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Ternary and Multinary Compounds

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ELECTRONIC STRUCTURE AND STABILITY OF $A^{\text{IB}}\text{IIC}^{\text{V}}$ FILLED TETRAHEDRAL COMPOUNDS
INVITED PAPER

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ABSTRACT

The familiar zincblende structure of III-V and II-VI semiconductors has, as one traverses the $[111]$ body diagonal, a cation at $\vec{r}_1=(0,0,0)a$ and an anion at $\vec{r}_2=(1/4,1/4,1/4)a$, where a is the conventional unit cell lattice constant. "Filled tetrahedral" compounds result from occupying, in addition, one of the tetrahedral interstitial sites (unoccupied in conventional III-V's or II-VI's) at $\vec{r}_3=(1/2,1/2,1/2)a$ or $\vec{r}_4=(3/4,3/4,3/4)a$ with another atom type. Such compounds exhibit a large range of physical properties, from metals and semiconductors to "half-metallic" magnetic compounds. Structural and electronic properties of an interesting class of $A^{\text{IB}}\text{IIC}^{\text{V}}$ compounds, e.g. LiZnAs , are discussed using first-principles pseudopotential and Full-Potential Linearized Augmented Plane Wave calculations. Simple models are given to understand the observed relative stability of distinct possible phases and the electronic structure is interpreted in the light of a simple rule developed to understand distortions of a zincblende band structure induced by interstitial insertion.

INTRODUCTION

Zincblende, wurtzite, and carborundum-type binary crystals are the most loosely packed of all space groups consistent with tetrahedral coordination for both types of atoms [1]. Their openness is highlighted by the fact that for the homopolar members the ratio of the volume of the touching atomic spheres

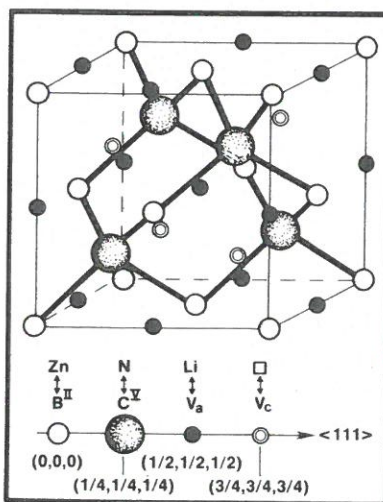


Fig. 1. Crystal structure of the Nowotny-Juza compound $V_c\text{ZnNLi}$.

to that of the unit cell is .34, less than half that for the close-packed element structures, 0.74. They may be characterized (see Fig. 1) by the existence of four vacant (V) lattice sites (holes) at the tetrahedral interstitial sites nearest the anion A (sites V_A) and four nearest the cation C (sites V_C), both at the normal nearest-neighbor tetrahedral distance $d=\sqrt{3}a/4$ with a the lattice constant. Hence as we traverse the $\langle 111 \rangle$ body diagonal in the zincblende CA crystal, with the origin, say, at the cation site $C=\vec{r}_1(0,0,0)a$, we encounter the anion A at $\vec{r}_2(1/4,1/4,1/4)a$, the V_A site at $\vec{r}_3(1/2,1/2,1/2)a$, and the V_C site at $\vec{r}_4(3/4,3/4,3/4)a$, the latter both unoccupied in normal tetrahedral structures. We may structurally designate this arrangement as $V_c\text{CAV}_A$. While this minimal packing fraction reflects the effectiveness of pure sp^3 tetrahedral bonding in forming stable compounds with low coordination number, denser packing is by no means unusual in these structure types[2-6]. This can be effected by diffusion of interstitial impurities (e.g., the 3d impurities[2a] or in silicon[2b], oc-

copying the $V_A=V_C$ sites), by stoichiometric substitution of one type of vacant site, e.g., the Nowotny-Juza $C^{II}A^IVV^I$ compounds[3] with $V^I=Li, Cu, Ag$, $C^{II}=Be, Mg, Zn, Cd$, and $A^V=N, P, As, Sb$, and Bi, the antifluorite compounds-[4] $MgAVMg$ with $A^V=Si, Ge, Sn$, or by substitution of both types of vacant sites (e.g., the B32 Zintl compounds[5] $LiAl, NaTl$, or the L2₁ Heusler alloys[6a,b,c] V_CMnAV_A , with $V_A=V_C=Co, Ni, Cu, Pd$ and $A=Al, In, Sb, Sn$). We refer to the structures with partially or completely occupied V_A and V_C sites as "filled tetrahedral structures" (FTS).

