RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 32, NUMBER 10 15 NOVEMBER 1985

Electronic interlayer states in hexagonal boron nitride

A. Catellani, M. Posternak, and A. Baldereschi*
Institut de Physique Appliquée, Ecole Polytechnique Fédérale, CH-1015 Lausanne, Switzerland

H. J. F. Jansen and A. J. Freeman
Department of Physics and Astronomy, Northwestern University, Evanston, Illinois 60201
(Received 6 August 1985)

Full-potential self-consistent linearized augmented-plane-wave calculations for hexagonal boron nitride show the existence of unoccupied interlayer states similar to those found in pure and intercalated graphite. Furthermore, in contradiction to the currently accepted picture, the resulting energy-band structure indicates that hexagonal BN is an indirect-gap insulator.

Hexagonal boron nitride (h-BN) is a layered compound which is isoelectronic to graphite. Both crystals consist of a stacking of two-dimensional arrays with honeycomb structure, and are characterized by strong intralayer bonds and weak interlayer interactions. The electronic states are also similar and, in a simple linear combination of atomic orbitals (LCAO) picture, the sequence of their energy bands with increasing energy is σ and π bonding, π and σ antibonding, with the Fermi energy E_F located in the middle of the π bands. The major difference between the two materials is that the π-bonding and π-antibonding bands overlap weakly at the Brillouin-zone boundary in graphite, which is thus a semimetal, whereas these bands are separated by an energy gap of several eV in BN, which is therefore an insulator.

It has been shown recently[1-3] that the LCAO method with a minimal basis set does not provide the correct energy-band structure of graphite above E_F. By contrast, when a set of basis functions with sufficient variational freedom is used, additional unoccupied bands appear, corresponding to interlayer states that exhibit free-electron character parallel to the atomic planes and which result from bonding and antibonding combinations of surface states bound to single graphite layers.[2,3] The existence of interlayer states has recently been demonstrated for pure graphite and LiC_6 using inverse photoemission spectroscopy.[4] Because of the similarity between grraphite and h-BN, the question arises whether interlayer states exist also in the latter material.

Available energy bands for h-BN are unable to answer this question. In fact, they have been obtained either (i) in the two-dimensional approximation,[5-7] or (ii) in minimal basis LCAO calculations,[8-11] or (iii) with the orthogonalized plane wave (OPW) method using a limited number of plane waves so that convergence was not achieved for the conduction bands.[12] A new three-dimensional calculation is therefore required in order to determine if interlayer states exist in h-BN. Results of such a study may also provide useful information with which to understand the nature of the optical properties of pyrolytic boron nitride, presently believed to be a direct-gap insulator as a result of considerable experimental[13] and theoretical[5-12] effort.

In this paper, we present the results of a precise three-dimensional all-electron full-potential self-consistent calculation of the energy bands of h-BN. We find that unoccupied interlayer states do exist in the lower portion of the conduction bands. This result confirms our earlier finding for graphite and LiC_6, and indicates that, as expected, interlayer states appear to be a general feature of layered materials.[2] We also show that our present understanding of the electronic structure and of the optical properties of h-BN near the fundamental band gap requires revision. We find that h-BN is an indirect-gap insulator.

Hexagonal BN has D_{6h} symmetry and the unit cell contains two formula units from two consecutive layers. The values of the lattice parameters are $a = 2.504$ Å and $c = 6.66$ Å.[14] Electronic energies and wave functions have been calculated with our all-electron local-density self-consistent full-potential linearized augmented-plane-wave (FLAPW) method.[15] The Hedin-Lundqvist exchange-correlation potential has been used. The resulting energy-band structure is displayed in Fig. 1. The classification of the electronic states at Γ follows the notation used by Robertson.[11] The valence bands are in close agreement with those reported previously (see, e.g., Ref. 11). In addition to the usual sequence of π- and σ-antibonding states above the Fermi energy, however, we find a new band which is the lowest conduction band at Γ. It has a strong parabolic behavior around its minimum at Γ and is located 4.7 eV above the top of the valence band at H. This band has Γ_1^+ symmetry, i.e., it is even under the reflection σ_h with respect to the atomic planes. Since the unit cell of h-BN extends over two consecutive layers, the parabolic interlayer band originating at Γ_1^+ folds back at the upper Brillouin-zone boundary. As found in graphite, it gives rise to a second higher-energy interlayer state at Γ with Γ_3^+ symmetry, i.e., antisymmetric under σ_h, and is located 10.0 eV above the top of the valence band. We also notice from Fig. 1 that the two new bands modify the conduction-band structure to some extent through hybridization between the interlayer states and the σ and/or π states with the same symmetry. It is apparent that experimental evidence for the existence of these new states could be obtained via inverse photoemission spectroscopy measurements, similar to those performed in graphite.[4]

