RAPID COMMUNICATIONS

*Rapid Communications are intended for the accelerated publication of important new results and are therefore given priority treatment both in the editorial office and in production. A Rapid Communication in **Physical Review B** may be no longer than four printed pages and must be accompanied by an abstract. Page proofs are sent to authors.*

―――――――――

Stability and charge transfer of C_3B ordered structures

Qiang Wang and Long-Qing Chen

Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802

James F. Annett

University of Bristol, H. H. Wills Physics Laboratory, Royal Fort, Tyndall Avenue, Bristol BS8 1TL, United Kingdom

The relative stability and charge-transfer behavior of C_3B ordered phases were investigated using the *ab initio* pseudopotential method. The total energies as well as the cohesive energies of four possible ordered structures of the C_3B were calculated at 0 K by relaxing both the unit-cell parameters and the local atomic positions. Among them, the one with the hexagonal symmetry was found to have the lowest total energy, and is thus the most stable structure. The amount of charge transfer between B and C was calculated and it was found that charge was transferred from the B to C atom in all four structures. [S0163-1829(96)51428-1]

The usefulness of graphite-based carbon-carbon (C/C) composites is mainly limited by their oxidation at high temperatures. Therefore, one of the major research efforts on C/C composites is to find ways to improve their oxidation resistance. There are experimental evidences that boron (B), when substituting C atoms in the graphite structure, may significantly improve the oxidation behavior of a C/C composite.[1–4] However, it was shown that if B doping was carried out by solid-state diffusion, the substitutional solubility of B in graphite was limited to about 2.35 at. % at 2350 °C, with the B randomly distributed in the lattice. A dramatic increase in the amount of substitutional B in graphite, ~25 at. %, has been achieved by reacting benzene and boron trichloride at about 800 °C, and it was suggested that the C_3B compound has an ordered structure as shown in Fig. 1(a) which has a hexagonal symmetry.[5–7] Its electronic and structural properties were calculated using the *ab initio* pseudopotential method.[8] On the other hand, based on the extended Hukel method, Lee and Kertesz[9] suggested two alternative ordered structures for C_3B as described in Figs. 1(b) and 1(c), which can explain the higher electric conductivity of C_3B than graphite. However, it is still unclear which ordered structure is the thermodynamically most stable one, and hence one of the main purposes of this work is to determine the relative stabilities of different ordered structures at

the C_3B composition using the *ab initio* pseudopotential total-energy calculations by relaxing both the unit-cell lattice parameters and the atomic positions. Similar calculations have been performed by Magri[10] for the ordered structures of B_xC_{1-x} with different x. However, in her calculation, the unit-cell lattice parameter changes as a function of composition and atomic relaxation were not taken into account. According to our calculations, the relaxation can be very important and can alter their relative stabilities.

To explain how B reduces the oxidation processes in C/C composite, several possible mechanisms have been proposed.[3] One of the proposed mechanisms considered the charge transfer between carbon and boron. Since B has three valence electrons and C has four, a B atom substituted into the graphite lattice would tend to draw electrons from neighboring C atoms, resulting in the reduction in the reactivity of C atoms with electronegative oxygen atoms, and thus the reduction in oxidation of graphite. Therefore, the second objective of this paper is to discuss the electron charge transfer between B and C at the C_3B composition. As will be shown below, we found the contrary, i.e., the electron charge actually transfers from B to C instead of from C to B, at least for the particular composition we studied.

