

$\sigma$ -STATES CONTRIBUTION TO THE CONDUCTIVITY OF  $BC_3$ 

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(Received 13 April, 1988; in revised form 27 May 1988 by A. A. Maradudin)

Recently the new graphitic material,  $BC_3$ , has been shown to exhibit electrical conductance which is 10% larger than graphite. In order to explain this behavior we show that in the  $BC_3$  monolayer the Fermi level lies at the top of the  $\sigma$  bands and that the semimetallic behavior, which appears upon stacking of the semiconducting monolayers, arises from the simultaneous presence of  $\sigma$  and  $\pi$  bands at the Fermi level.

A remarkable advance in the technology of layered materials has been made recently<sup>1</sup> by the direct chemical syntheses of graphite-like phases in which carbon is extensively replaced by boron and/or nitrogen. Among the new phases,  $BC_3$  is particularly interesting because it is lighter and has improved conductivity with respect to graphite. The proposed structure of  $BC_3$  is motivated by its syntheses which combines benzene and  $BCl_3$  at 800°:  $2 BCl_3 + C_6H_6 \rightarrow 2 BC_3 + 6 HCl$ . The B's, which replace the H's in benzene, interlink the C rings forming a layered structure of B rings surrounding C rings (See Fig. 1).

The observed lower density of  $BC_3$  is caused primarily by a larger B-C interatomic distance, which is  $\approx$

10% larger than C-C distance, and by the smaller mass of B.<sup>2,3</sup> On the other hand, the origin of its improved conductivity has remained an open question. The picture in which the B's electron deficiency creates 'hole-carriers' in the valence bands has not been confirmed by theoretical inspections of the proposed structure.<sup>2,3</sup>

An extended Huckel<sup>2</sup> calculation of  $BC_3$ 's monolayer band structure pointed out that the topology of the proposed structure opens a gap of 1.8 eV at the Fermi level which lies on top of a  $\pi$  band at  $\Gamma$ . This finding left small room for a semimetallic behavior to be derived from interlayer interactions. Further considerations led to the proposal of alternative structures with either smaller gaps or systems displaying fully metallic behavior.<sup>2</sup> However, because of the energetic stability, the structure in Fig. 1 remained the best candidate among the alternative structures.

Consistent results were obtained by a first principles pseudopotential calculation<sup>3</sup> of the density of states of a monolayer and bulk  $BC_3$ . This calculation revealed that the monolayer is semiconducting with a LDA (local density approximation) gap of 0.66 eV and that the semimetallic behavior arises from the interaction between layers. This conclusion is similar to graphite but quite different from anionic intercalated graphite in which the Fermi level shifts downward rigidly. The role of different stacking sequences has also been examined and shown<sup>3</sup> to be an important factor in determining the density of states at the Fermi level.

In this paper we report for the first time the details of a first principles band structure of the  $BC_3$  monolayer and a comparison with that of a graphite monolayer containing 8 atoms/cell. We also point to an important difference in the electronic structure of these two materials, i.e., the presence of  $\sigma$  states at the Fermi level of  $BC_3$ , which in graphite are inert from the point of view of electronic conductance, and, on the basis of a tight-binding model for the  $\pi$  bands and a symmetry analyses, we offer a justification for such occurrence. Since Ref. 3 reported the semimetallic behavior in bulk structures with

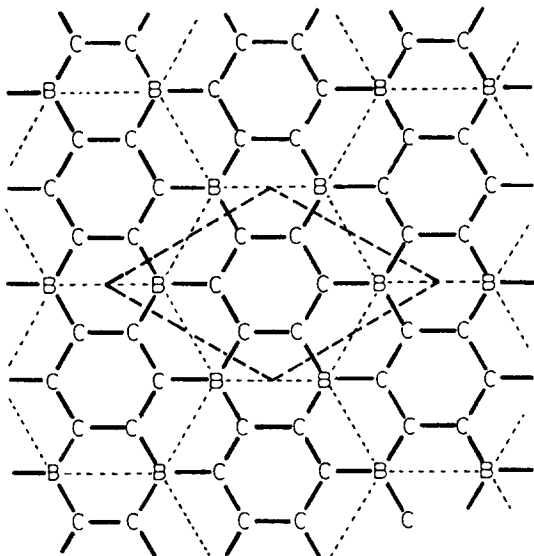


Fig. 1 - Proposed structure of  $BC_3$ .

