

## Structural theory of graphite and graphitic silicon

M. T. Yin

*AT&T Bell Laboratories, Murray Hill, New Jersey 07974*

Marvin L. Cohen

*Department of Physics, University of California, Berkeley, California 94720  
and Materials and Molecular Research Division,**Lawrence Berkeley Laboratory,  
Berkeley, California 94720*

(Received 13 January 1984)

The graphitic phases of C and Si are studied with the use of the pseudopotential local-density-functional approach. For graphite, good agreement with experiment is obtained for the in-plane lattice constant, interlayer spacing, isotropic bulk modulus, and graphite-diamond structural energy difference. Graphitic Si has relatively weak bonding and its formation is unlikely since its energy is 0.71 eV/atom higher than the diamond phase and a large negative pressure of  $-69$  kbar is required.

Carbon and silicon in the diamond structure are the prototypical covalent solids and many of their structural properties are well understood. Graphite has also been studied extensively and this material serves as the prototype of layer materials. Hence there is considerable interest in the carbon graphite-diamond transition and the properties of the weak binding between layers which is believed to be of the van der Waals type. The nature of the interlayer bonding is of particular importance for the study of intercalated graphite compounds.

Despite the fact that Si is one of the most studied and best understood materials in science and technology, the question of the existence of graphitic Si remains open. Research<sup>1</sup> on Si in the hexagonal diamond and *BC-8* structures has resulted in detailed information about these metastable phases. Although suggestions that graphitic Si may exist at negative pressures have been made, this material has not been observed and precise theoretical estimates indicating the likelihood of success have not been available.

The present study addresses the questions raised above and also serves as a test of the pseudopotential approach<sup>2,3</sup> and the local-density-functional (LDF) approximation.<sup>4</sup> It is found that this method which was very successful<sup>5,6</sup> for computing ground-state properties of tetrahedral semiconductors and metals can be used to study layered systems with  $\sigma$  and  $\pi$  bonds. In addition, some information is obtained about the use of the LDF approximation for the exchange-correlation potential and its role in van der Waals bonding. The results include the in-plane and interlayer spacings, the isotropic bulk modulus, and the total energy difference between the diamond and graphite structures. For C, the results are in good agreement with observations, while for Si it is predicted that the graphite phase is 0.71 eV/atom higher than the diamond phase and therefore very unlikely to occur.

*Ab initio* pseudopotentials<sup>7</sup> within the LDF formalism<sup>3</sup> are used to compute the total structural energy ( $E_{\text{tot}}$ ) using the momentum space representation.<sup>8,9</sup> The pseudopotentials for Si and C have been shown<sup>5,6,9-11</sup> to yield very accurate results for the diamond phase. When  $E_{\text{tot}}$  is evaluated for a variety of crystal structures as a function of atomic separation, a determination of the lowest-energy structure, lattice constants, elastic moduli, and phase diagrams is possible.

This is the first application to the graphitic phase. In the present calculation the pseudopotential Schrödinger equation is solved self-consistently<sup>12</sup> for each structural case considered. A plane-wave basis set is used with kinetic energy up to a cutoff,  $E_{\text{pw}}$ , of 35 Ry for C and 11.5 Ry for Si. The valence charge density used to generate screening potentials in the self-consistent procedure is evaluated at six special  $k$  points<sup>13</sup> in the irreducible Brillouin zone for the graphitic phases.<sup>14</sup> Although graphite is a semimetal, since the overlap between the valence and conduction bands occupies such a small part of phase space, this contribution is considered to be negligible in calculating  $E_{\text{tot}}$ . The exchange-correlation contribution to  $E_{\text{tot}}$  was evaluated using the Wigner interpolation formula,<sup>15</sup> but other forms were also tested as described below.

For (hexagonal) graphite, the ratio of the lattice constants  $c/a$  was fixed at first at the measured<sup>16</sup> value (2.726) and  $E_{\text{tot}}$  was calculated for five values of  $a$  in 2% steps. A least-squares fit to the Murnaghan equation of state<sup>17</sup> yields the calculated equilibrium lattice constants,  $a_0 = 2.47$  Å and  $c_0 = 6.73$  Å, in good agreement with the experimental values of 2.461 and 6.709 Å.<sup>17</sup> This suggests that the pseudopotential LDF approach is describing the in-plane  $\sigma$ - and  $\pi$ -bonding quite accurately. The calculated isotropic bulk modulus is 2.36 Mbar, which is in reasonable agreement with the value of 2.86 Mbar derived from experiment.<sup>18</sup> We expect numerical uncertainties of 1% and 20% for the equilibrium lattice constants and the isotropic bulk modulus, respectively.<sup>19</sup> When different functional forms<sup>20-22</sup> are used for the exchange-correlation energy, the equilibrium lattice constants are found to be smaller by  $\sim 1\%$  and the isotropic bulk modulus is  $\sim 5-8\%$  larger than for the corresponding results using the Wigner form.<sup>15</sup>

