PH YSICA L RE VIE% B VOLUME 13, NUMBER 12 15 JUNE 1976

O~& proyerties of hexagons& boron nitride

13 OPTICAL PROPERTIES OF HEXAGONAL BORON NITRIDE 5561

6.5 6.0 5.5

Energy (eV)
5.0 4.5 4.0

E
O

O 4- be

O

A. ZUNQ EH, A. KAT ZIR, AND A. HALP ERIN 13

5.5 5,0
1

Energy (eV)
4.5
I

4.0

4„(K, r)=N '~ Pe'"'&X„'(r —R„),

tp

OPTICAL PROPERTIES OF HEXAGONAL BORON NITRIDE 5563

i =1...ehN, (5)

is employed, the BZ integration is replaced by a direct sum, yielding
N c

(6)
T

'

indicates the normalization of the crystal func-tion 4,(r) Eq. (5) and N„de ntoes the number of occupied levels in the crystal. The diagonal P„,(0) element represents the p,-orbital charge on site a due to all occupied levels in the crystal. The net atomic charge is given by
ty

q.„=z.„-P J„„(o), (7)

on the

5564 ZUNGER, A. KATZIR, AND A. HALPERIN

Expression (10) for the diagonal element has a
simple physical interpretation. The first term
represents the contribution of an isolated neutral
atom, the second term corrects for deviation from
neutrality at a particular site due to the bonding
in the crystal, while the third term represents screened Madelung-type electrostatic forces exerted by

OPTICAL PROPERTIES OF HEXAGONAL BORON NITRIDE 5565

potentials

FIG. 5. Molecular hexagonal BN clusters. Open and dark circles denote different types of atoms. The verti-cal arrows on clusters 1, 2, 3, 4, and 7 denote the direc-
tion in 2rs.

5566 A. ZUNGEH, A. KAT ZIB, AND A. HALP ERIN

p+
3
p+

(c)

p r
OP

-IO-
0

p-
UJ
UJ

p+ -20-&

p+
5

p+2-

JI'

p~ r

Pl
la

p+

jp

pi

p+2

p+

I

+ ~ Q] p-

p+
3

~p

FIG. 6. Sand structure
of two-dimensional hexa0,-
onal boron nitride. Dashed
lines indicate 7) bands. The
highest occupied valence
state is I'&. (a) Extended
Huckel (EXH); (b) simple
iterative extended Huckel

(SIEXH); (c) modified iterated
extended Huckel (MIEXH).

-30

p+ Q+ Pi p+

I

p+

Q P P Q P P Q P

and borazine~~'45 (1.2 eV) and seems to be con-sistent with the interpretation of the x-ray photo-emission data of hexagonal boron nitride. 4~
An examination of the various terms appearing
in the Hamiltonian elements [Eq. (5)] reveals
the reason for the contrasting behavior of SIEXH compared with both EXH and MIEXH results. The simple iterative scheme (SIEXH) tends to lower the atomic orbital energies of the positively

ene3she of 5g /Xi6 8.5 Tf 113.9s.

13 OPTIONAL PROP ERTI ES OF H EXAGONAL BORON NITRIDE 5567

energy due to the linear one-center terms is most
pronouncedly revealed by the decrease in the band
gap between the zone corner P, and P~ states that
are pure nitrogen and boron 2p, Bloch states,
respectively, while the zone center (I') and zone-
edge (Q} points are affected to a smaller extent due to interference of boron and nitrogen Bloch functions at these points in the BZ (compare Figs. 6(a} and 6(b). This leads to an increased dis-persion of the mbands, a a- m separation and, an increase in the m valence-band width and to a de-crease in the ionization potential (= —SNI) in the SIEXH results relative to the EXH results. %hen the two-center electrostatic terms are in-
cluded in the Hamiltonian elements (MIZKH), they
tend to cancel the one-center terms due to the

