<sup>3</sup> Steven G. Louie,<sup>1,2</sup> and Marvin L. Cohen<sup>1,4</sup>

<sup>1</sup>Department of Physics, University of California, Berkeley, California 94720-0001, USA

<sup>2</sup>Material Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720-0001, USA

<sup>3</sup>The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California 94720-0001, USA

<sup>4</sup>Material Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720-0001, USA

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In this work we performed *ab initio* pseudopotential, density functional calculations of the structure and electronic properties of two hypothetical carbon structures with cubic symmetry:  $C_6$  bcc, body centered with 12 atoms per cubic unit cell, and  $C_{20}$  sc, simple cubic with 20 atoms per unit cell. The former is semiconducting with an indirect gap of 2.5 eV—within the local density approximation to the exchange and correlation energy functional—while the latter is metallic. Both have similar zero-pressure densities of about one atom per  $6.9 \text{ \AA}^3$ , which is intermediate between graphite and diamond, and similar bulk moduli of about 350 GPa at ambient conditions. Both are metastable with respect to graphite and diamond, and no phase transition is expected in the range of pressures studied.

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### I. INTRODUCTION

The most commonly known solid phases of pure carbon are graphite and diamond. Graphite is the stable phase at low pressures while diamond is stable at high pressures. Several other known metastable phases include hexagonal diamond or lonsdaleite, amorphous forms of carbon, and crystalline fullerenes.<sup>1</sup> Recently, Goresy *et al.*<sup>2</sup> reported on a new hard transparent phase found in a rock sample from the Popigai impact crater in Russia. Their x-ray results indicate that the new phase is not amorphous but cubic with  $Pm\bar{3}m$  space group symmetry, and a lattice constant of  $14.697(1) \text{ \AA}$ . At an estimated density of  $2.5 \text{ gm/cm}^3$ , the number of atoms per unit cell is about 400, or about one carbon atom per  $8 \text{ \AA}^3$ . For comparison, in graphite and diamond there is one carbon atom per  $8.8 \text{ \AA}^3$  and  $5.67 \text{ \AA}^3$ , respectively.<sup>3,4</sup>

In this work we study the electronic and structural properties of two possible, very simple, cubic polymorphs of carbon, that, because of the constraints of the cubic symmetry, are most likely present in some form as building blocks in the Popigai phase. The two structures are  $C_6$  bcc with 12 atoms/cell and body-centered cubic symmetry, and  $C_{20}$  sc with 20 atoms/cell and simple cubic symmetry.

### II. STRUCTURES

Figures 1(a) and 1(b) show two different views of the proposed  $C_6$  bcc structure. This structure which is body-centered cubic with  $Im\bar{3}m$  space group symmetry, has 12 atoms per body-centered cubic unit cell—or six atoms in the primitive unit cell—each in the Wyckoff position  $12d$ . The geometry of the structure can be described by a single internal free parameter such as the interatomic distance, the lattice constant, or the volume. Each carbon atom is bound to four other carbon atoms, and the angles between bonds are either  $90^\circ$  or  $120^\circ$ .

In Figs. 1(c) and 1(d), two different views of the  $C_{20}$  sc structure are shown. This structure is composed of 20 atoms per unit cell, and the unit cell is simple cubic with  $Pm\bar{3}m$  space group symmetry and has three internal degrees of free-

dom. In each unit cell there are eight and 12 atoms in the  $8g$  and  $12j$  Wyckoff positions, respectively. Each  $8g$  atom has three  $12j$  nearest neighbors with bond angles close to  $120^\circ$ . Each  $12j$  atom has two  $8g$  and two  $12j$  nearest neighbors and one bond angle of  $90^\circ$  and five bond angles close to  $113^\circ$ . See Table I for more details on the structural parameters.

