

Calculation of electronic and structural properties of BC_3

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We have determined the equilibrium geometry and electronic structure of the compound BC_3 using the *ab initio* pseudopotential local orbital approach and the local-density functional formalism. The boron-carbon compound BC_3 is a layered material with graphitic structure, where every fourth carbon atom is substituted by boron. The nearest-neighbor distances are predicted to be 1.42 Å for the C—C bond and 1.55 Å for the B—C bond. A monolayer of BC_3 is found to be a semiconductor, and the observed metallic behavior of the bulk sample arises from interactions between neighboring layers in BC_3 with *AA* and *AB* stacking. Based on total-energy calculations, we find BC_3 to be less stable than graphite for the structures investigated.

Recently, a novel material with the composition BC_3 has been synthesized.¹ Its sheetlike character and metallic appearance suggest a graphitelike structure which has been confirmed by electron diffraction data.¹ However, since the films are not grown epitaxially, information about the atomic structure of this compound is limited. Based on the observed graphitelike symmetry, an ordered structure has been suggested¹ which is reproduced in Fig. 1. Since B has one valence electron less than C, it is reasonable to assume that the in-plane properties of BC_3 should lie close to those of acceptor-intercalated graphite. Indeed, a correspondingly increased electronic conductivity is observed.¹ On the other hand, it is not clear how large a perturbation of the electronic system of graphite will arise from B substitution. To investigate these questions, we have performed an *ab initio* calculation of the electronic and structural properties of this compound.

The calculations are done using the local-density approximation (LDA).² We employ the *ab initio* pseudopoten-

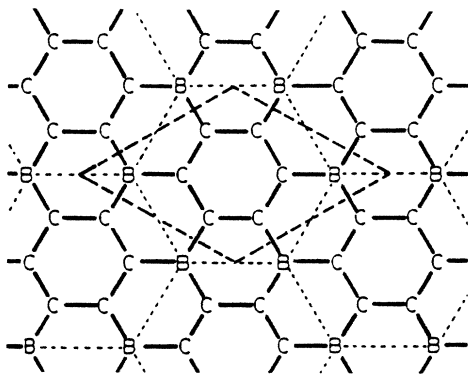


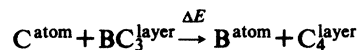
FIG. 1. Atomic arrangement in a layer of BC_3 , as suggested in Ref. 1. The unit cell is enclosed by a dashed line. The boron superlattice is connected by dotted lines.

tial local-orbital method,³ which has been used successfully to describe properties of graphite.⁴ Norm-conserving pseudopotentials⁵ and the Hedin-Lundqvist form of the exchange-correlation potential⁶ were used. The wave-function basis set consists of local orbitals with s , p_x , p_y , and p_z character. The radial part of the orbitals is described by Gaussians with decay constants (in a.u.) $\alpha = 0.17, 0.54, 1.69$ for B, and $\alpha = 0.24, 0.80, 2.65$ for C, i.e., 12 independent basis functions at each site.⁷ The plane-wave components of the charge density and the potential have been determined self-consistently up to an energy cutoff of 49 Ry.

Because of the weak interaction between adjacent layers in BC_3 , which are separated by 3.35 Å (Ref. 1), the intralayer bond lengths can be evaluated for an isolated monolayer. For this case, the unit cell consists of six C atoms and two B atoms, as shown in Fig. 1. If the hexagonal symmetry is to be maintained, the structure is fully determined by only two parameters, the nearest-neighbor distances between carbon atoms, d_{CC} , and between boron and carbon atoms, d_{BC} . From a total-energy minimization, we find the equilibrium values $d_{CC} = 1.42$ Å and $d_{BC} = 1.55$ Å. These values are consistent with Slater atomic radii⁸ $r_C = 0.70$ Å and $r_B = 0.85$ Å. This corresponds to an increase of the lattice constant by 5% compared to graphite. Next, we calculate properties of the bulk material with *AA* and *AB* stacking using the optimized intralayer geometry and an interlayer distance of 3.35 Å. Both of these structures have eight atoms in the unit cell and all atoms have a neighbor in adjacent layers above and below (both neighbors of B atoms are B atoms in the *AA* structure and C atoms in the *AB* structure).