alternating signs of the charges on the two sub-lattices. The electrostatic terms thus screen effectively the one-center terms, resulting in a much lower dependence of the atomic orbital en-ergies on charges (and hence the iteration pro-cedure converges more rapidly) and in a reduction in the degree of charge neutralization characteriz-ing the SIEXH scheme. The noniterative EXH method thus becomes a good approximation to the complete self-consistent MIEXH method regarding
one-electron energies, whereas the latter method
is still better for charges (QN = —Q„=O. 55 e in MIEXH}. The inclusion of the Madelung-type terms
results in an over-all stabilization of the bands.
Owing to the larger stabilization of the bonding va-lence bands, the onset of o -a~ transition (I'2- I",)
increases to 10.4 eV and a smaller increase oc-

curs in the saddle-point transitions at Q (see Table
I). The o'- v overlap at the valence-band zone
center increases to 2. 2 eV and the m band width to
5. 1 eV. This behavior of the Madelung-type
terms is consistent with the apparent success of the simple EXH method and explains the abnormal-ly low-energy gap previously

in

SIEXH

calculations. '7 Similar near-cancellation effects between Madelung and linear terms in the charge have been

and

(in)Tj ET BT /Xi7 8.

charge

M e

5570 A. ZUNG ER, A. KAT Z IR, AND A. HALP ERIN

I I

500—

0.0

=

I)

8 N

- 500

-I000

CO

-I500
E

-2000
C3

-2500

-5000

—5500

-4000

-4500 I
-5.5 -5.0 - 2.5 -2.0 -

I,S

—I.O

- 0.5

I

0.0

I
I
I
I
I
I
I

0.5 I.O

I

~

i
I

l.5 2.0 2.5 5.0 5.5

R (a. u)

FIG. 8. Electrostatic potentials computed from CNDO charge density for small clusters, along the central B-N bond (Fig. 5). The B-N distance was taken as 1.446 A.. Distance denoted in atomic units. Dashed line, BSN; solid line, N3B, dash-dot line, Cluster 7 (Fig. 5).

(3) are computed from the finite clusters. A
similar comparison for the CNDO calculations is
shown in Table 7' where the CNDO band structure
calculated by Kapsomenos' and confirmed by our
independent calculation is compared with the CNDO cluster band structure. It is seen that although the CNDO and SIEXH results differ markedly, the re-sults of the cluster band-structure approximate very well those of the direct self-consistent method,
in both cases. It thus appears, that it is possible
to obtain good approximations to the self-consistent band structure by replacing the "free-atom" po-

tentials used in noniterative tight-binding methods, with the matrix elements obtained from self-con-

sistent-field (SCF) calculations on finite clusters. CNDO band-structure calculations were previously shown to yield very poor results (overestimation of the band widths by a factor of 5-10 and overestima-tion of the lowest interband transitions by a factor of -3) both in graphite56 ~8, and in boron nitride, ss'ss mainly due to the neglect of overlap. In these covalent systems, characterized by short bonds, the overlap integrals play an essential role in de-termining the

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in

5572 A. ZUNGER, A. KAT ZIR, AND A. HALP ERIN

using the modified iterative extended Hifckel
(MIEXH) method. It should also be noted that re-
flection measurements indicated9 that E & 5. 5 eV

and showed'0 a prominant peak at 6.2 eV which fits
well the results of the present work. In addition,
photoconductivity measurement in the present work (Fig. 4) as well as glow-curve measure-ments also indicate E &4. 5 eV. Vfe conclude

therefore that the "knee" in the absorption spec-trum near 4 eV does not correspond to the gap of the pure crystal.
The experimental temperature dependence of the band gap fitted to the expression E,(T) = E~(0) —PT
reveals a very low-temperature coefficient (P&4
&&10 ' eV/'K). This value is lower by at least an
order of magnitude compared to shifts in cubic III-V compounds. This abnormally low value is explained theoretically by the absence of the two-
center boron-nitrogen terms in the expression for
the gap due to the special symmetry of the P-point in the hexagonal Brillouin zone.
The main conclusions to be made from the the-oretical study in this work can be summarized as follows:

(i) Owing to the substantial electronegativity dif-ference characterizing the atoms constituting the III-V unit cell of the III-V compounds,

OPTICAL PROPERTIES OF HEXAGONAL BORON NITRIDE

5A.