Our first-principles approach for calculating the ground-

(a)   S1

(b)   S2
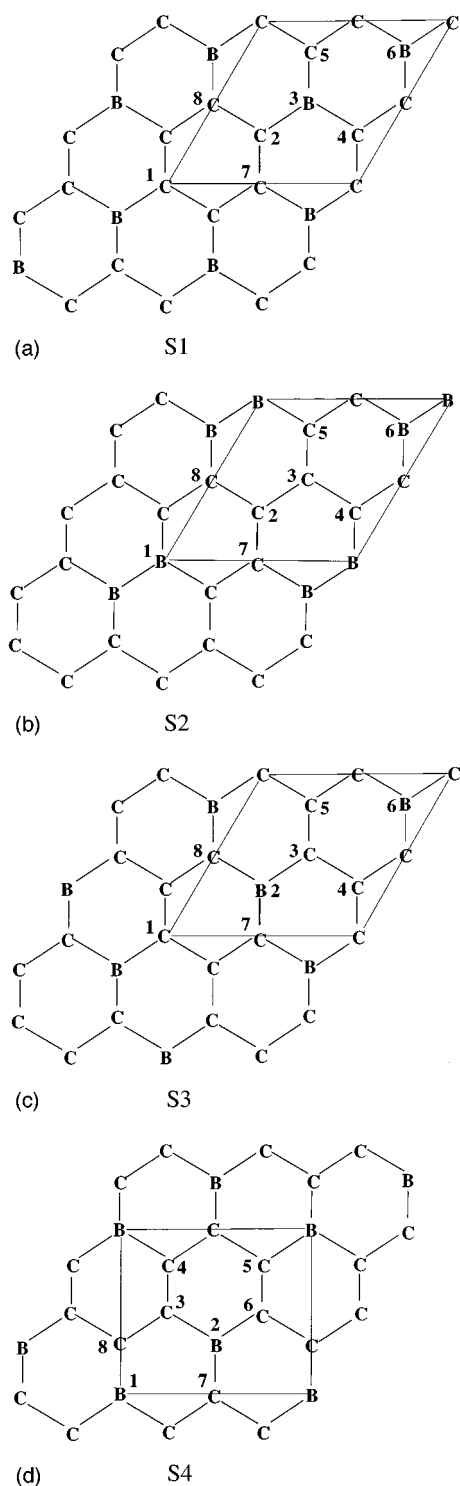
(c)   S3

(d)   S4

FIG. 1. (a), (b), (c), and (d) are 2D atomic configurations of different ordered structures labeled as $S1$, $S2$, $S3$, and $S4$, respectively, where the C denotes the carbon site and B denotes the boron site. The basic unit cell for $S1$, $S2$, and $S3$ was described by the rhombus and the unit cell for $S4$ is described by the rectangle.

four special k points according to the Monkhorst-Pack scheme.[14] The minimization of the total energy E was carried out by a preconditioned conjugate-gradient method in two steps.[15,16] At first, the cell parameter (i.e., lattice constant a) was optimized with atom positions fixed. Then, the atom positions were relaxed using the steepest-descents method with the cell parameters fixed at their optimized values. The optimization with respect to atom positions was carried out until the difference in total energies between two consecutive iterations is less than 0.01 eV (i.e., the relative error is less than 10^{-4} per atom).

We first calculated the structural properties of graphite carbon as a test for the C pseudopotential. The optimized in-plane lattice constant was 2.453 Å and the interlayer distance c was approximately 6.60–6.70 Å, which compare very well with the experimental values [$a = 2.456$ Å and $c = 6.674$ Å (Ref. 17)]. The cohesive energy of the graphite was found to be 8.59 eV/atom, which is in reasonable agreement with the experimental value, 7.374 eV/atom.[18]

In addition to the three structures for C_3B mentioned above, we also included in our calculation the fourth structure [Fig. 1(d)]. The unit cell chosen for $S1$, $S2$, and $S3$ is different from that for $S4$, although both of them include eight atoms, six carbon atoms and two boron atoms. Because the interactions between atoms in different graphite layers are much weaker than the in-plane interactions, to reduce the computation time, we only consider one graphite sheet by choosing an artificially large cell parameter along the normal to the plane, with periodic boundary conditions applied along all three directions. The reduced time results from not including any cell relaxation in this direction. A comparison between a true three-dimensional (3D) calculation and that using only one sheet shows that there is essentially no difference in the structural parameters, such as lattice parameters and bond lengths, and the electronic charge density distributions.[10]

