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Electronic structure of LiZnN: Interstitial insertion rule

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LiZnN, like other Nowotny-Juza filled tetrahedral $A^{\mathrm{I}}B^{\mathrm{II}}C^{\mathrm{V}}$ compounds, consists of a $B^{\mathrm{II}}C^{\mathrm{V}}$ zinc-blende lattice with the A^{I} atoms filling half of the available tetrahedral interstitial sites. Using band calculations we deduce an "interstitial insertion rule" which shows, following an earlier argument of Wood, Zunger, and de Groot, how the electronic structures of such ternary compounds constitute recognizable distortions of those of the underlying zinc-blende $B^{\mathrm{II}}C^{\mathrm{V}}$ material. The *s*, *p*, and *d* components of the electronic charge density at the tetrahedral interstitial sites of the zinc-blende structure are shown to play a decisive role in understanding quantitatively these distortions.

Filled tetrahedral semiconductors (FTS) are zinc-blende-like compounds in which one or both of the normally empty tetrahedral interstitial sites (i.e., site V_a nearest the anion, or site V_c nearest the cation) are occupied by an atom. The Nowotny-Juza compounds[1] $A^{\mathrm{I}}B^{\mathrm{II}}C^{\mathrm{V}}$ (e.g., LiZnP), comprise a special class of such FTS; they can be viewed structurally[2] (Fig. 1) as consisting of a binary zinc-blende lattice $(B^{\mathrm{II}}C^{\mathrm{V}})^-$ consisting of B^{II} at the origin $\tau_1=(0,0,0)$ and C^{V} at $\tau_2=(\frac{1}{4},\frac{1}{4},\frac{1}{4})$, interpenetrated by a lattice of closed-shell ions $(A^{\mathrm{I}})^+$ at the tetrahedral interstitial sites V_a at $\tau_a=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ or V_c at $\tau_c=(\frac{3}{4},\frac{3}{4},\frac{3}{4})$, measuring all distances in units of the cubic-cell lattice constant *a*. We designate the underlying zinc-blende compound as $V_cB^{\mathrm{II}}C^{\mathrm{V}}V_a$ (where V_c and V_a are empty interstitial sites), and the two filled tetrahedral structures that result from occupying sites V_c or V_a, respectively, as $A^{\mathrm{I}}B^{\mathrm{II}}C^{\mathrm{V}}V_a$ and $V_cB^{\mathrm{II}}C^{\mathrm{V}}A^{\mathrm{I}}$. The filled compounds are analogous to the III-V zinc-blende semiconductors in the sense that they can be viewed conceptually as resulting from a "nuclear disproportionation" of the column III cation (e.g., Ga in GaP) into a B^{II} cation (e.g., Zn) at τ_1 and an A^{I} cation (e.g., Li) at τ_a or τ_c. Many members of this interesting class of materials (e.g., LiMgN, LiMgP, LiMgAs, LiZnN, LiZnP, LiZnAs, LiCdP, LiCdAs, and AgMgAs) were synthesized over 35 years ago,[1] but have not been characterized optically or electronically.

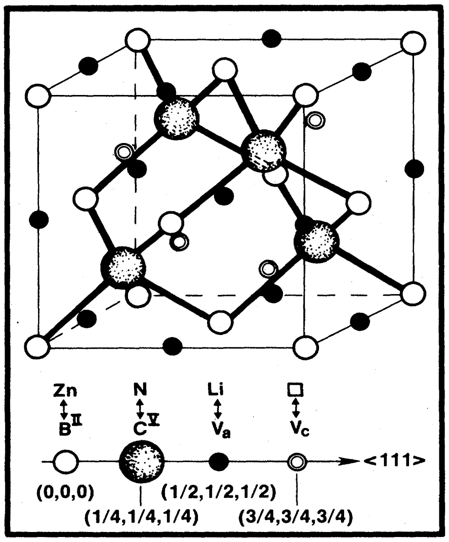

FIG. 1. Crystal structure of the Nowotny-Juza compound V_cZnNLi. Note that Zn is coordinated by four N atoms, but that N is eightfold coordinated with four Zn and four Li nearest neighbors.