different stackings, we address the bulk cases only briefly here, however the presence of  $\sigma$  states at the Fermi level, which is the central issue in this paper, is also observed in the calculations of bulk structures. A first principles pseudopotential calculation within the LDA<sup>4</sup> and using the localized basis formalism,<sup>5</sup> according to the specifications already reported in Ref. 3, was used in the calculation of the band structures displayed in Fig. 2. In this figure the heavy lines indicate the  $\pi$  bands while the lighter ones refer to the  $\sigma$  bands.

where

$$\Delta = [2\epsilon_B^2 + 12V_2^2 + 4V_1^2 - (2\epsilon_C + 4V_1)\epsilon_B + 4V_1\epsilon_C]^{1/2} \quad (2)$$

The band folding of graphite introduces six new  $\pi$  states at  $\Gamma$ , which originate from the first two stars of states associated with M containing three elements each.<sup>6</sup> When projected onto the representations of the small group of  $\Gamma$  ( $D_{6h}$ ), these stars must split into two singlets,  $\Gamma^{(4)}$  and  $\Gamma^{(8)}$ , and two doublets,  $\Gamma^{(5)}$  and  $\Gamma^{(12)}$ .<sup>7</sup> In graphite the two stars of states remain degenerate (by accident from the perspective of a larger unit cell) but in the  $BC_3$  monolayer the splitting of  $\Gamma^{(5)}$  and  $\Gamma^{(4)}$  gives rise to its semiconducting behavior.

Physically the splittings can be interpreted by inspection of the symmetrized combinations of Bloch sums corresponding to these states. As can be seen in Fig. 3 the symmetries reveal that the two doublets,  $\Gamma^{(5)}$  and  $\Gamma^{(12)}$ , contain only orbitals localized on C rings which completely decouple from the B rings, while the singlets contain B's as well. Therefore the singlets have their energies shifted upward with respect to the doublets because of the smaller binding energies of the B's  $p_z$ -orbitals compared to those of C. Specifically a tight-binding model of the  $\pi$  bands, which considers only nearest neighbor interaction, yields the following expressions for the new  $\Gamma$  states:

In these equations  $V_1$  and  $V_2$  are the C-C and C-B hopping terms, while  $\epsilon_C$  and  $\epsilon_B$  are the C and B  $p_z$  atomic term values. Within this approximation, the expressions for  $E_5$  and  $E_{12}$  remain unperturbed by the presence of B in the neighborhood of C's, which can be observed by the alignment of these states in Fig. (2-a,b). The above expressions together with others for the other  $\Gamma$ , M and K states eigenvalues yield the values  $V_1 = 2.2$  eV,  $V_2 = 2.4$  eV,  $\epsilon_C = -8.1$  eV, and  $\epsilon_B = -7.0$  eV from which the LDA  $\pi$  bands can be reproduced within few tenths of eV.<sup>8</sup>

It is interesting that the same phenomenon which creates the gap also raises the highest valence  $\sigma$  bands into the gap region. The presence of B orbitals in the original  $\Gamma^{(6)}$  graphitic doublet, which remains degenerate in  $BC_3$ , lifts these states above the  $\Gamma^{(5)}$   $\pi$ -doublet, which does not contain any B orbital and brings the Fermi level now to the top of the  $\sigma$  bands. The symmetry of these states is shown in Fig. 4.

The immobility of  $BC_3$  bands containing exclusively C orbitals is also manifested in the  $\sigma$  manifold. This can be seen in a new  $\sigma$  multiplet ( $\Gamma^{(11)} + \Gamma^{(9)}$ ) which appears in the folded bands of graphite, and is originated from the