The total energies per atom and the cohesive energy of each ordered structure are listed in Table I. The cohesive energy was defined as the difference between the total energy of a particular structure and the total energy of the con-
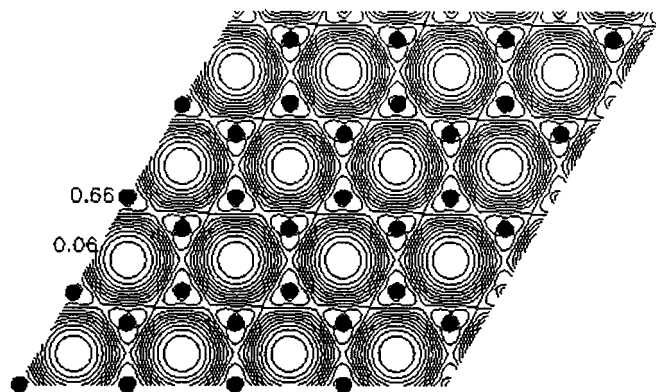

FIG. 2. The valence-charge density distribution in a graphite monolayer, ● refers to the carbon site. Charge density is given in units of 3.57 electrons $/Å^2$. Consecutive contours are separated by 0.214 electrons $/Å^2$. The highest density around the carbon is 0.66 unit and the lowest density close to the center of the hexagon is 0.06 unit.

state charge density and energy is based on the local-density-functional theory. The exchange and correlation energy was calculated using the Perdew-Wang expression.[11] Nonlocal pseudopotentials are employed for both C and B.[12,13] We used a plane-wave basis set with kinetic energy cutoff at 71 Ry and sample the first Brillouin zone of each structure with

TABLE I. The minimized total energies and cohesive energies for the four ordered structures.

Structure	Total energy per atom (eV)	Cohesive energy per atom (eV)
$S1$	-135.41	7.86
$S2$	-135.22	7.67
$S3$	-135.29	7.75
$S4$	-135.36	7.81

stituent atoms at infinite separation. As shown in Table I, the relative stabilities of the four structures follow the sequence $S1 > S4 > S3 > S2$. $S1$ was found to be the most stable ordered structure at the C$_3$B composition which maintains the hexagonal symmetry of the graphite layer and therefore the smallest local lattice distortion. However, all four structures have the same optimized in-plane lattice constant $a = 2.57$ Å. The second most stable ordered structure $S4$ is quite similar to structure $S1$ except for the hexagonal symmetry. The cohesive energy of $S1$ is about 0.05 eV/atom larger than that of $S4$. They have identical C-C and similar C-B bond lengths. The nearest- and second-neighbor atomic arrangements associated with the C-C and C-B bonds are the same for both structures; however, the third neighbors are different [Figs. 1(a) and 1(d)]. This difference is the main origin for the difference in the cohesive energy between $S3$ and $S4$.

The bond lengths for all the structures were calculated. In $S1$, the bond length of the C-C bond is 1.42 Å, which is identical to that in graphite, and that of the C-B bond is 1.55 Å, which agrees well with previous predictions.[8,9] These values are also consistent with the atomic radii of B and C (0.85 Å for boron and 0.70 Å for carbon[8]). However, the C-C bond length could be different in different ordered structures or even in the same ordered structures, such as $S2$ and $S3$. For example, C2-C3, C3-C4, and C4-C8 bonds in structure $S2$ have bond lengths 1.53, 1.47, and 1.41 Å, respectively, and the bond lengths associated with the $S3$ structure were 1.50 Å for the C3-B2 bond, 1.54 Å for the C8-B2 bond, 1.47 Å for C3-C4 and 1.38 Å for C4-C8.