NOWOTNY-JUZA COMPOUNDS

The Nowotny-Juza compounds[3], henceforth denoted $A^I B^{II} C^V$ (e.g., $LiZnAs$), comprise a special class of such FTS; they can be viewed structurally (Fig. 1) as consisting of a binary zincblende lattice ($B^{II}C^V$) with B^{II} at the origin \vec{r}_1 and C^V at \vec{r}_2 , interpenetrated by a lattice of closed-shell ions (A^I)⁺ at the tetrahedral interstitial sites V_a at \vec{r}_3 or V_c at \vec{r}_4 . We designate the underlying zincblende compound as $V_c B^{II} C^V V_a$ (where V_c and V_a are empty interstitial sites) and the two filled tetrahedral structures that result from occupying sites V_a or V_c , respectively, as $V_c B^{II} C^V A^I$ (which we will call the α phase) and $A^I B^{II} C^V V_a$ (the β phase). The third distinct way in which we can distribute three different atoms along the body diagonal, denoted $B^{II} A^I C^V$, we will term the γ phase (Fig. 2). The α and β phases are analogous to the III-V zincblende 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 GaAs) into a B^{II} cation (e.g., Zn) at \vec{r}_1 and an A^I cation (e.g., Li) at \vec{r}_3 or \vec{r}_4 . 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[3] but were characterized only in terms of their crystal structures and colors. We have recently investigated the properties of some of these compounds theoretically[7-9].

In this paper we first present results of the first electronic struc-

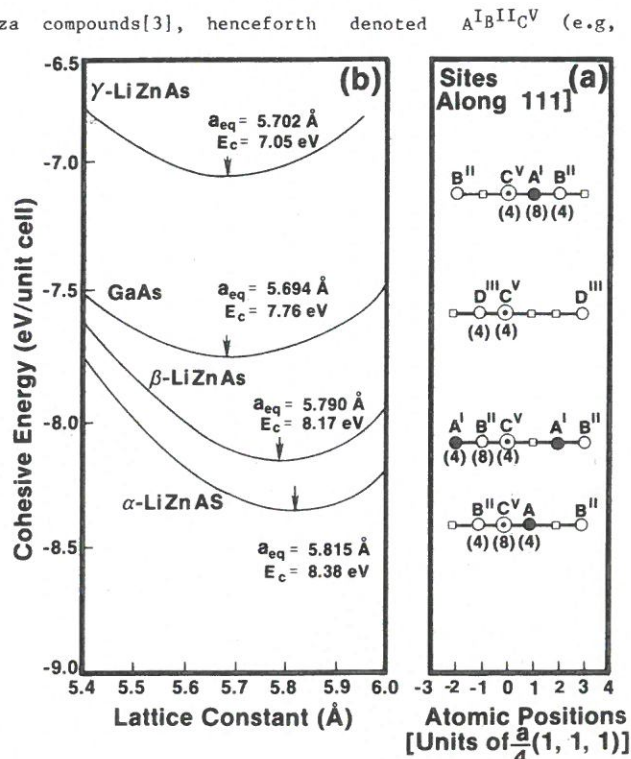
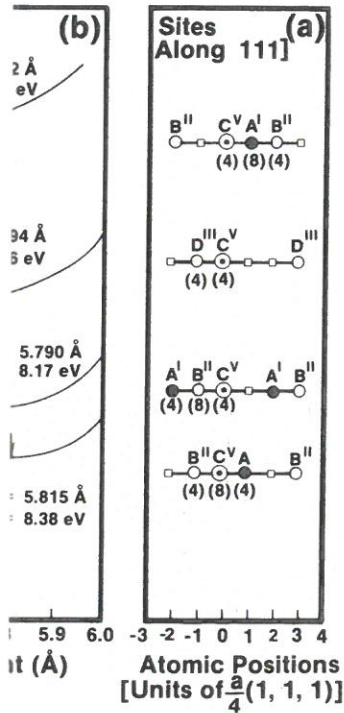


Fig. 2(a) Atomic positions along the [111] body diagonal for α , β , and γ phases of $LiZnAs$. Numbers in parentheses are coordination numbers; squares are empty sites; (b) cohesive energies.

substitution of one type of valence ions [3] with $V_A = \text{Li, Cu, Ag, Al}$, the antifluorite compound structure of both types of vacant sites, NaTl, or the L₂ Heusler alloy and $A = \text{Al, In, Sb, Sn}$. We refer to the occupied V_A and V_C sites as

which denoted $A^I B^{II} C^V$ (e.g.,



along the [111] body diagonal of LiZnAs . Numbers in parentheses are the number of ions; squares are the equilibrium energies.