The total occupied charge-density contours for BN in the basal plane and in a vertical plane through a BN bond is given in Fig. 2. The striking part of the right side of this figure is the clear separation of charge density in this interlayer region. The interlayer nature of the new Γ_1^+ and Γ_3^+

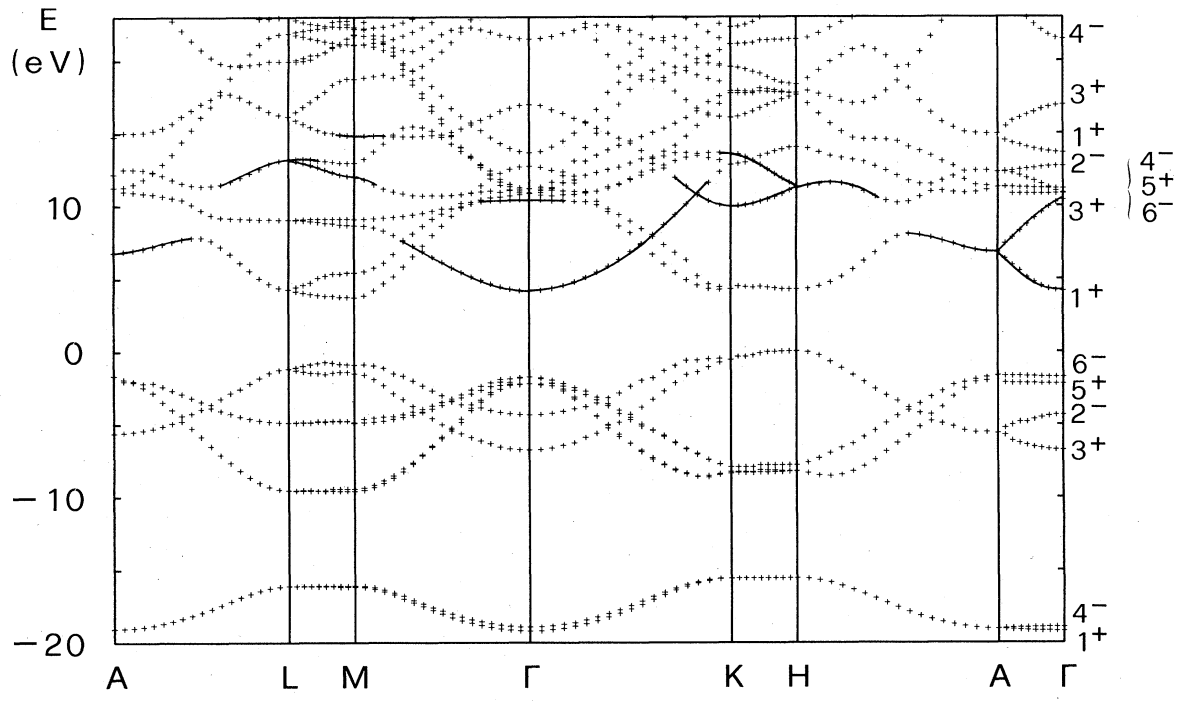
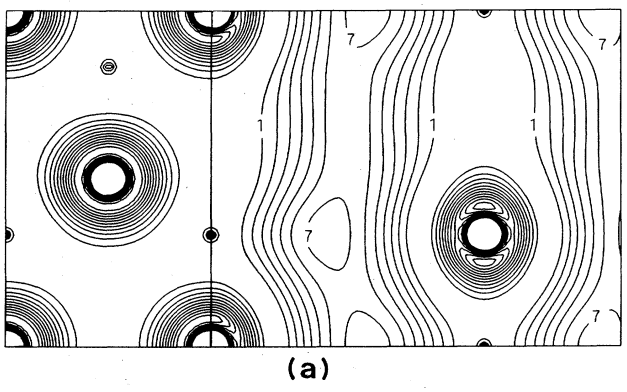