Figure 3(a) presents the valence-charge density distribution for the $S1$ structure in which 64×64 grid points were employed for discretizing the $2a^* \sqrt{3}a$ unit cell in Fig. 1(a). As a reference, the valence-charge density distribution of a graphic monolayer was shown in Fig. 2. Comparing Figs. 2 and 3(a), we can see that the charge distribution around the C-C bond has only a slight change from that of graphite in Fig. 2. A comparison between the charge density distributions for different structures shows that $S1$ structure has a much smaller deformation of the charge distribution around the C-C bond compared to graphite than the other three structures. As expected, the neighboring atomic arrangement of a bond affects its charge density distribution. Figure 3(b) shows the charge density distribution of structure $S2$. It can be seen that the charge distributions differ from each other around the C2-C3, C3-C4, and C4-C8 bonds. By carefully checking the neighbor atomic arrangements, we found the differences between those C-C bonds are associated with neighbors, such that the C2-C3 bond connects with four C-C bonds (i.e., 2-8, 2-7, 3-4, and 3-5), C3-C4 with three C-C
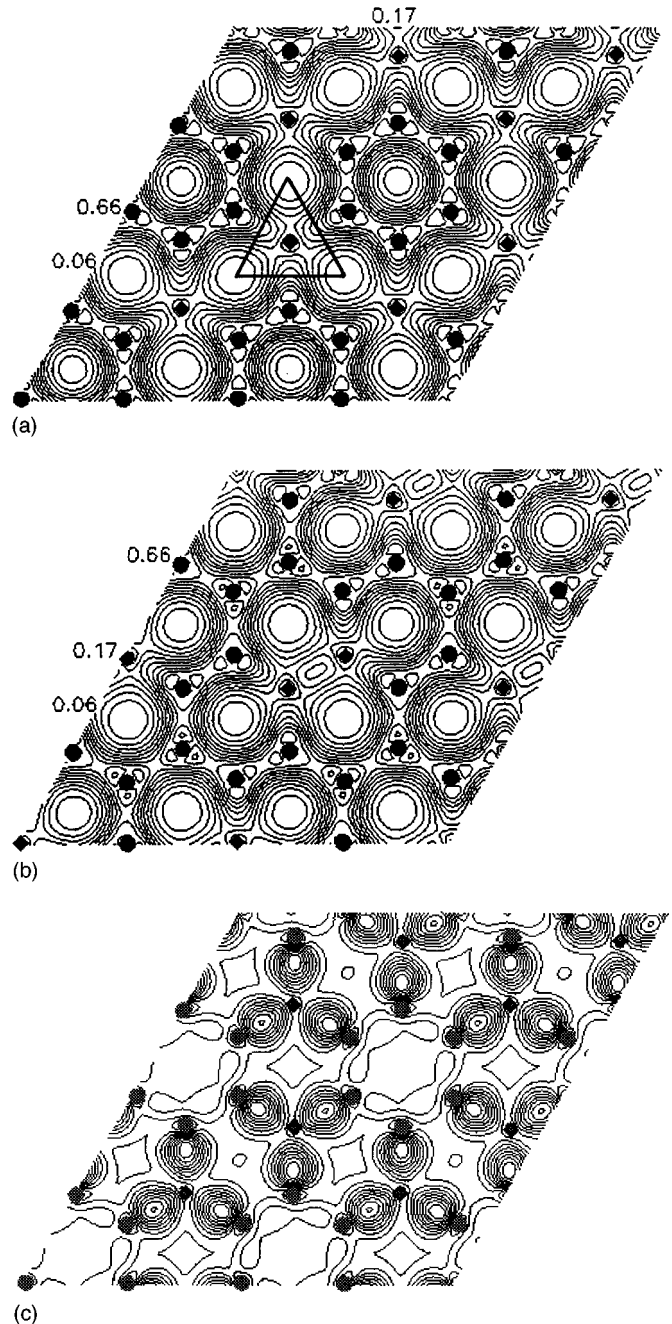

FIG. 3. The valence-charge density distribution (a) in $S1$ and (b) in $S2$, where ■ denotes the boron site; (c) the corresponding subtractive charge density distribution in $S1$.

bonds (i.e., 2-3, 3-5, and 4-8) and one C-B bond (i.e., 1-4), and C4-C8 with two C-C bonds (i.e., 3-4 and 2-8) and two C-B bonds (i.e., 1-4 and 6-8).

