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sides on these substitutional sites. In contrast, the
conduction-band state I &

(I'2 in Si) is antibonding s-like
around both V, and V, and can have amplitude on both
sites [in a proportion reflecting the relative ionicity of the
two atoms in the cell, e.g., residing mostly on the Cl site in
CuC1 (Ref. 7)]. Insertion of a closed-shell atom or ion
(e.g., He, Li+) into the sites V, or V, then leads via the
orthogonality requirement to a Pauli repulsion of conduction
electrons2 and an upward shift of the energy of the conduc-
tion band having largest s amplitude on that site. Since the
conduction bands of GaP at X have much larger relative
amplitudes on the interstitial sites than does the conduction

band I' t, insertion of He into V, (V,) was found to push X~ (X3) to higher energies than I'~, converting indirect-band-
gap GaP into the direct-band-gap material HeGaPHe. The
same principle was applied to LiZnP, where it was shown2
that it is a direct gap material since insertion of Li+
(isoelectronic with He) into the interstitial site of (ZnP)
(isoelectronic and isostructural with GaP) pushes upward
, the conduction bands at Xmore than I ~.
In the present work we extend this study to a different
member of the Nowotny-Juza compounds, LiZnN..Our aim
is twofold: (i) Since Al and Ga binary zinc-blende phos-
phides (A1P,GaP) are indirect-gap materials, but their ni-
trides (A1N, GaN) are direct-gap systems, it is interesting to
see whether the same rule that governs the conduction-band
structure of ternary phosphides (e.g., LiZnP) also applies
the ternary nitrides (e.g., LiZnN); (ii) in some of the ter-
nary nitrides (e.g., LiMgN) the A' atom does not order on
either the V, or V, sites, but remains statistically distribut-
ed, '

implying a small energy difference between the sites.
We then wish to determine the site-preference energy as
well as the insertion energy.
We have applied the nonrelativistic augmented-spherical
wave method to V,ZnNLi and LiZnN V, using the observed
LiZnN lattice constant' a =9.2162 a.u. We use the Hedin-
Lundqvist exchange-correlation functional and equal sphere

radii (r =2.2689 a.u.) for all four (Zn, N, V„and V,)
space-filling spheres. Self-consistency is achieved to a toler-
ance of —0.1 mRy, and partial waves up to an angular
momentum l of 2 for each sphere (up to i=3 for multi-
center integrals in the Hamiltonian) are retained. The
resulting band structures of V,ZnNLi (Li nearest the N
anion), V,ZnN V, [(ZnN) with both interstitial sites emp-
ty and a uniform compensating positive charge added for
neutrality to the Ewald potential], and LiZnN V, (Li nearest
the zinc cation) are depicted in Figs. 2(a), 2(b), and 2(c),
respectively. We use the same lattice constant of a =9.2162
a.u. for all three structures [whereas in the work of WZD2
the band structures of (ZnP) and LiZnP, Fig. 4 of WZD,
were calculated close to the respective equilibrium volumes,

i.e., a =10.2976 and 10.9201 a.u., respectively1. We also indicate in Fig. 2 the total charges Q, and Q, (including s, p,
and d components) enclosed within spheres of radius 2.2689
a u. about the V, and V, sites, respectively, in each

conduction-band state at I, X, and L. We find the hy-
pothetical zinc-blende compound (ZnN) [Fig. 2(b)] to be a
direct-band-gap semiconductor, in analogy with its binary
compound GaN (the latter crystallizing at low pressures in
the wurzite structure with a direct principal band gap cal-
culations for GaN in a cubic zinc-blende structure with its

wurzite unit-cell volume also show a direct band gap). In-
spection of the charges Q, and Q, for the conduction bands

a,=o.~o x, (a)

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:,e tc Q 0 q) Q = 0.10

—Kqy

.„-W—~~K
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ZA, 3d

5

0 0

"""""'-"-""""' """'""'""''-'

- 5

- 10— V,Z.NLi

- 15— W~v

- ',:~ggv' 'Q&
-':,
, X I

= 013

i' 'p '

-...