2). The α and β phases are in the sense that they can undergo "disproportionation" of a B^{II} cation (e.g., Zn) at $\frac{1}{2}$ of the V_C sites of this interesting structure. LiZnN , LiZnP , LiZnAs , LiCdP , etc. [3] but were characterized by their colors. We have recently calculated the first electronic structure

calculation of the three possible ordered phases of a prototypical $A^I B^{II} C^V$ compound (LiZnAs , Ref. 9), including cohesive and structural properties. We also give semiclassical arguments which provide an intuitive understanding of the first-principles results for the relative stability of these phases. Second, we discuss the great resemblance of the bands of the two competing most stable phases to those of a III-V zincblende compound and to those of the fictitious "parent" compound ($B^{II} C^V$) [7-8]. It is shown how the details of the electronic structure of the ordered ternary compounds may be semiquantitatively predicted from the bands and interstitial charge contents of the binary ($B^{II} C^V$) using a recently-developed "interstitial insertion rule" [8] to understand the distortions induced in a zincblende III-V-like band structure attendant upon inserting He or Li^+ -like atoms. [We refer the reader to Refs. 7-9 for details.] Finally, we discuss trends for other $A^I B^{II} C^V$ and interpret via the FTS analogy recently-calculated properties of LiAlSi [5], a member of the closely-related $A^I B^{II} C^V$ class.

STRUCTURE AND COHESION OF LiZnAs

Figure 2b [9] depicts, as a function of lattice parameter, the calculated cohesive energies [10] of the α , β , and γ forms (Fig. 2a) of LiZnAs , together with that of the binary analog GaAs , showing also the equilibrium lattice constant a_{eq} and equilibrium cohesive energy E_c . The calculated a_{eq} for α - LiZnAs and GaAs (5.815 Å and 5.69 Å [11]) are close to the observed values (5.92 Å [12] and 5.65 Å [11], respectively), and so is the bulk modulus of GaAs (76.2 GPa [11]), relative to its measured value (78.9 GPa [11]).

Wei and Zunger [9], using the General Potential LAPW method [12] find the α phase to be the stablest among the α , β , and γ forms (Fig. 2b). This can be understood semiclassically both in terms of the electrostatic configurational (Madelung) energies, and in terms of bond strain energy models [13]. First, considering the classical Madelung ion-ion electrostatic energy of these cubic phases with point-ion charges q_A , q_B and q_C , (where $q_A + q_B = |q_C|$) and interatomic distances $d = \sqrt{3} a/4$, we find

$$E_M^\alpha = -\frac{1}{d} [\alpha_{ZB} (q_A^2 + q_B^2) + \alpha_{B2} q_A q_B], \quad E_M^\beta = -\frac{1}{d} [\alpha_{ZB} q_B^2 + \frac{\sqrt{3}}{2} \alpha_{B1} q_A (q_A + q_B)],$$

$$E_M^\gamma = -\frac{1}{d} [\alpha_{ZB} q_A^2 + \frac{\sqrt{3}}{2} \alpha_{B1} q_B (q_A + q_B)]. \quad (1)$$

Here, $\alpha_{ZB} = 1.6381$, $\alpha_{B1} = 1.7476$ and $\alpha_{B2} = 1.762$ are the Madelung constants for the zincblende, B1 (NaCl-like) and B2 (CsCl-type) structures, respectively and E_M for the ZB structure is $-\alpha_{ZB} q_C^2/d$. Assuming the polarity of the A, B and C atoms to be approximately structure-independent, we find from Eq. (1) $E_M^\alpha < E_M^\beta < E_M^\gamma$, i.e., the correct order of stability $\alpha > \beta > \gamma$. Second, semiclassical valence force field models [13] relating the stability of a structure which has bond lengths R_{AC} and R_{BC} to the strain-inducing size mismatch $(R_{AC} - R_{AC}^0)^2$ and $(R_{BC} - R_{BC}^0)^2$ (where R^0 are the "ideal" tetrahedral bond lengths) also indicate the stability of the α phase. Compared with the ideal average bond lengths $R_{ZnAs}^0 = 2.47 \text{ \AA}$ (2.453 Å, 2.489 Å, and 2.471 Å in [14] ZnSiAs_2 , ZnGeAs_2 , and ZnSnAs_2 , respectively) and $R_{LiAs}^0 = 2.53$ -2.59 Å (in Li_3As [15]), the α phase has both Zn-As and Li-As bond lengths ($R_{ZnAs} = R_{LiAs} = \sqrt{3} a/4$; see Fig. 2a) closer to the ideal values than the β phase ($R_{ZnAs} = 2.56 \text{ \AA}$, $R_{LiAs} = a/2 = 2.96 \text{ \AA}$) or the γ phase ($R_{ZnAs} = a/2 = 2.96 \text{ \AA}$, $R_{LiAs} = 2.56 \text{ \AA}$). Since the two-electron Zn-As bond is stronger than the one-electron Li-As bond, this argument also predicts the correct order of phase stability $\alpha > \beta > \gamma$.