Cohesive energies with respect to isolated spin-polarized atoms⁹ have been evaluated for the equilibrium structures within the LDA. The cohesive energy of one formula unit of a BC_3 monolayer was calculated to be -31.41 eV (corresponding to an average cohesion per atom of -7.85 eV), which is slightly less favorable than

the calculated graphite value of -8.45 eV per atom. The cohesive energies of BC_3 with AA and AB stacking lie at -7.8 eV, very close to the monolayer value.¹⁰ Then, all conclusions about relative stability are nearly independent of the stacking. The enthalpy ΔE of the reaction



is calculated to be $\Delta E = -2.37$ eV per formula unit of a BC_3 monolayer, i.e., this reaction is exothermic.

In Fig. 2, the valence-charge density of BC_3 is compared to that of graphite. The contour plots, evaluated in the plane of the BC_3 and graphite layers, show that the B atoms keep their lower valence-charge density and do not significantly perturb the stable electronic system of the carbon ring. This is the main reason why d_{CC} is nearly the same in BC_3 as it is in graphite.

Information about the electronic structure and conductivity can be obtained from the density of states near the Fermi level, which is given in Figs. 3(a) and 3(b) for bulk BC_3 with AA and AB stacking. We find bulk BC_3 in the investigated structures to be a metal with a low density of states near E_F . The AA stacked material, which might not be realized in nature, appears to be a better conductor than the AB stacked material. This result is not obvious and requires further investigation, since both in the AA and AB stacked materials all atoms have neighbors in adjacent layers above and below.

In order to isolate the role of interlayer coupling, we also calculate the electronic structure of a monolayer of

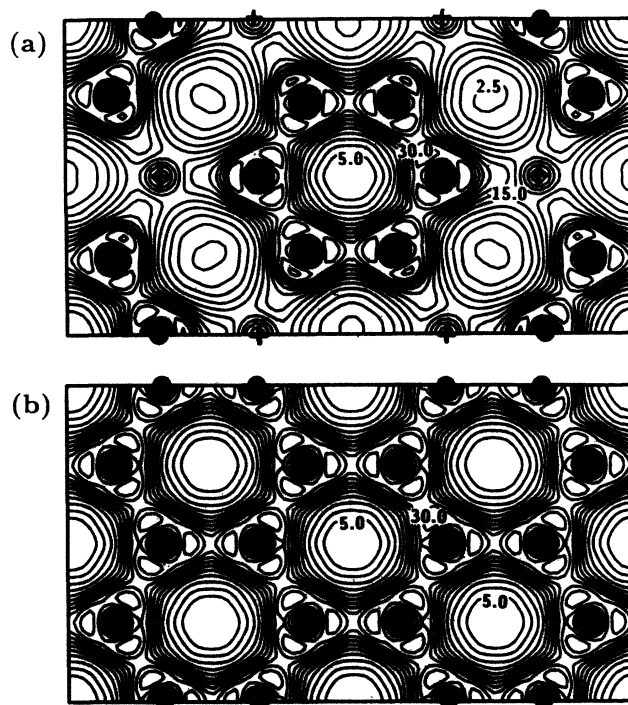


FIG. 2. Valence-charge density of a (a) BC_3 and (b) graphite monolayer in the plane of the layer. Atomic positions are indicated by (\bullet) for carbon and $(+)$ for boron sites. Charge density is given in units of 10^{-2} electrons/a.u.; consecutive contours are separated by 2.5×10^{-2} electrons/a.u.