In this work we provide a simple rule which describes qualitatively the band structure of FTS as recognizable distortions of the bands of the parent zinc-blende compound. Recently, Wood, Zunger, and de Groot[2] calculated the first electronic band structure for a Nowotny-Juza compound (LiZnP) and found it to be a direct-band-gap semiconductor, despite the fact that its "binary analog" (GaP) is a strongly indirect-gap material. Using the tools of self-consistent band theory and the *ab initio* total energy minimization method[3] they examined the principles determining the electronic structure (e.g., the occurrence of direct versus indirect gaps) of the FTS and the modifications away from that of the parent zinc-blende material.[2,4,5] Following WZD, we wish to emphasize that conduction-band states of both real zinc-blende semiconductors (e.g., III-V) and those of the hypothetical $(B^{\mathrm{II}}C^{\mathrm{V}})^-$ semiconductors are classified most naturally according to the wave-function character on the vacant interstitial V_a and V_c sites, rather than on the occupied substitutional sites, simply because the conduction bands have most of their amplitude on or near the interstitial sites.[2,4,5] This approach departs from the more traditional practice of classifying the extended conduction-band states according to their character relative to the substitutional sites—a tight-binding viewpoint useful for the more atomiclike valence-band states. For example, whereas the lowest conduction band at X (X_3, if the origin is on the cation[6]) is *s*-like around V_c [(p,d)-like around V_a] and has most of its amplitude near V_c, the next higher conduction band at X (X_1), as well as the lowest conduction band at L (L_1), are complementary: they are *s*-like around V_a [(p,d)-like around V_c] and have most of their amplitude on V_a. Notice that if classified from the traditional *substitutional sites* τ_1 and τ_2, X_3 (X_1) is formally characterized as cation- (anion-) like,[6] although little amplitude actually resides on these substitutional sites.[2] In contrast, the conduction-band state Γ_1 (Γ_2' in Si) is antibonding *s*-like around both V_a and V_c 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 CuCl (Ref. 7)]. Insertion of a closed-shell atom or ion (e.g., He, Li^+) into the sites V_a or V_c then leads via the orthogonality requirement to a Pauli repulsion of conduction electrons[2] and an upward shift of the energy of the conduction 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 Γ_1, insertion of He into V_a (V_c) was found to push X_1 (X_3) to higher energies than Γ_1, converting indirect-band-gap GaP into the direct-band-gap material HeGaPHe. The same principle was applied to LiZnP, where it was shown[2] 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 *X* more than Γ_1.

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 phosphides (AlP,GaP) are indirect-gap materials, but their nitrides (AlN,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 ternary nitrides (e.g., LiMgN) the A^1 atom does not order on either the V_a or V_c sites, but remains statistically distributed,[1] implying a small energy difference between the sites. We then wish to determine the site-preference energy as well as the insertion energy.

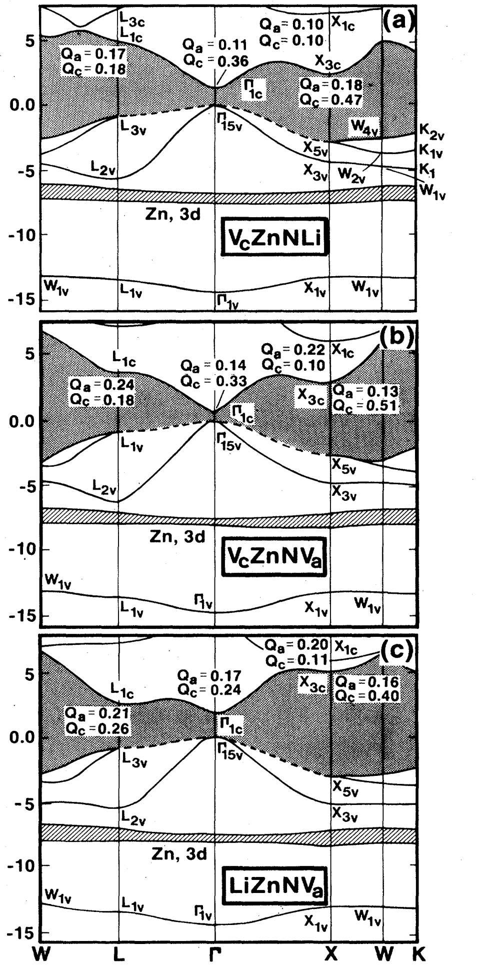

FIG. 2. Calculated band structures (method of Ref. 8) of (a) V_cZnNLi, (b) V_cZnNV_a, and (c) $LiZnNV_a$, for lattice parameter $a=9.2162$ a.u.