Despite the fact that the III-V structure is strain-free ($R_{AC} = R_{AC}^0$) and that its classical point-ion Madelung energy is considerably more negative (even at the same lattice constant) than that of the I-III-V structure [16], we find that the cohesive energy of LiZnAs considerably exceeds that of GaAs

(Fig. 2b). We highlight this point by considering the (fictitious) transmutation of GaAs into its isovalent LiZnAs analog in a two-step process. First, dilate GaAs from its calculated equilibrium lattice constant ($a_1 = 5.69\text{\AA}$) to that calculated for LiZnAs ($a_2 = 5.81\text{\AA}$). We find that this requires an investment of an elastic volume-deformation (VD) energy $\Delta E_{VD} = 0.04\text{ eV}$ (Fig. 2b) [proportional to the strain $\sim B(a_2 - a_1)^2$]. Second, transmute the Ga nucleus into "Li + Zn", placing Li at its interstitial lattice site in LiZnAs. According to Fig. 2b, this releases a chemical (C) energy ΔE_C (partially [16] an electrostatic effect). The predominance of ΔE_C over ΔE_{VD} suggests that the excess stability of LiZnAs over GaAs is a chemical (i.e., bonding), not a bulk elastic effect. To clarify this behavior we show in Fig. 3 the calculated ground state valence charge densities in the (110) plane of the different phases of LiZnAs and GaAs at the same lattice

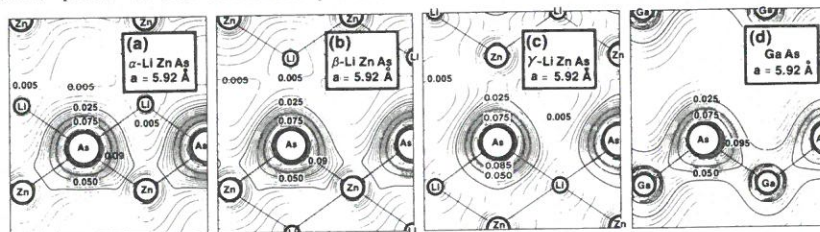


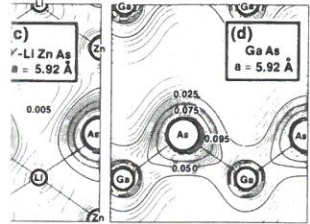
Fig. 3. Calculated valence charge densities (omitting Zn 3d band) of α , β , γ phases of LiZnAs, (a)-(c); of GaAs, (d). Contour interval 0.005 elec/a.u.³

constant. Notice the following features: (i) the Zn-As bonds in the α and β phases of LiZnAs (Fig. 3a,b) are remarkably similar to the covalent Ga-As bond in GaAs (Fig. 3d, all exhibiting local maxima along the bonds), whereas the Li-As bond is almost purely ionic (with no maxima anywhere along the bond direction). This material can hence be characterized as strongly ionic and strongly covalent at the same time. The ionic contribution to this structure stabilizes it over the purely covalent III-V zincblende structure. (ii) Examination of the charge density differences at the same lattice constant $\Delta\rho(\vec{r}) = \rho(\text{LiZnAs}) - \rho(\text{GaAs})$ reveals a small directional accumulation of charge ("residual covalency") on the Li-As bond in the α phase (far weaker in the β phase), indicative of additional stabilization of this structure. The stability of the α over the β phase is hence a consequence both of its superior electrostatic stability and the existence of residual Li-As bonds. (iii) Examination of the source of extra charge on the Li-As bond relative to the GaAs structure reveals that it originates from the residual valence charge of Li. Following a transfer of most of its valence electron to the Zn-As bond, the (screened) Li sublattice remains weakly attractive to electrons. It then forms an additional weak bond with the As neighbors. (iv) The γ phase forms no covalent bonds (Fig. 3c); its eight-fold coordinated Li sublattice gives rise to a charge distribution which can be best characterized as metallic.

