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Electronic structure of filled tetrahedral semiconductors

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is far smaller than the experimental value Ef," '=24.6 eV.
Most of this discrepancy can be removed by canceling the
spurious self-interaction associated with the LDA, yielding a
self-interaction corrected (SIC) value'5 Ets,'c of 25.8 eV.
%ere He to interact negligibly with the host crystals, it
would give rise to a narrow He 1s band located approxi-
mately at Ei,—4 below the valence-band maximum
(EvaM), where 4 is the intrinsic host work function (5.2, 5.9, and 5.5 eV, respectively, for Si, GaP, and GaAs). Us-ing Et, =EfP" in these semiconductors puts such a band at
about EvaM 10 eV—, where it was found by RSW (Ref. 8)
and in our earlier, conventional LDA calculations. '6 This
spurious positioning of the He ls band in resonance with
the host valence band (the valence-band width is —12.5
eV) induces substantial repulsion of host states of the same
symmetry. Using, however, either Ei,' or Ei',"P' One
predicts instead a dispersionless He 1s band at 19-20 eV
below EvsM, i.e., well belo~ the valence-band minimum.
When constructing a pseudopotential for He, then, it is na-tural to adopt a configuration which places the 1s orbitals in
the core (unlike that used by Bachelet, Hamann, and
Schluter in their He potential'4), thereby generating (using
the SIC procedure'7) an essentially repulsive potential (since the 1s orbital is pseudized by the 2s). Its radius reflects the core size of He, much as does an empty core pseudopoten-
tial, defining a volume excluding other e1ectrons through
Pauli repulsion. Hence, in our calculations the presence of
helium atoms will be manifest not by where valence elec-
trons are found, but rather by where they are not found The.
problem of finding the changes induced in the electronic
structure by insertion of He atoms in the empty interstitial
sites is now mapped into the more transparent problem of calculating the response of the host electronic structure to
electron-repelling potential wells at these sites.
With this formulation of the problem, it is straightforward
to understand the potential susceptibility of zinc-blende ma-
terials to band modification by insertion of closed-shell
atoms at the interstitial sites. The high tetrahedral sym-
metry, but different chemical content, of the occupied C and
A sites in the (highly directional) sp -bonded zinc-blende
materials implies very different, quite spatially inhomogene-
ous charge distributions for Bloch states P„a(r) (of band in-
dex n, wave vector k) for different high-symmetry points in
the BZ (band-by-band or state selectivity of the charge den-
sity), unlike the roughly uniform valence charge density for, e.g., s electron metals. Moreover, the vacant interstitial V~
and V~ sites possess this same high symmetry, and perturb-
ing potentials centered on these sites will selectively affect
bands associated primarily with these sites. One expects the
principal effect of insertion of a closed-shell atom on a
given state to be simply expulsion from the Pauli exclusion
volume of its contribution to the valence charge density
(thereby raising the kinetic energy of the corresponding or-bitals, and hence the single-particle band eigenvalue for this state). These circumstances raise the possibility that filling
the tetrahedral sites will have a chemically specific, selective
effect on certain bands.
The emphasis above on sites and excluded volume makes
it natural to seek an explanation in the charge densities for
the relevant states. Whereas the charge densities of the oc-
cupied (bonding) bands at Vz and Vc are small, even a
minor rearrangement can have a major effect on their anti-
bonding (i.e., conduction band) counterparts In Fig. 1 we.
display for GaP and Si the partial (pseudo) charge density

p„a(r) =

bandr9 Tf T BT 6Xi1 8.33 Tf89 191.22 Td (effeceA)Tj Ei1 8.9T /Xi1 7.88X67.78 50.78 Td (fnd)Tj T /Xi1 671 8.53 Tf(X3 44.89 605.56 Td (9,)Tj 4T BT /X

differ(the)Tj 4ET BT /Xi1 8.74 TTf 67.78 50.78 Td (fo)Tj ET BT /X671 10.5 Tf 189.56 605.56 Td (EvaM)Tj 5155724XT /Xi1 8.5X 44.89 605.56 Td (9)Tj ET0BT /Xi

state)a closed-shel=

circumstancea distributergy

banda8r244 494.5r7.5978n.22 50 Tl=

a

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i5Cg
L

(a) ~& (b)
L3C -~ X3C
C LIC 15C

~s$+~.-:::::::::+&x, c.

'

C::::::::.:-:.:.:::::::::-'::::;:::j '.....::-'.:::::::--'::.:::::::

L2V GaP

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]iv

I I a

= o.55 I

0-Llv

~-14

p
c
4l 4 L3

g ~1

0

w'.