### III. CALCULATION

The total energies of the studied systems were calculated using density functional theory (DFT),<sup>5,6</sup> where the local density approximation<sup>7,8</sup> (LDA) to the exchange and correlation energy functional was used. The interaction between the cores (core electrons and nucleus) and the valence electrons was modeled by *ab initio*,<sup>9</sup> separable,<sup>10</sup> norm-conserving Troullier-Martins<sup>11</sup> pseudopotentials. The electronic wave functions were expanded as linear combinations of plane waves with energies up to 70 Ry. The Brillouin zone was sampled on a uniform grid of  $k$  points.<sup>12</sup> The electronic densities of states were calculated using the tetrahedron method.<sup>13</sup>

Forces and stresses were obtained with the Hellmann-Feynman theorem and the internal degrees of freedom of the

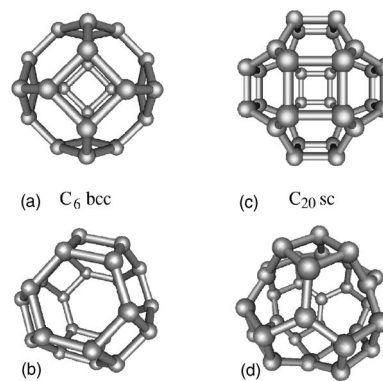


FIG. 1. Views of the two proposed cubic structures. (a) Front and (b) slanted views of the  $C_6$  bcc structure and (c) front and (d) slanted views of the  $C_{20}$  sc structure.

$C_{20}$  sc system were relaxed using a quasi-Newton method.<sup>14</sup> The zero-pressure energy, volume, and bulk modulus were obtained by fitting the values of the calculated energies at various volumes to a five-parameter empirical function described elsewhere.<sup>15</sup> Using the derivatives of this fitting function the pressure-dependent enthalpy and bulk modulus were obtained.

Molecular dynamics simulations<sup>16</sup> based on the extended Tersoff-Brenner potential<sup>17</sup> were performed on the equilibrium configurations of the proposed structures to investigate their dynamic stability.

#### IV. RESULTS

Figures 2(a)–2(c), show results for the calculated energy versus volume, enthalpy versus pressure, and bulk modulus versus pressure, respectively for diamond, graphite,  $C_6$  bcc, and  $C_{20}$  sc. Graphite and diamond results are included for the purpose of comparison. In Table II, for the same structures, the calculated zero-pressure energies, volumes and bulk moduli are given, together with existing experimental values. The total energy values are given with respect to the total energy of diamond at zero pressure. Experimentally the cohesive energy of diamond is lower than the cohesive energy of graphite by about 25 meV,<sup>21</sup> which contrasts with our calculated energy difference of  $-12$  meV. Nevertheless, our result is in agreement with previous DFT LDA calculations,<sup>22–24</sup> and the difference with experiment is likely to be connected to the fact that the van der Waals interaction is incorrectly described by the LDA. This inaccuracy is small compared to the cohesive energy differences of the  $C_{20}$  sc and  $C_6$  bcc structures and does not affect the conclusions of this work.

The zero-pressure total energies per atom of the two proposed structures,  $C_6$  bcc and  $C_{20}$  sc, are 0.46 and 0.69 eV/atom above that of diamond, respectively. In both structures the bonds associated with the atoms of coordination number 4 ( $12j$  in  $C_{20}$  sc and  $12d$  in  $C_6$  bcc) are very distorted compared to the ideal  $sp^3$  hybridization present in diamond. In other words, the four member rings present in both structures are responsible for most of the energy difference. Moreover, in  $C_{20}$  sc the electrons of the atoms with coordination number 3 that are not  $sp^2$  hybridized ( $p_z$ ) do not form a bond and therefore raise the energy further.

The volumes per atom of the  $C_6$  bcc and  $C_{20}$  sc phases are 6.84 and 6.91  $\text{\AA}^3$ , respectively, which correspond to densities lower than the density of diamond and higher than the den-

TABLE I. Calculated zero-pressure structure parameters for  $C_6$  bcc and  $C_{20}$  sc: cubic unit cell lattice constant  $a$ , Wyckoff positions, and nearest neighbor (NN) distances.