3~ |Q =0.5't» 3
:~1g
r, rf.:.a
15v
Xsv

0.0
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Q)
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X3q

FPPXAPp ~i'Wizzxziiizzxx gggggyyjy/////////~////~ ~///& ++/++&

ZFI, 3d -10— VcZnNVa

- 15—

Qa=o'7 '-: x::~a o.ii= 0 -040'

L~3v

x5v -5— L2v X3y

&/////iiFj ~iuuzuaaui wzzaazzzzayiggyggj P///lz FEIST
- 10—

- 15—

Vlf

1v

Zfl, 3CI

LN~Rv LiZnNY~

W1

X W K

FIG. 2. Calculated band structures (method of Ref. 8) of (a)
V,ZnNLi, (b) V,ZnNV~, and (c) LiZnN V~, for lattice parameter a =9.2162 a.u.

of (ZnN) at high-symmetry points [Fig. 2(b)] reveals that
X3 has most of its charge at the V, site and X» has much of its charge at the V, site. Insertion of Li at V, [Fig. 2(a)]
hence raises the energy of Xt, insertion at V, [Fig. 2(c)1
raises the energy of X3. Since the I ~ state has significant
amplitude at both V, and V„substitution at either site
raises the energy of I ~. However, since the conduction
bands at L for zinc-blende compounds have relatively much
more interstitial charge than do those at I, the former are
more strongly perturbed by interstitial substitutions than are
the latter. As a result the "degree of band-gap directness"
(i.e., the amount by which the lowest

OP

56 Td 76 Tf 461 8.15 Tf 389.11 204.44 Td (a)Tj ET Brni1 8.51 8.15 Tf 3 184.33 Td (I,)Tj 0BT /X

the 303.78 194.78 Td (bands)u.15 vXi1 8.4 ET BT7T /Xi1245.67 Td'N 356.1eaf 346.vXi1 8.4 g67 Td (d (at)Tj ET BT /Xi1 8.62 Tf 492.335.67 TT BT7T /Xi1in)Tj -sh BT /Xi1 8

potwX3y

d (at)Tj

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sites. This is depicted in Fig. 3(a). The results can be sum-
marized in the form of a rule: "substitution of the
tetrahedral interstitial sites in

a zinc-blende semiconductor

by He- or Li -like species (i.e.

, repulsive

s core potentials,
attractive non-s core potentials) raises (lowers) the energy
of the conduction bands that have

s (non-s) character on
these sites.

" For example, L3 has strong

s character at V,

[Q,'(X3)

= 51.5%1, so that substitution of this site raises the
energy of X3 dramatically (by 2.17 eV). Xt has strong

s

character at V, (Q,'=18.8%); hence, substitution of this site

raises its energy [by 0.83 eV, in proportion to Q,'(Xt)/ Q (X3)=0.37, close to 0.83/2. 17= 0.38]. Lt, likewise, has a strong s character at V, [Q,'(L~) =20.7%], leading to an

upward shift of this state (by 0.94 eV) upon substituting the V, site (again, following approximately linearly the intersti-tial charge Q'). The I t state has s character at both V, and
V,

; hence, its energy shifts upwards upon substitution of ei-
ther site. On the other hand, L~ and X~ have substantial
non-s character on the V, site, leading to

a lowering of these
energies upon substitution on

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the latter are lowered (raised) by H (He) insertion.
The apparently general validity of this new rule suggests
that the main features of the band structures of ternary FTS
materials may be deduced from the band structures and in-
terstitial charge analyses of the underlying binary materials.
Similarly, although it is not known with certainty if shallow
interstitial impurities [e.g., ZnSe:Li (Ref. 14)) occupy V, or
V„our rule can be used to characterize their gap levels in
terms of perturbed conduction bands: If the interstitial
atom is next to the anion its level will be lower in the gap than a V, interstitial.
The remarks above deal with effects of interstitial site in-
sertion on conduction-band states of the host zinc-blende
electronic structure. Hodges" has invoked similar argu-
ments for the valence bands of nontransition metals to ex-

plain trends in alloying heats of solution (i.e., neglecting en-tropy effects, in ground-state energies) in terms of the inhi-bition of response of the host system in high-/channels be-

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cause of the centrifugal barrier l(l+ 1)/2mr2 about the im-
purity site, the angular-momentum-resolved host charge
densities, and the character of the (-dependent pseudopoten-tials associated with an added impurity. In this context, we touch upon the question of the ordering energy of the

metals thrtio

thterstitial thOtot

coxt