FIG. 1. Energy-band structure of hexagonal BN. Electron states at the zone center are classified following the notation used by Robertson (Ref. 11). Solid lines help to identify the interlayer bands which show several (anti)crossings with σ and π states.

bands is now clearly evident from the single-state densities given in Fig. 3 which plots their charge-density contours in the same planes as shown in Fig. 2. Note the large concentration of charge in the interlayer region between two consecutive layers where most of the charge (86% and 57%, respectively) is localized. It is evident from Fig. 2 that the charge-density contours of the interlayer states (cf. Fig. 3) reflect the larger extent of boron with respect to nitrogen. Their contour structure close to the B nuclei originates from orthogonalization to states which lie at lower energy.

As is clear from the bands shown in Fig. 1, the lowest direct band gap occurs at the H point; its value is 4.3 eV. However, our results show that h-BN is an indirect-gap in-



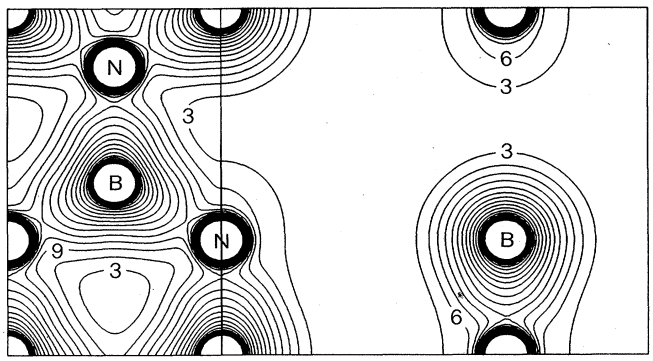


FIG. 2. Contour plots of the total electronic charge density for hexagonal BN in the basal plane (left) and in a vertical plane through a BN bond (right). Contour values are given in units of $0.1e/\text{Å}^3$. Subsequent contours differ by $0.3e/\text{Å}^3$.

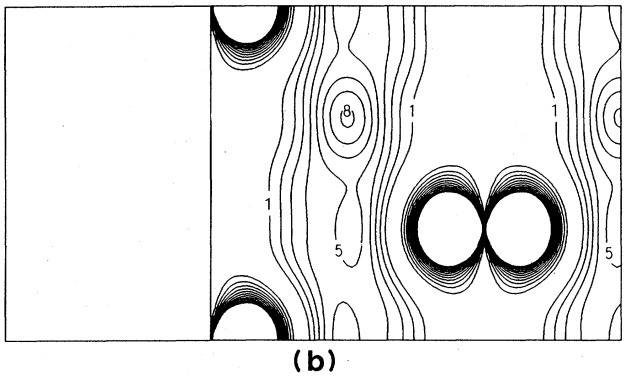


FIG. 3. Charge-density contour plots in the same planes as Fig. 2 for (a) the symmetric Γ_1^+ and (b) the antisymmetric Γ_3^+ interlayer states. Contour values are given in units of $0.01e/\text{Å}^3$, with subsequent contours separated by $0.01e/\text{Å}^3$.

sulator with an energy gap of 3.9 eV between the valence-band maximum at H and the conduction-band minimum at M. It is well known that the local-density approximation (LDA) underestimates the values of energy gaps. The relative values of different LDA gaps are, however, more reliable, in particular for gaps in the same energy range and which correspond to transitions between states of a similar atomic nature. These two conditions are fulfilled for the lowest direct and indirect gaps in h-BN, which are both ~ 4 eV and involve transitions between π states originating from atomic p_z orbitals. Thus, while LDA results cannot accurately predict the absolute values of the lowest band gaps, we have strong evidence from the relative gaps that the material is an indirect-gap insulator. This result disagrees with all previous theoretical predictions, except possibly that of the OPW calculation.[12] Although the authors do not comment on the nature of their lowest gap, inspection of the published OPW band structure suggests an indirect character.