Structure	$a$ ( $\text{\AA}$ )	Wyckoff positions ( $r/a$ )	NN distance ( $\text{\AA}$ )
$C_6$ bcc	4.34	$12d$ (0.500, 0.250, 0.000)	1.53 ( $12d$ )
$C_{20}$ sc	5.17	$12j$ (0.500, 0.151, 0.151)	1.56 ( $12j$ )
		$8g$ (0.262, 0.262, 0.262)	1.47 ( $12j$ )

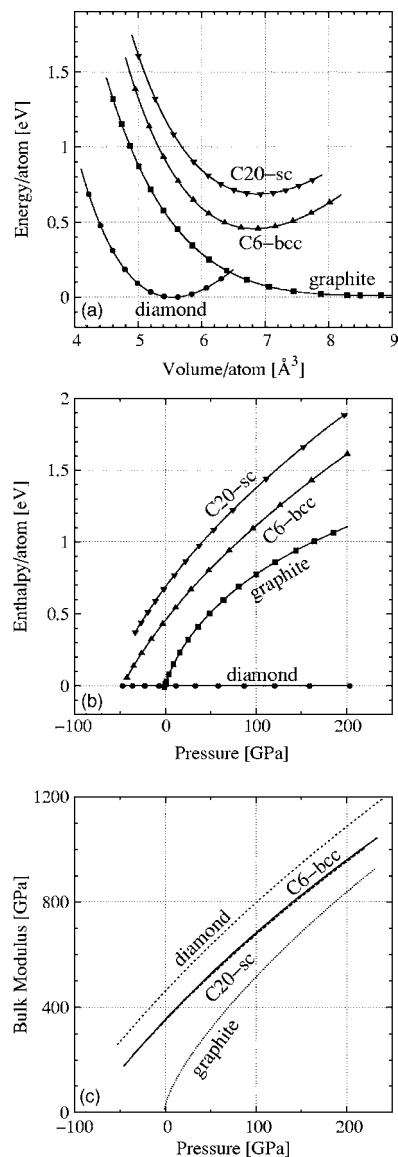


FIG. 2. Calculated (a) energy versus volume, (b) enthalpy versus pressure, and (c) bulk modulus versus pressure for diamond, graphite,  $C_6$  bcc, and  $C_{20}$  sc. In (a) and (b) the data points correspond to calculated values and the lines are numerical fits, and in (c) the lines were obtained from the second derivative of the numerical fit to the energy. The enthalpies at each pressure are plotted relative to the enthalpy of the diamond structure.

sities of graphite and the Popigai cubic phase.

Molecular dynamics simulations of both structures at temperatures exceeding 1000 K at zero pressure and extending for tens of picoseconds indicate that the structures are dynamically stable.<sup>16</sup> In Fig. 2(b) the intersection between the graphite and diamond enthalpy curves shows that both phases can coexist in thermodynamical equilibrium with each other close to zero pressure. Any pressure fluctuation tips the balance and favors the phase with lowest enthalpy. For the range of pressures studied, the enthalpies of both  $C_6$  bcc and  $C_{20}$  sc remain higher than the enthalpies of either graphite or diamond. Therefore, both cubic structures remain metastable with respect to graphite and diamond and cannot

TABLE II. Calculated zero-pressure energies/atom ( $E_{0 \text{ calc}}$ ), volumes/atom ( $V_{0 \text{ calc}}$ ), bulk moduli ( $B_{0 \text{ calc}}$ ), and Vickers hardness ( $H_v \text{ calc}$ ) for diamond, graphite, and the two proposed cubic structures. Total energies are shown relative to the energy of diamond. The Vickers hardness on  $C_6 \text{ bcc}$  was estimated using the semiempirical method of Ref. 18. Available experimental values ( $E_{0 \text{ exp}}$ ,  $B_{0 \text{ exp}}$ , and  $H_v \text{ exp}$ ) are also given for comparison.