2V

L3

HOGaPHe

a =56OA

X3V

X)V

I S = -o.54)

S

- 14
L

~~ tg= i.26(
I XL

I
q
I

Q=o.2si
C X

FIG. 2. Band structures of GaP (a), HeGaPHe (b), Si (c), aud
HeSiSiHe (d), at their respective theoretical equilibrium lattice con-
stants. Origin for (a), (b) is at Ga, for (c),(d) is at bond center. Dotted lines in (b),(d) indicate lowest conduction bands for GaP, Si at equilibrium lattice constant of HeGaPHe and HeSiSiHe, respec-tively.

Fig. 1(c)], and it is largely the differential susceptibility to He
insertion between the X and I BZ points which accounts for
the dependence of 8 on the presence/absence of He. Inser-
tion of- He dramatically reduces the indirectness parameter 5

by comparable amounts for GaP and for Si (changes in S of —0.99 and —0.98, respectively), converting GaP into a
direct gap material (s-ince its theoretical initial So,v=0.55 was small), but leaving Si, in contrast with the results of RSW,
slightly indirect (since its theoretical initial Ss;=1.26 was
larger), with the direct gap little changed from pure Si. We note that, whereas the X3,-X~, splitting in HeGaPHe is little changed from GaP, the order ofthe X3, and Xt, bands has in terchanged, due to the large energy shift of the phosphorus-like X3, state in response to the occupation of the Vc site
next to Ga. In contrast to the RSW results, we find none
of the substantial (—2.4 eV) He-induced broadening of the
valence bands (indeed, we find some narrowing), and the
upward shift in the lowest conduction band at X (1.2 eV) is only about

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Interestingly, EEvo for HeGaPHe and HeSiSiHe constitutes
only a small part (18% and 11% in GaP and Si, respectively)
of A Et„, the rest being a chemically specific electronic effect
resulting from the He-induced charge redistribution (Fig. 3).
%hile such effects have been considered for He in metals, '
their neglect in the pioneering calculations for He in
semiconductors' ' has resulted in an underestimation of
hE, (by a factor of about 8) and an associated overestima-tion (by 10s) of its solubility; a more recent calculation'9(. "~
overestimates AE, by about the same factor.
The foregoing analysis indicates that directness of the band gap can be enhanced by placing electron-repelling ob-jects in the tetrahedral interstitial sites where the lowest conduction band has a higher electron density than other bands and hence is selectively shifted upwards. Can we use this rule to predict direct gap filled tetrahedral structures,
where the stuffing atom is stabiy bound to the lattice (i.e.,
hE„,(0, unlike the He case)'? We suggest that this is the

case for the Nowotny-Juza compounds of the LiZnP type.
In this structure, the Zn and P atoms take up the regular ca-tion and anion positions, respectively, of the zinc-blende lat-tice, whereas the Li atoms fill half of the tetrahedral inter-
stitial sites. We suggest that in analogy with GaPHe, this
structure be viewed conceptually as a zirnc-blende (ZnP)
crystal (where the extra electron is compensated by a uni-formly distributed positive background of one charge) plus
an interstitial Li+ cation (isoelectronic with He). Figure
4(a) depicts the band structure of (ZnP) calculated with the augmented spherical wave method2 showing, in fact, the same qualitative features as the bands of GaP (except

(a}

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L1c

~15c

~e ~«Xsc ~ ~ e~e «g g~o ~ ~ ~ ~ ~ ~ ~ ~ ~ ~

gy -4
O
c -8- ~~
lal

1)v

3v

Xq„--

XL

3v

1v

FIG. 4. Band structures of (a), the hypothetical zinc-blende
(ZnP) compound and its filled analog LiznP, (b).

for the narrow Zn 3d band in the lo~er part of the valence band). In particular, the system has an indirect gap. When we insert Li at the interstitial Vp site [Fig. 4(b)l, the Xs, conduction band is shifted to higher energies more than do the other bands, exposing the I ~, point as the conduction-
band minimum. The system has become a direct-gap ma-
terial. However, in contrast with HeoaPHe, we find LiZnP
to be stable towards disproportionation. In fact, we find a preference for Li to reside at Vp rather than at Vz„, suggest-
ing an ordered interstitial compound. While to our
knowledge it is not yet experimentally known if the
Nowotny-Juza compounds are semiconductors, let alone
direct, this study predicts such systems to be direct gap (in the range of 1.3-2 eV) stable semiconductors, hence of po-tential technological interest.

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