We have applied the nonrelativistic augmented-spherical wave method[8] to V_cZnNLi and $LiZnNV_a$ using the observed LiZnN lattice constant[1] $a=9.2162$ a.u. We use the Hedin-Lundqvist exchange-correlation functional[9] and equal sphere radii ($r=2.2689$ a.u.) for all four (Zn, N, V_c, and V_a) space-filling spheres. Self-consistency is achieved to a tolerance of ~ 0.1 mRy, and partial waves up to an angular momentum l of 2 for each sphere (up to $l=3$ for multicenter integrals in the Hamiltonian) are retained. The resulting band structures of V_cZnNLi (Li nearest the N anion), V_cZnNV_a [$(ZnN)^-$ with both interstitial sites empty and a uniform compensating positive charge added for neutrality to the Ewald potential], and $LiZnNV_a$ (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 WZD[2] 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., respectively]. We also indicate in Fig. 2 the total charges Q_a and Q_c (including *s*, *p*, and *d* components) enclosed within spheres of radius 2.2689 a.u. about the V_a and V_c sites, respectively, in each conduction-band state at Γ, *X*, and *L*. We find the hypothetical 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;[10] calculations for GaN in a cubic zinc-blende structure with its wurzite unit-cell volume also show a direct band gap). Inspection of the charges Q_a and Q_c for the conduction bands of $(ZnN)^-$ at high-symmetry points [Fig. 2(b)] reveals that X_3 has most of its charge at the V_c site and X_1 has much of its charge at the V_a site. Insertion of Li^+ at V_a [Fig. 2(a)] hence raises the energy of X_1; insertion at V_c [Fig. 2(c)] raises the energy of X_3. Since the Γ_1 state has significant amplitude at both V_a and V_c, substitution at either site raises the energy of Γ_1. However, since the conduction bands at *X* for zinc-blende compounds have relatively much more interstitial charge than do those at Γ, 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 conduction band at *X* is higher than at Γ) *increases* by closed-shell atom substitution of, say, the V_c site. This confirms the rule deduced by WZD in their earlier work[2] on LiZnP and substantiates its generality.

The rule governing the distortion of the conduction bands of a zinc-blende system through interstitial substitution of a closed-shell species can be further refined by considering the decomposition of the interstitial charges Q_a and Q_c into *s*-like (Q_a^s, Q_c^s) and non-*s*-like (i.e., *p* and *d* character, denoted $Q_a^{p,d}$ and $Q_c^{p,d}$) components *about the respective interstitial* *sites.* This is depicted in Fig. 3(a). The results can be summarized 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, X_3 has strong s character at V_c [$Q_c^s(X_3)=51.5\%$], so that substitution of this site raises the energy of X_3 dramatically (by 2.17 eV). X_1 has strong s character at $V_a(Q_a^s=18.8\%)$; hence, substitution of this site raises its energy [by 0.83 eV, in proportion to $Q_a^s(X_1)/Q_c^s(X_3)=0.37$, close to $0.83/2.17=0.38$]. L_1, likewise, has a strong s character at V_a [$Q_a^s(L_1)=20.7\%$], leading to an upward shift of this state (by 0.94 eV) upon substituting the V_a site (again, following approximately linearly the interstitial charge Q^s). The Γ_1 state has s character at *both* V_a and V_c; hence, its energy shifts upwards upon substitution of *either* site. On the other hand, L_1 and X_1 have substantial non-s character on the V_c site, leading to a *lowering* of these energies upon substitution on V_c; conversely, X_3 has substantial non-s character on the opposite V_a site, leading to a lowering of the energy of this state upon substitution of V_a. This general rule is also obeyed by the results of WZD (using the self-consistent pseudopotential method as described in Ref. 2) for HeGaPV_a and V_cGaPHe, as illustrated here in Fig. 3(b). We observe the same response of the X_3, X_1, and Γ_1 conduction bands of GaP to insertion of He into the interstitial sites as was found for (ZnN)$^-$ in response to insertion of Li$^+$. Note that p-like conduction states (e.g., Γ_{15}) respond more weakly to substitution since their associated charge densities are more uniformly spread throughout the cell. This rule directly illustrates the utility of classifying conduction-band states with respect to their angular character around the *interstitial* sites: it would have been impossible to deduce the rule from the conventional substitutional site classification.