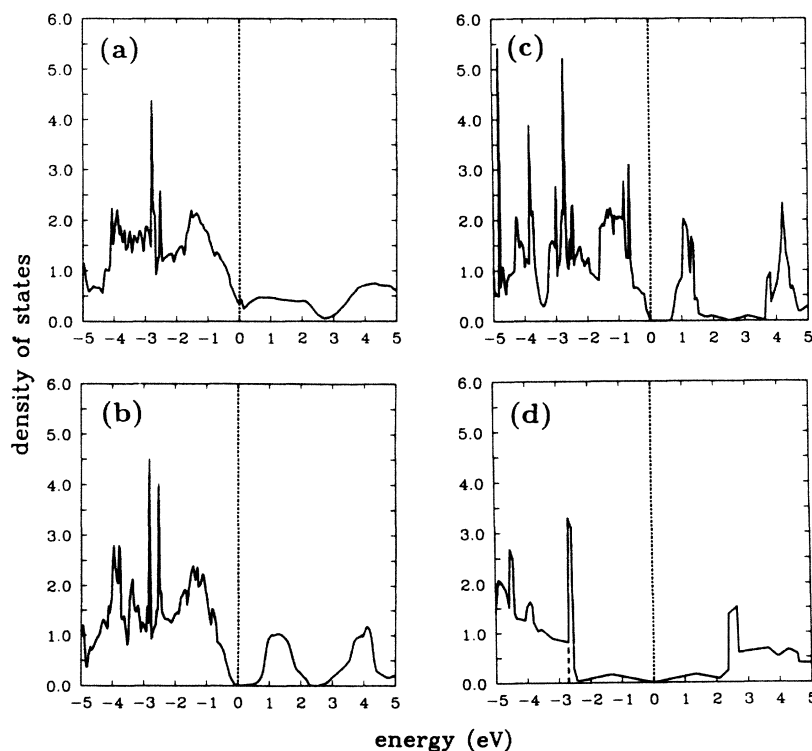


FIG. 3. Electronic density of states of bulk BC_3 with (a) AA stacking and (b) AB stacking, indicating a metallic behavior. Density of states of a monolayer of (c) BC_3 and (d) graphite. The units are states per eV for a unit cell containing eight atoms. The Fermi level, given by a dotted line, is used as energy zero.

BC₃ and compare the results to a graphite monolayer calculation. Our results, given in Fig. 3(c), indicate that a monolayer of BC₃ should be an indirect-gap semiconductor¹¹ with a gap of 0.66 eV between the highest occupied states at $\bar{\Gamma}$ and the lowest unoccupied state at \bar{M} . This result shows that the metallic behavior of BC₃ arises from coupling between adjacent layers, similar to graphite. The role of B atoms in BC₃ is significantly different from that of anionic intercalate in graphite. In graphite, the effect of the intercalate on states near E_F consists mainly of rigidly shifting the Fermi level and thereby increasing the density of states at E_F . A shift of E_F , corresponding to a deficit of 0.25 electrons per carbon atom in a graphite monolayer, is indicated by a dashed line in Fig. 3(d). A closer investigation shows that a rigid-band shift can actually be observed for some p_z bands of BC₃. This effect is, however, negligible when compared to the role of B atoms, which weakens the coupling between the π systems of neighboring carbon rings and opens up a gap near E_F at $\bar{\Gamma}$ between states which in graphite were of p_z character and form a part of the valence band.

In summary, our calculations indicate that the B atoms in BC₃ exert a very small perturbation on the charge density and structure of the carbon ring. This results in the graphitelike value for the C—C bond length $d_{CC} = 1.42 \text{ \AA}$.

The B—C bond length shows a slightly larger value of $d_{BC} = 1.55 \text{ \AA}$. A monolayer of BC₃ is an indirect-gap semiconductor with an LDA gap of 0.66 eV. The metallic behavior of bulk BC₃ arises from the interaction between neighboring layers.

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⁹Atomic spin-polarization energies of -0.27 eV for B and -1.25 eV for C have been obtained using the Gunnarsson-Lundqvist formula [*Phys. Rev. B* **18**, 3126 (1978)] for the exchange-correlation potential.

¹⁰The present sampling of the three-dimensional Brillouin zone of the bulk material limits the precision of the calculated interlayer coupling to $\approx 0.1 \text{ eV}$.

¹¹A BC₃ monolayer in an unrelaxed graphite structure with $d_{BC} = d_{CC} = 1.42 \text{ \AA}$ is calculated to be an indirect-gap semiconductor with a negligibly small gap. This gap opens upon structural relaxation. In general, the true gap is larger than the calculated LDA gap, as discussed, e.g., by M. S. Hybertsen and S. G. Louie, *Phys. Rev. B* **34**, 5390 (1986).