The charge transfer between the carbon and boron atoms was an important parameter to understand the mechanism by which the B substitution can improve the oxidation resistance of graphite. For each structure, based on the optimized geometry, the charge density distributions of the following two cases were separately calculated. Case 1: in the unit cell, six carbon atoms were fixed at their optimized positions and the other two boron atoms were removed from their lattice sites. Case 2: two boron atoms were kept on their optimized
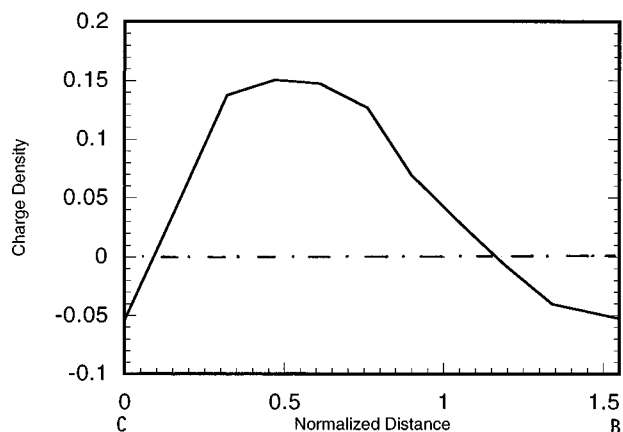
FIG. 4. One-dimensional subtractive charge density distribution along a C-B bond in the $S1$ structure.

TABLE II. The charge distribution in the ordered structures, specified by the notation $X^e_{(n1,n2,\ldots)}$ where X denotes the atom type, C for carbon and B for boron; e refers to the number of valence charge belonging to the atom X with index $n1,n2,\ldots$.

Structure	Charge distribution
$S1$	$C^{4,15}_{(1,2,4,5,7,8)}B^{2.55}_{(3,6)}$
$S2$	$C^{4.0}_{(2,3)}C^{4.1}_{(4,5,6,7,)}B^{2.8}_{(1,6)}$
$S3$	$C^{4.0}_{(4,5)}C^{4.2}_{(7,8)}C^{4.3}_{(1,3)}B^{2.5}_{(2,6)}$
$S4$	$C^{4.16}_{(3,4,5,6,7,8)}B^{2.52}_{(1,2)}$

lattice positions and the six carbon atoms were removed. We then sum the two charge density distributions calculated for the two cases together (6C+2B). The difference between the charge density distribution for a given structure and that for (6C+2B), i.e., D_C (Si)-[($D_C(Si$-6C)+$D_C(Si$-2B)], where D_C means charge density distribution and Si refers to the ith ordered structure, provides an indication where the charge gains and loses when a C-B bond forms. This method was previously used[19] for discussing the charge transfer in small atom clusters. Figure 3(c) shows the subtractive distributions for structure $S1$. From Fig. 3(c), we can easily find charge transfer occurs mostly around C-B bonds. Based on Fig. 3(c), a one-dimensional distribution of charge density distribution along a B-C bond was plotted in Fig. 4. From Fig. 4 it is quite clear that charge transfers from B to C. The result seems to be reasonable because C is more electronegative than B (E_C=2.5; E_B=2.01).[20] Therefore, we suggest an alternative explanation for the improvement in the oxidation resistance of C graphite by B doping. Since C is more electronegative than B, an electronegative O will prefer to react with B than C in a graphite doped with B, and the resulting B_2O_3 or C_2BO or CBO_2 (Ref. 21) staying on the surface would protect the oxidation of C. Furthermore, the charge transfer from B to C enhances to reactivity between B and O.