To obtain a convergent value for the cohesive energy, we calculate  $E_{\text{tot}}$  for graphite at the measured lattice constants using 18 special  $k$  points and a large  $E_{\text{pw}}$  ( $E_{\text{pw}} = 42$  Ry; about 1100 plane waves are used.) For comparison, the total energy is also calculated for diamond at the measured lattice constant (3.567 Å) using 28 special  $k$  points and the same  $E_{\text{pw}}$ .<sup>23</sup> These results are compared in Table I along with results for the isolated atom. The total energy is decomposed into various components in Table I.  $E_{\text{pot}}$  is the sum of electron-electron and core-core electrostatic energy

TABLE I. Comparison of various energy contributions (in units of Ry/atom) to the total energy for graphite ( $E^g$ ) and diamond ( $E^d$ ) using measured lattice constants ( $E_{pw} = 42$  Ry). Data in the last column are energy differences between the diamond and the graphite phase of Si ( $E_{vib}$  is neglected for Si).

	Graphite $E^g$	Diamond $E^d$	C $E^d - E^g$	Si $E^d - E^g$
$E_{kin}$	8.3244	8.4051	0.0807	0.102
$E_{xc}$	3.4175	-3.4753	-0.0578	-0.077
$E_{pot}$	16.2709	-16.2939	-0.0230	-0.077
$E_{vib}$	0.0122	0.0133	0.0011	...
$E_{tot}$	-11.3518	-11.3508	0.0010	-0.052

and electron-core interaction. We note that the kinetic energy ( $E_{kin}$ ) and the zero-point vibrational energy<sup>24</sup> ( $E_{vib}$ ) favor a graphite phase. The opposite is true for  $E_{pot}$  and exchange-correlation energy ( $E_{xc}$ ). The signs are majorly due to the fact that graphite has larger equilibrium volume than diamond. The calculated cohesive energies<sup>25</sup> of graphite and diamond are, respectively, 7.70 and 7.69 eV/atom.<sup>26</sup> Compared with the corresponding experimental values of 7.374 and 7.349 eV/atom,<sup>27</sup> both cohesive energies are too large by  $\sim 0.3$  eV/atom. Similar results for the cohesive energy of graphite have been found by Weinert, Wimmer, and Freeman.<sup>28</sup> It was suggested that the discrepancy comes mainly from the configuration-interaction-type correlation.

As shown in Table I, the total energy of graphite is lower than that of diamond by 0.001 Ry/atom. Since this energy difference is very small, we repeated the calculation of this quantity using different forms of exchange-correlation energy. The energy difference is -0.002, -0.003, and -0.003 Ry/atom for the forms in Refs. 20, 21, and 22, respectively. Taking these results into consideration, the present study shows that graphite has almost the same total energy as diamond within an estimated error of 0.003 Ry/atom resulting from numerical computation and various forms of exchange-correlation energy. This is in agreement with the experimental finding<sup>27</sup> and the calculated number is of the same order as the experiment value (graphite is more stable by 0.002 Ry/atom). However, a more straightforward comparison of this quantity is not warranted because of the calculational uncertainties.

It is of great practical interest to transform graphite to diamond. Although our study and experimental data<sup>29</sup> indicate that the thermodynamic transition pressure is within the kbar pressure range, the transition rate is extremely slow because it involves a large activation energy to break strong directional covalent bonds. Practical diamond synthesis is usually carried out by the solvent-catalyst method in which graphite is dissolved in a metal solvent to reduce the activation energy and subjected to high temperature and high pressure (of the order of 1500 K and 100 kbar, respectively).

If the lattice constants  $a$  and  $c$  are varied independently, we find that the variation of  $a$  has the dominant effect on the total energy. This is because the in-plane covalent bonding is much stronger than the interlayer van der Waals bonding. To study the interlayer interaction independently, we keep  $a$  fixed at its measured value and vary  $c$  in the total energy calculations for graphite. The calculated total ener-

gies are fitted to a second-degree polynomial and the resulting  $c_0$  value and the elastic modulus  $C_{33}$  are 7.05 Å and 0.54 Mbar, respectively, accompanied by large computational errors of 10% and 50%.<sup>30</sup> The  $c_0$  value is larger than the experimental value by 5% and  $C_{33}$  has larger deviation [measured value is 0.365 Mbar (Ref. 18)]. The percentage deviation is of the same order of magnitude as those for rare-gas solids<sup>31</sup> and trigonal Se,<sup>32</sup> which also involve van der Waals interactions. These calculations suggest that a LDF approximation is capable of determining equilibrium spacings for van der Waals interactions to an accuracy of  $\sim 10\%$  even though the fluctuating dipole nature of this interaction is not adequately described. We suggest that it is because equilibrium lattice constants (and elastic moduli) are determined mainly by the short-range repulsive force which is adequately described by the LDF theory. The weak long-range van der Waals attraction plays a minor role in this aspect, even though it determines the interlayer cohesion.<sup>33</sup>