Structure	$E_{0 \text{ calc}}$ (eV)	$V_{0 \text{ calc}}$ ( $\text{\AA}^3$ )	$V_{0 \text{ exp}}$ ( $\text{\AA}^3$ )	$B_{0 \text{ calc}}$ (GPa)	$B_{0 \text{ exp}}$ (GPa)	$H_v \text{ calc}$ (GPa)	$H_v \text{ exp}$ (GPa)
Diamond	0	5.55	5.67 <sup>a</sup>	460	443 <sup>b</sup>	93.6 <sup>c</sup>	96(5) <sup>c</sup>
Graphite	0.012	8.61	8.80 <sup>d</sup>	30	34 <sup>e</sup>		
$C_6 \text{ bcc}$	0.46	6.84		352		84.5	
$C_{20} \text{ sc}$	0.69	6.91		349			
Popigai			$\sim 8^f$				

<sup>a</sup>Reference 4.

<sup>b</sup>Reference 19.

<sup>c</sup>Reference 18.

<sup>d</sup>Reference 3.

<sup>e</sup>Reference 20.

<sup>f</sup>Reference 2.

be obtained in a direct way in high-pressure experiments. In addition, there is no obvious transition path from either graphite or diamond to  $C_6 \text{ bcc}$  or  $C_{20} \text{ sc}$ , suggesting very high energy barriers for these phase transitions.

The zero-pressure bulk modulus for both phases is very high at 352 and 349 GPa for  $C_6 \text{ bcc}$  and  $C_{20} \text{ sc}$ , respectively. The similarity between the calculated zero-pressure bulk moduli of both phases is not surprising given that both phases have similar zero-pressure densities with volumes per atom of 6.84 and 6.91  $\text{\AA}^3$  for  $C_6 \text{ bcc}$  and  $C_{20} \text{ sc}$ , respectively. Figure 2(c) shows that the bulk modulus increases monotonically with pressure for all the structures considered and is essentially the same for both  $C_6 \text{ bcc}$  and  $C_{20} \text{ sc}$ . Both cubic structures remain more compressible than diamond as the pressure is increased, and the trends of the curves suggest that diamond will remain the least compressible of the studied structures for much higher pressures.

The bulk modulus is not always a good indicator of the hardness of a substance. Using a semiempirical method for the calculation of the Vickers hardness for semiconductors<sup>18</sup> based on the electron density and bond lengths, the estimated hardness of  $C_6 \text{ bcc}$  of 84.5 GPa is close to but below the corresponding estimate for diamond of 93.6 GPa (the experimental Vickers hardness).

In Figs. 3(a) and 3(b), the electronic band structure and density of states of  $C_6 \text{ bcc}$  and  $C_{20} \text{ sc}$ , respectively, are shown. Electronically,  $C_6 \text{ bcc}$  is an insulator with an indirect LDA band gap of 2.5 eV. The real band gap should be higher since the LDA tends to underestimate band gaps. The top of the valence band of  $C_6 \text{ bcc}$  is located at the  $H$  symmetry point, in contrast to diamond where it is located at  $\Gamma$ . As pointed out earlier, the valence electrons in  $C_6 \text{ bcc}$  populate  $sp^3$ -like hybridized orbitals and give rise to  $\sigma$  bonds between nearest neighbors. It has been shown that, in  $\text{MgB}_2$ ,<sup>25–27</sup> and more recently in boron-doped diamond,<sup>28–31</sup> superconductivity is associated with a strong coupling between phonons and