A comparison of our data with experiment[13] indicates that the use of LDA underestimates the low-energy gaps of h-BN by ~ 1 eV. With this in mind, our results provide the following model for the optical spectra near the fundamental threshold: (i) In the intrinsic perfect material, absorption starts at ~ 5 eV with indirect transitions from H (valence band) to M (conduction band). (ii) The lowest direct threshold occurs at the point H at a photon energy of ~ 5.5 eV. (iii) The $e \perp c$ spectrum is dominated by a doublet at photon energy near 6.5 eV, corresponding to direct transitions which occur close to the L-M direction. Our LDA bands show, in fact, the existence of two saddle points in the joint density of states at 5.4 and 5.8 eV corresponding to transitions at M. (iv) The experimentally observed electronic absorption from ~ 1 to ~ 5 eV must be attributed to extrinsic transitions involving impurity and defect states.[13] This absorption masks the intrinsic indirect edge at ~ 5.0 eV and makes the lowest direct edge at ~ 5.5 eV difficult to detect.

Finally, we want to comment on the possible existence of electronic surface states[3] in h-BN. Because of the similarity between the interlayer bands in graphite and in h-BN, one is tempted to suggest that there will also be an electronic surface split off from the bottom of the bulk interlayer band in h-BN. Considering, however, that insulators are much less polarizable than are metals and semimetals, it is expected that the potential experienced by an electron in the vacuum region near the surface of h-BN is less binding than the corresponding potential for graphite. Calculations directed at verifying if surface states exist in h-BN are in progress.

This work was supported by the Swiss National Science Foundation and the U. S. National Science Foundation (Grant No. DMR 82-16543 and a computing grant from its Office for Advanced Scientific Computing at the University of Minnesota Computing Center). One of us (A.C.) acknowledges the financial support of the Consiglio Nazionale delle Richerche (CNR), Italy.

---

*Also at Istituto di Fisica Teorica and Gruppo Nazionale di Struttura della Materia, Consiglio Nazionale delle Ricerche, Università di Trieste, I-34014 Trieste, Italy.

[1]N. A. W. Holzwarth, S. G. Louie, and S. Rabii, Phys. Rev. B **26**, 5382 (1982).

[2]M. Posternak, A. Baldereschi, A. J. Freeman, E. Wimmer, and M. Weinert, Phys. Rev. Lett. **50**, 761 (1983).

[3]M. Posternak, A. Baldereschi, A. J. Freeman, and E. Wimmer, Phys. Rev. Lett. **52**, 863 (1984).

[4]Th. Fauster, F. J. Himpsel, J. E. Fischer, and E. W. Plummer, Phys. Rev. Lett. **51**, 430 (1983).

[5]E. Doni and G. Pastori, Nuovo Cimento **64B**, 117 (1969).

[6]A. Zunger, J. Phys. C **7**, 76 (1974); **7**, 96 (1974).

[7]R. Dovesi, C. Pisani, and C. Roetti, Int. J. Quantum Chem. **17**, 517 (1980).

[8]J. Zupan, Phys. Rev. B **6**, 2477 (1972).

[9]J. Zupan and D. Kolar, J. Phys. C **5**, 3097 (1972).

[10]A. Zunger, A. Katzir, and A. Halperin, Phys. Rev. B **13**, 5560 (1976).

[11]J. Robertson, Phys. Rev. B **29**, 2131 (1984).

[12]M. S. Nakhmanson and V. P. Smirnov, Fiz. Tverd. Tela **13**, 3288 (1971) [Sov. Phys. Solid State **13**, 2763 (1972)].

[13]D. M. Hoffman, G. L. Doll, and P. C. Eklund, Phys. Rev. B **30**, 6051 (1984), and references therein to earlier experiments.

[14]R. W. G. Wyckoff, *Crystal Structures* (Interscience, New York, 1965), Vol. 1.

[15]H. J. F. Jansen and A. J. Freeman, Phys. Rev. B **30**, 561 (1984).