The properties of graphitic Si were examined in the same manner as for graphite. The ratio of the lattice constants  $c/a$  was fixed at the measured<sup>16</sup> value (2.726) for graphite. The calculated  $a_0$ ,  $c_0$ , and isotropic bulk modulus are 3.90 Å, 10.62 Å, and 0.50 Mbar, respectively. To estimate the  $\pi$ -bonding influence in the graphitic phases of C and Si, we show in Table II the calculated and measured bond lengths for the graphitic and diamond phases of C and Si. As a consequence of extra  $\pi$  bonding, both graphitic phases have contracted bond lengths compared with their corresponding diamond phases. The graphitic bond length of Si has a smaller contraction than that of C. Since a short bond length usually indicates a strong bond, it suggests that the graphitic  $\pi$  bonding for Si is not as strong as for C. Other evidence comes from the total energy comparison between the two phases (see the last two columns in Table I). While the two phases of C are very close in energy, the graphitic phase of Si is unstable against its diamond phase by 0.71 eV/atom. This confirms the suggestion<sup>34</sup> that  $\pi$  bonds are relatively weaker (as compared with  $\sigma$  bonds) for third-row elements than for second-row elements. We believe that the origin of these differences between Si and C arises from difference in their atomic configurations. There are no  $p$  electrons in the atomic core of C yielding a more compact charge distribution for the valence  $p$  orbitals and strong  $\pi$  bonds.

There has been some suggestion from the phase diagrams<sup>35</sup> of Si and C that the graphitic phase of Si might be

TABLE II. Bond lengths (Å) of the graphite and diamond phases and their ratio of C and Si. The experimental values are from Ref. 16. The calculated values for diamond phases are from Refs. 5 and 10.

	Bond length (Å)	
	Calc.	Expt.
C		
Graphite phase	1.426	1.421
Diamond phase	1.537	1.545
Ratio	0.928	0.920
Si		
Graphite phase	2.249	...
Diamond phase	2.361	2.351
Ratio	0.952	...

stable at negative pressures. The present study indicates that the pressure is  $-69$  kbar which is too large a negative pressure to be practically possible.

We acknowledge Professor S. G. Louie, Dr. J. C. Phillips, and Professor L. J. Sham for helpful discussions. One of us

(M.L.C.) would like to acknowledge support by the National Science Foundation under Grant No. DMR7822465 and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