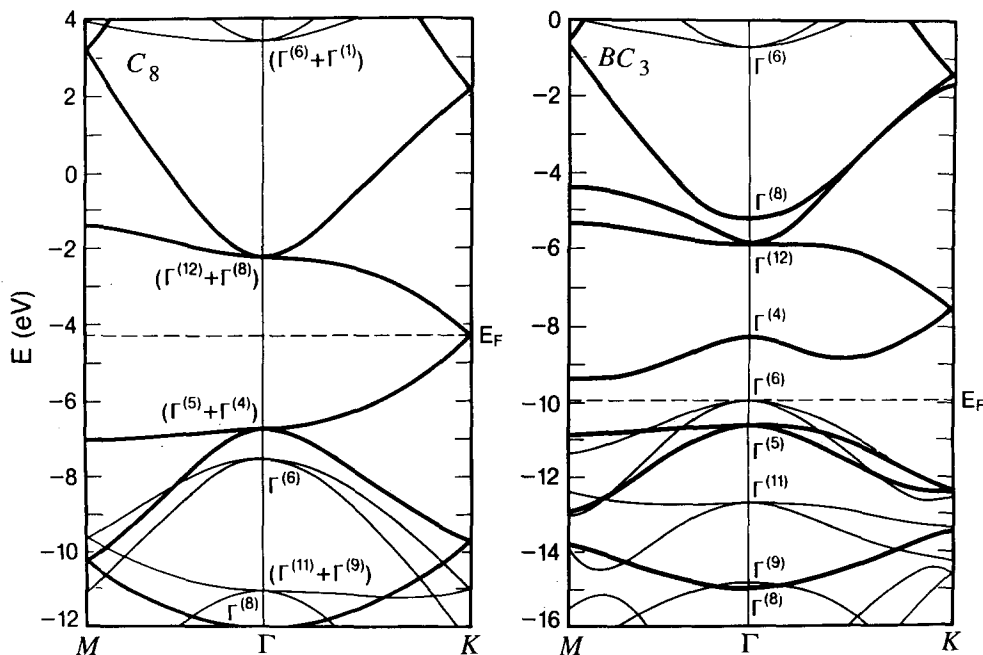


Fig. 2 - Band structures of a) graphite containing 8 atoms/cell, and b)  $BC_3$  monolayers.

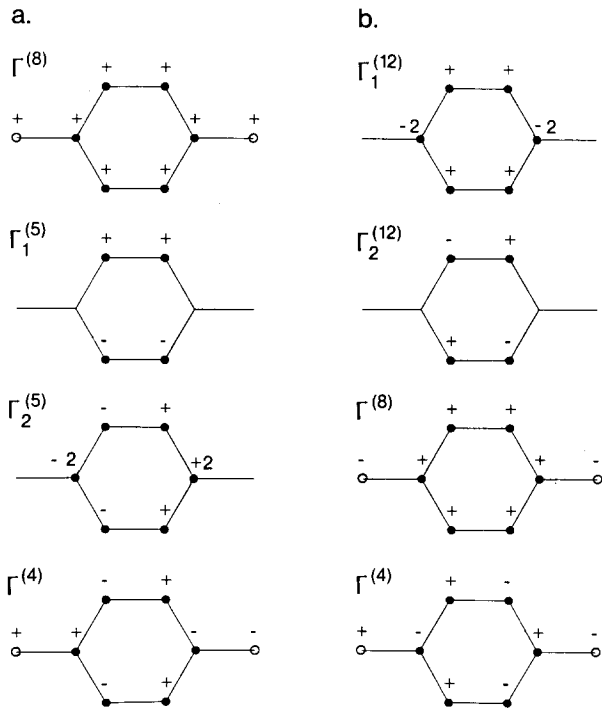


Fig. 3 - Symmetries of the  $BC_3$   $\pi$  states at  $\Gamma$ , containing one  $p_z$  orbital per site; a) derived from graphitic valence and b) graphitic conduction states.

star of states associated with the highest valence  $\sigma$  states at M. This accidentally degenerate multiplet must split into a doublet  $\Gamma^{(11)}$  and a singlet  $\Gamma^{(9)}$  in  $BC_3$ , in which case  $\Gamma^{(9)}$  is free of B. As the calculation demonstrates, the doublet is raised in energy, due to the presence of B in these orbitals, while the singlet remains essentially stationary with respect to the original multiplet in pure graphite.