It is natural to express this rule in terms of the effective l-dependent potentials v_l of the inserted atom (e.g., nonlocal pseudopotentials) and the angular-momentum-resolved electron density[3] $n_{l,\alpha}^{(i)}(r)\equiv\psi^{(i)}\hat{P}_l(R_\alpha)\psi^{(i)}$ of a given band state i around the interstitial site $\alpha=a$ or c.[11] [Here $\psi^{(i)}$ is a band wave function and $\hat{P}_l(R_\alpha)$ is the angular-momentum projection operator with respect to $\mathbf{R}_\alpha=\boldsymbol{\tau}_a$ or $\mathbf{R}_\alpha=\boldsymbol{\tau}_c$.] The first-row elements He and Li$^+$ have "repulsive" (i.e., non-Coulombic) s core potentials but attractive (i.e., Coulombic) non-s core potentials[12] (since no non-s states are available in the core for pseudopotential cancellation). States i which have substantial s amplitude at the interstitial site α (e.g., X_3 at $\alpha=c$ or X_1 and L_1 at $\alpha=a$) will hence be *raised* in energy by an amount $\Delta\epsilon^{(i)}\propto\int d\mathbf{r}\,v_0(r)\,n_{0,\alpha}^{(i)}(r)$ [and resulting in a *reduction* in their s content; see Fig. 3(a)], whereas states i having substantial non-s amplitude at site α (e.g., X_3 at $\alpha=a$ or X_1 and L_1 at $\alpha=c$) will be *lowered* in energy by $\Delta\epsilon^{(i)}\propto\int d\mathbf{r}\,v_{l\neq0}(r)\,n_{l\neq0,\alpha}^{(i)}(r)$ (resulting in an *enhancement* of their non-s character). This suggests that as we move to heavier group IA alkali-metal atoms, having more repulsive s and p potentials than does Li (cf., Fig. 5 in Ref. 12), the raising (lowering) of the conduction bands will increase (decrease). Insertion of hydrogen (a coreless atom) into site α will result in a *lowering* of all conduction states having amplitude at α, since $v_l(r)$ for hydrogen is attractive for all l values.[4,13] Note that the interstitial insertion rule cannot be simply described in terms of a raising of the (antibonding) conduction bands in response to interaction with the orbitals of the interstitial atom: whereas both H and He have occupied s orbitals far below the conduction bands of the host,