- <sup>1</sup>R. H. Wentorf and J. S. Kasper, *Science* **139**, 338 (1963); J. S. Kasper and S. M. Richards, *Acta Crystallogr.* **17**, 752 (1964); J. D. Joannopoulos and M. L. Cohen, *Phys. Rev. B* **7**, 2644 (1973).
- <sup>2</sup>M. L. Cohen and V. Heine, *Solid State Phys.* **24**, 37 (1970).
- <sup>3</sup>See, e.g., M. T. Yin and M. L. Cohen, *Phys. Rev. B* **25**, 7403 (1982), and references therein.
- <sup>4</sup>P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).
- <sup>5</sup>M. T. Yin and M. L. Cohen, *Phys. Rev. Lett.* **45**, 1004 (1980); *Phys. Rev. B* **26**, 5668 (1982).
- <sup>6</sup>M. L. Cohen, *Phys. Scr.* **T1**, 5 (1982).
- <sup>7</sup>D. R. Hamann, M. Schlüter, and C. Chiang, *Phys. Rev. Lett.* **43**, 1494 (1979).
- <sup>8</sup>J. Ihm, A. Zunger, and M. L. Cohen, *J. Phys. C* **12**, 4409 (1979).
- <sup>9</sup>M. T. Yin and M. L. Cohen, *Phys. Rev. B* **26**, 3259 (1982).
- <sup>10</sup>M. T. Yin and M. L. Cohen, *Phys. Rev. B* **24**, 6121 (1981).
- <sup>11</sup>M. T. Yin and M. L. Cohen, *Phys. Rev. Lett.* **50**, 2006 (1983).
- <sup>12</sup>M. Schlüter, J. R. Chelikowsky, S. G. Louie, and M. L. Cohen, *Phys. Rev. B* **12**, 4200 (1975).
- <sup>13</sup>D. J. Chadi and M. L. Cohen, *Phys. Rev. B* **8**, 5747 (1973); H. J. Monkhorst and J. D. Pack, *ibid.* **13**, 5189 (1976).
- <sup>14</sup>The convergence in crystalline total energy difference with respect to  $E_{pw}$  is estimated to be  $\sim 2$  mRy/atom. The convergence in total energy with respect to number of sampling  $k$  points is estimated to be  $\sim 1$  mRy/atom.
- <sup>15</sup>E. Wigner, *Trans. Faraday Soc.* **34**, 678 (1938); D. Pines, *Solid State Phys.* **1**, 375 (1955).
- <sup>16</sup>The measured lattice constants for hexagonal graphite are obtained from J. Donohue, *The Structures of Elements* (Wiley, New York, 1974).
- <sup>17</sup>F. D. Murnaghan, *Proc. Natl. Acad. Sci. U.S.A.* **30**, 244 (1944); O. L. Anderson, *J. Phys. Chem. Solids* **27**, 547 (1966).
- <sup>18</sup>O. L. Blakslee, D. G. Proctor, E. J. Seldin, G. B. Spence, and T. Weng, *J. Appl. Phys.* **41**, 3373 (1970). The bulk modulus for ideal isotropic compression (called isotropic bulk modulus) is  $\frac{1}{9}(2C_{11} + C_{33} + 2C_{12} + 4C_{13})$ .
- <sup>19</sup>We neglect the effect of lattice vibrations which is estimated to cause about 0.1% and 1% errors in the equilibrium lattice constant and the bulk modulus, respectively.
- <sup>20</sup>L. Hedin and B. I. Lundqvist, *J. Phys. C* **4**, 2064 (1971).
- <sup>21</sup>U. von Barth and L. Hedin, *J. Phys. C* **5**, 1629 (1972).
- <sup>22</sup>O. Gunnarsson, B. I. Lundqvist, and J. W. Wilkins, *Phys. Rev. B* **10**, 1319 (1974).
- <sup>23</sup>Because the calculated equilibrium lattice constants are close to experimental values, this total energy differs from the minimal total energy by  $\sim 1$  mRy/atom for the same  $E_{pw}$ .
- <sup>24</sup>It is calculated by taking the total energy difference between the spin-polarized and the unpolarized pseudoatoms with the valence configuration  $s^2p^2$  using the form of the exchange-correlation energy proposed by Gunnarsson, Lundqvist, and Wilkins (Ref. 2).
- <sup>25</sup>We use the phonon density of states of graphite fitted by R. Al-Jishi and G. Dresselhaus, *Phys. Rev. B* **26**, 4514 (1982) and that of diamond fitted by W. Weber, *ibid.* **15**, 4789 (1977). See the references therein for original experimental data.
- <sup>26</sup>The convergence error is  $\sim 0.5$  eV/atom for cohesive energies. The calculated cohesive energy for diamond using a larger  $E_{pw}$  (50 Ry) is 8.06 eV/atom. Because of cancellation of errors, the total energy difference between graphite and diamond has a smaller convergence error ( $\sim 0.02$  eV/atom).
- <sup>27</sup>See the compilation by L. Brewer, Lawrence Berkeley Laboratory Report No. LBL-3720 (unpublished) (for the cohesive energy at 0 K).
- <sup>28</sup>M. Weinert, E. Wimmer, and A. J. Freeman, *Phys. Rev. B* **26**, 4571 (1982).
- <sup>29</sup>See G. Muncke, in *Properties of Diamond*, edited by J. E. Field (Academic, London, 1979), p. 473; R. Berman and F. Simon, *Z. Elektrochem.* **59**, 333 (1955).
- <sup>30</sup>Since the total energy change is very small ( $\sim 1$  mRy/atom) as  $c$  varies, the spurious discontinuity in total energy as a function of  $c$  resulting from a discrete change of plane-wave basis set becomes significant.
- <sup>31</sup>S. B. Trickey, F. R. Green, Jr., and F. W. Averill, *Phys. Rev. B* **8**, 4822 (1973). The  $X\alpha$  formalism was used with the  $\alpha$  value ( $\sim 0.7$ ) adjusted to satisfy the virial theorem in the atomic limit.
- <sup>32</sup>D. Vanderbilt and J. D. Joannopoulos, *Phys. Rev. B* **27**, 6269 (1973).
- <sup>33</sup>In the LDF theory, the corresponding attractive part comes mainly from the exchange-correlation energy.
- <sup>34</sup>R. S. Mulliken, *J. Am. Chem. Soc.* **72**, 4493 (1952); **77**, 884 (1955).
- <sup>35</sup>See F. P. Bundy, *J. Chem. Phys.* **41**, 3809 (1964) (for phase diagrams).