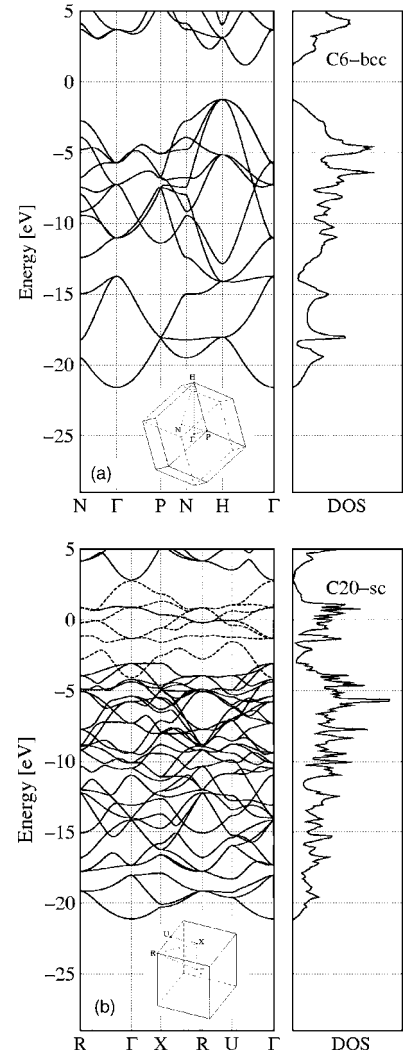


FIG. 3. Calculated electronic band structure and density of states of (a)  $C_6 \text{ bcc}$  and (b)  $C_{20} \text{ sc}$  at zero pressure. In the  $C_{20} \text{ sc}$  band structure the solid lines stand for  $sp^2$  and  $sp^3$  hybridized states while the dashed lines stand for the  $p_z$ -orbital-derived states (see text for details). The Fermi levels are at 0 eV.

$\sigma$ -bonding electrons. Since  $C_6 \text{ bcc}$  is also  $\sigma$  bonded, it is likely that boron-doped  $C_6 \text{ bcc}$ , if synthesized, would also undergo a superconducting transition. The detailed calculation of the superconducting transition temperature in this system is beyond the scope of this work.

In contrast to  $C_6 \text{ bcc}$ ,  $C_{20} \text{ sc}$  is a metal. In the band structure plot of  $C_{20} \text{ sc}$  in Fig. 3(b) the states with energies close to the Fermi energy (dashed lines) are associated with the  $p_z$  orbitals<sup>32</sup> of the atoms in the 8g Wyckoff positions. Because the  $p_z$  orbitals of different atoms overlap very weakly—the 8g atoms are only second-nearest neighbors to each other—the dispersion of the corresponding electronic bands is small and the density of states is very high. In graphite the bands that cross the Fermi level are also derived from  $p_z$  orbitals. However, in graphite the overlap between neighboring  $p_z$  orbitals is much stronger than in  $C_{20} \text{ sc}$ . This leads to a very wide electronic band and a much lower electronic density of states. Therefore  $C_{20} \text{ sc}$  should have a higher conductivity than graphite. If the high density of states at the Fermi en-

ergy is combined with strong electron-phonon coupling,  $C_{20}$  sc could potentially have interesting superconducting properties. However, the states at the Fermi level are not  $\sigma$ -bonding states and so there is no *a priori* reason to expect a strong coupling between electrons and phonons, as in the case of  $C_6$  bcc.

## V. CONCLUSIONS

In this work we have presented the results of calculations of two carbon structures with cubic symmetry that could be present in some form in a recently identified cubic polymorph of carbon found in a rock sample from the Popigai impact crater. We have shown that the proposed phases  $C_6$  bcc and  $C_{20}$  sc have cohesive energies that are 0.46 and 0.69 eV/atom smaller than diamond, respectively, and related this difference to the presence of four-member rings. Both structures have similar densities of about one atom per  $6.9 \text{ \AA}^3$  which is intermediate between diamond and graphite. At one atom per  $8 \text{ \AA}^3$ , the Popigai cubic phase is less dense than both  $C_{20}$  sc and  $C_6$  bcc. The calculations of the enthalpies as a function of pressure showed that, within the range of pressures studied, the proposed structures are metastable relative to both graphite and diamond. Also, there is no ob-

vious path for a phase transition to either of these structures, suggesting that energy barriers might be very high. Therefore it is not expected that these phases are achievable in high-pressure experiments. However, vapor deposition on a carefully engineered surface could be a viable alternative. At zero pressure the bulk moduli are 352 GPa for  $C_6$  bcc and 349 GPa for  $C_{20}$  sc and they increase monotonically with pressure without ever exceeding the bulk modulus of diamond. Also, the estimated Vickers hardness of the  $C_6$  bcc phase is 84.5 GPa which is lower than that of diamond at 93.6 GPa. Electronically,  $C_6$  bcc is a semiconductor with an indirect LDA gap of 2.5 eV, and, if synthesized and doped with boron, could have interesting superconducting properties similar to boron-doped diamond. In  $C_{20}$  sc, which is a metal with a relatively high density of states at the Fermi level, the possibility of superconductivity was also discussed.

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