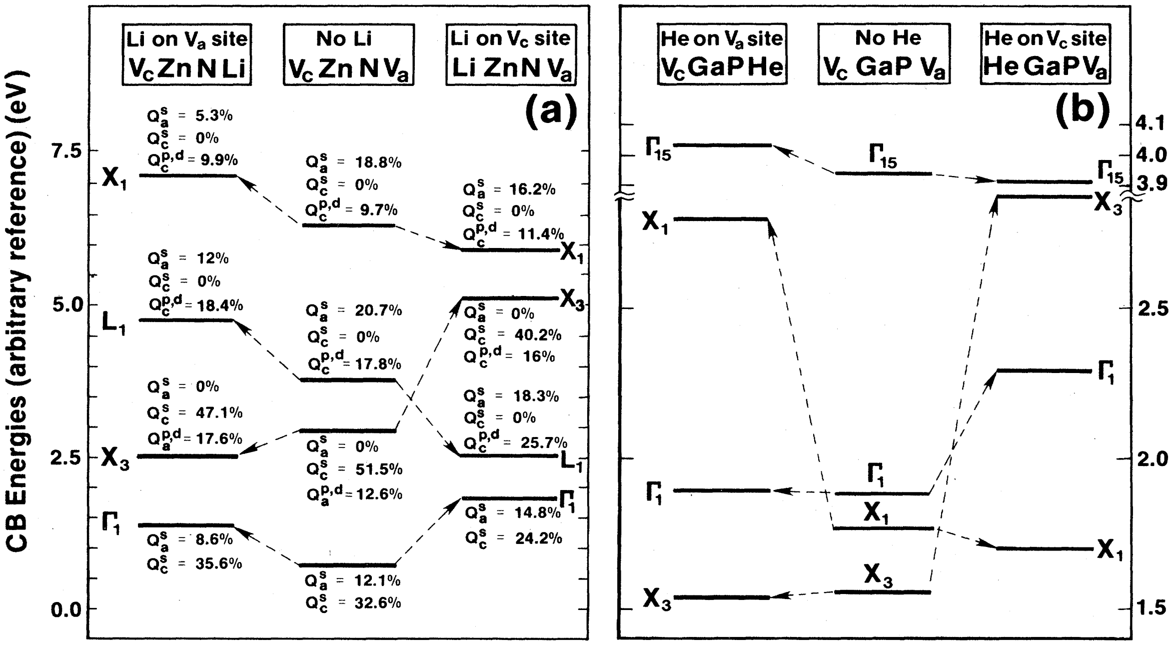

FIG. 3. Variation of energies of conduction-band states of (a) (ZnN)$^-$ and (b) GaP, with interstitial insertions of Li$^+$ and He, respectively. Results for (a) were calculated by the method of Ref. 8 for $a=9.2162$ a.u.; we also indicate the band and site charges Q_α^l for $\alpha=a,c$ and $l=s,p,d$. Results for (b) use the method of Ref. 2 with $a=10.3$ a.u.

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 interstitial 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_a or V_c, 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_c interstitial.

The remarks above deal with effects of interstitial site insertion on *conduction-band* states of the host zinc-blende electronic structure. Hodges[11] has invoked similar arguments for the *valence bands* of nontransition metals to explain trends in alloying heats of solution (i.e., neglecting entropy effects, in ground-state energies) in terms of the inhibition of response of the host system in high-l channels because of the centrifugal barrier $l(l+1)/2mr^2$ about the impurity site, the angular-momentum-resolved host charge densities, and the character of the l-dependent pseudopotentials associated with an added impurity. In this context, we touch upon the question of the ordering energy of the inserted interstitial atoms. Our total energy calculations indicate that insertion of Li next to N at V_a (creating a strong Li–N bond in the V_cZnNLi structure) lowers the total energy E_t by 1.8 eV/cell more than does insertion next to the Zn site at V_c (creating a weaker Zn–Li bond in the LiZnNV_a structure). This agees with the x-ray determination[1] and suggests, in accord with the data, that LiZnN is an ordered interstitial compound (to be understood, in our notation, as V_cZnNLi). Our results on the site preference energy suggest that Li occurring interstitially in ZnSe (Ref. 14) will prefer the V_a site; it is interesting to note that a valence force field calculation for Li$^+$ interstitial impurities in ZnSe predicted a similar preference for the V_a site (by 1 eV) over the V_c site.

If we neglect lattice relaxation, the enthalpy of solution ΔE_s [i.e., the enthalpy of reaction $(\mathrm{ZnN})^- + \mathrm{Li(g)} \rightarrow \mathrm{LiZnN}$] can, further, be estimated as the difference $E_t(V_c\mathrm{ZnNLi}) - E_t(V_c\mathrm{ZnN}V_a) - E_t(\mathrm{Li})$. We find $\Delta E_s = -4.75$ eV [using $E_t(\mathrm{Li})$ from spin-polarized local-density calculations[15] for Li], suggesting substantial cohesion of Li in this lattice; theoretical estimates for enthalpies of solution of Li in homopolar semiconductors, e.g., Si (Ref. 16) are considerably (~ 3 times) smaller. Empirical force field calculations[14] give an enthalpy of reaction $\mathrm{ZnSe} + \mathrm{Li(g)} \rightarrow \mathrm{ZnSe{:}Li}$ of $\Delta E_s \sim 2$–3 eV (calculated from the data of Ref. 14). Our calculated ΔE_s assumes constant volume (i.e., neglects relaxation); however, our estimates indicate a maximum relaxation energy of ~ 0.05 eV, suggesting a very small relaxation effect upon Li insertion. For Li at either site the lattice is compressed relative to equilibrium $(\mathrm{ZnN})^-$, with the V_a site becoming even more energetically favorable upon relaxation.

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