It is also interesting to note that the energy separation between the  $\sigma$  and  $\pi$  states free of B ( $E_{\Gamma^{(5)}} - E_{\Gamma^{(9)}} = 4.2$  eV) remains almost unchanged when B is introduced in the structure. This is not an obvious result because the occupation of  $\pi$  bands, and consequently the charge density in the inter-layer region, change considerably in  $BC_3$ , what may affect enough the potential in this region and cause an overall shift of the  $\pi$  with respect to the  $\sigma$  manifold. This observation lends stronger support to the interpretation that the relative shift of the  $\Gamma^{(6)}$   $\sigma$ - and  $\Gamma^{(5)}$   $\pi$ -doublets around the Fermi level in  $BC_3$ , is caused by the presence (absence) of B orbitals in the  $\Gamma^{(6)}$  ( $\Gamma^{(5)}$ ) states.

Upon stacking of  $BC_3$  monolayers, the  $\pi$  bands are expected to acquire dispersions along the  $z$ -direction of the order of 1 eV similar to graphite, but the details of how the dispersions are going to occur is difficult to predict because of the many possibilities created by different ways of stacking the large unit cell. Inspection of two stacking sequences, whose density of states were already reported in previous publication, indicate that in both cases the Fermi level lies on  $\sigma$  bands. In the first

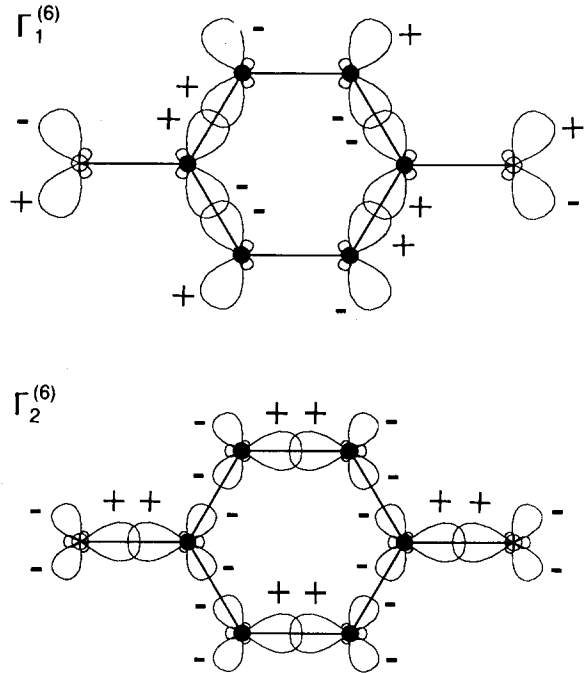


Fig. 4 - Symmetries of the highest valence  $\sigma$  states at  $\Gamma$  in  $BC_3$ . The orbital sizes indicate approximately the amplitudes of the  $sp^2$  orbitals.

case, AA stacking, all atoms lie over equivalent atom and the interacting orbitals from adjacent layers have the same phase along the basal plane. In the second case, AB stacking, all B atoms lie over C atoms. This case is marked by a small dispersion along the  $z$ -direction for  $\pi$  states which do not contain B orbitals, for instance the  $\Gamma^{(5)}$   $\pi$  states, and the contribution of the  $\sigma$  bands at the Fermi level becomes even more important.

Hence the comparison between the band structure of  $BC_3$  monolayer and the folded bands of the graphite monolayer, shows that the  $\sigma$  bands of  $BC_3$ , which are inert from the point of view of electrical conduction in pure graphite, are very likely candidates to receive hole-carriers together with the  $\pi$  bands upon stacking of the layers and subsequent shift of the Fermi level. Therefore the simultaneous presence of  $\sigma$  and  $\pi$  bands at the Fermi level enhances the conductivity of  $BC_3$  with respect to graphite as observed.

**Acknowledgements** - The authors acknowledge N. Bartlett and M. Kertesz for making their results available prior to publication. RMW acknowledges Conselho Nacional de Desenvolvimento Científico e Tecnológico, CNPq, from Brazil for financial support in the initial stages of this work. SGL acknowledges the support of the Center for Advanced Materials at Lawrence Berkeley Laboratory. This work was supported by NSF Grant No. DMR8319024 and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Material Science Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098. Cray computer time was provided by the San Diego Supercomputer Center.

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- (8) The agreement of few tenths of eV is obtained for the valence and the lowest conduction  $\pi$  bands from which these values are obtained. For the higher conduction bands the deviations are of the order of 2 eV.