The amount of charge transfer in four ordered structures were listed in Table II. An approximation was made for the convenience of calculating the amount of charge transfer between carbon and boron atoms. Because the carbon and boron have a very small difference in atomic radius, half of the C-B bond was attributed to the carbon atom and another half to the boron atom and then a triangle around each atom was

made up as seen in Fig. 3(a). The total charge within this triangle presents the charge on the atom located at the center of the triangle. Using this approximation, we found out that the boron atom gives the charge only to the nearest-neighbor carbon atom. There is no charge transfer between a B atom and a second-neighbor C atom. In structure $S2$, carbon atoms 2 and 3 are the second neighbors of B and the amount of charge is 4.00 on both atoms, which is the same as in graphite. In structure $S3$, the same situation can also be seen on carbon 4 and 5.

An additional semiempirical molecular orbital package MOPAC calculation was performed and the results are in good agreement with those from the above *ab initio* pseudopotential calculation.[22]

In conclusion, the $S1$ structure with hexagonal symmetry is the most stable ordered structure of the C_3B compound. The $S4$ structure is the second possible stable ordered structure with similar short-range atomic arrangement to that in $S1$. The nearest-neighbor bond lengths in the most stable structure are 1.42 Å for C-C and 1.55 Å for C-B, consistent with previous studies. Charge transfer occurs between nearest-neighbor C-B bonds with charge transfer from B to C, and the amount of charge is about 0.45 from boron to three C atoms with 0.15 each. This charge transfer from boron to carbon is partly responsible for reducing the oxidation of C in C/C composite. The results from both *ab initio* and MOPAC calculations agree well with each other.

[1] C. E. Lowell, J. Am. Ceram. Soc. **50**, 142 (1967).

[2] H. Murty, D. Beiderman, and E. Heintz, Fuel **56**, 305 (1977).

[3] L. E. Jones and P. A. Thrower, J. Chim. Phys. **84**, 1431 (1987); Carbon **29**, 251 (1991).

[4] R. B. Kaner, J. Kouvetakis, C. E. Warble, M. L. Sattler, and N.

Bartlett, Mater. Res. Bull. **22**, 399 (1987).

[5] B. M. Way, J. R. Dahn, T. Teidje, K. Myrtle, and M. Kasrai, Phys. Rev. B **46**, 1697 (1992).

[6] J. Kouvetakis, R. B. Kaner, M. L. Sattler, and N. Bartlett, J. Chem. Soc. Chem. Commun. **1986**, 1758.

[7] K. M. Krishnan, Appl. Phys. Lett. **58**, 1857 (1991).

[8] D. Tomanek, R. M. Wentzcovitch, S. G. Louie, and M. L. Cohen, Phys. Rev. B **37**, 3134 (1988).

[9] Y. S. Lee and M. Kertesz, J. Chem. Soc. Chem. Commun. **1988**, 75.

[10] R. Magri, Phys. Rev. B **49**, 2805 (1994).

[11] J. P. Perdew and Y. Wang, Phys. Rev. B **46**, 12 947 (1992).

[12] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[13] J. F. Annett, in *Towards Teraflop Computing, the New Grand Challenges*, edited by R. Kalia and K. Vashista (Nova, Commack, NY, 1995).

[14] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[15] G. S. Welsh and J. F. Annett, Phys. Rev. B **49**, 13 921 (1994).

[16] J. F. Annett, Comput. Mater. Sci. **4**, 23 (1995).

[17] Y. Baskin and L. Mayer, Phys. Rev. **100**, 544 (1955).

[18] M. T. Yin and M. L. Cohen, Phys. Rev. B **29**, 6996 (1984).

[19] Q. Wang, M. P. Iniguez, J. A. Alonso, and M. Silbert, J. Phys., Condens. Matter **5**, 4271 (1993).

[20] I. S. Butler and J. F. Harrod, *Inorganic Chemistry: Principles and Applications* (Benjamin Cummings, Menlo Park, CA, 1989), p. 61.

[21] W. Germignani (unpublished).

[22] X. L. Ma (private communication).