ELECTRONIC STRUCTURE OF ORDERED PHASES AND "PARENT ZINCBLLENDE" COMPOUNDS

Despite the substantial partial ionic character of α and β LiZnAs (or, to be precise, because the ionic character is spatially separated from the strong covalent III-V-like bond), Wei and Zunger[9] predict these phases to be semiconducting. Calculated band structures of the α and β phases (Fig. 4a,b) show great overall similarity to that of GaAs (Fig. 4e), whereas the γ phase as indicated above is metallic (Fig. 4c). The heteropolar $L_{1V}-L_{1V}$ and $X_{1V}-X_{3V}$ gaps separating the lower from the higher valence bands are substantially larger in LiZnAs (5.30 eV and 5.34 eV, respectively, for the α -phase) than in GaAs at the same lattice constant (4.52 eV and 3.67 eV, respective-

ing the (fictitious) transmutation in a two-step process. The equilibrium lattice constant ($a_1 = 3.76$ Å). We find that this reformation (VD) energy $\Delta E_{VD} = \frac{1}{2} B(a_2 - a_1)^2$. Second, transition at its interstitial lattice releases a chemical (C) energy. The predominance of ΔE_C over ΔE_{VD} in α -LiZnAs over GaAs is a chemical effect. To clarify this behavior we compare charge densities in the α -LiZnAs at the same lattice constant as GaAs at the same lattice



ly), testifying to the larger polarity of LiZnAs. We may regard the fact that the α and β phases are direct-gap as a measure of the similarity of LiZnAs to its binary analog GaAs, also a direct gap material. The great similarity between the band structures of the two semiconducting phases and that of a III-V deserves further comment. The strongly ionic character of the Li atom in LiZnAs suggests that, more generally, the

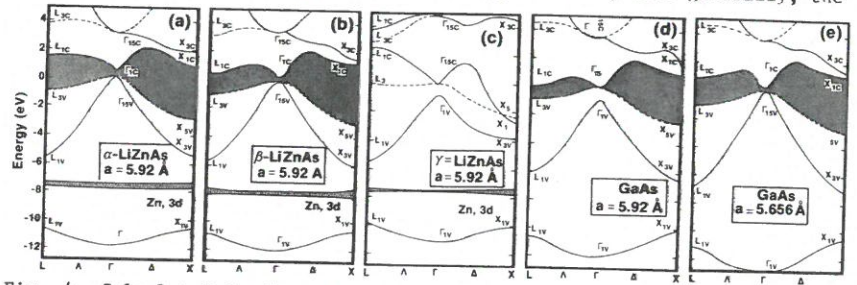


Fig. 4. Calculated band structures of LiZnAs phases at $a=5.92$ Å, (a)-(c); (d), GaAs at the same lattice constant and (e) GaAs at its equilibrium, $a=5.656$ Å. Band labels take origin at As [19]. Band gap is shaded.

ting Zn 3d band) of α , β , γ interval 0.005 elec/a.u.

e Zn-As bonds in the α and β similar to the covalent Ga-As (along the bonds), whereas maxima anywhere along the characterized as strongly ionic ionic contribution to this ent III-V zincblende structural differences at the same lattice a small directional accumulation Li-As bond in the α phase. The stabilization of this phase is hence a consequence of the existence of residual extra charge on the Li-As. It originates from the transfer of most of its valence electrons to the As sublattice remains weakly directional weak bond with the As bonds (Fig. 3c); its eightfold charge distribution which can

band structure of α - or β - $A^{II}B^{III}C^V$ should be close to that for the fictitious compound $(B^{III}C^V)^-$, in which the loosely-bound valence electron of A^I has been freed to participate in formation of the III-V-like covalent bond, but in which the remaining $(A^I)^+$ ion (for LiZnAs, Li^+ , isoelectronic with the simple closed-shell atom He) is completely omitted. Work of Carlsson, Zunger and Wood[8] demonstrates that this is in fact the case for another Nozotny-Juza compound LiZnN. They find a strong "family" resemblance between the α and β phases and the "parent zincblende" compound, $(ZnN)^-$ [shown in Fig. 5]; systematic distortions, however, are induced in the band structure (especially the conduction bands) of $(ZnN)^-$ upon insertion of the Li^+ ion. It is obvious from inspection of Fig. 4 (for LiZnAs) or Fig. 5 (for LiZnN) that the perturbation associated with Li^+ , though relatively weak, has an important effect in particular at the X point of the Brillouin zone for the conduction bands. For yet another $A^{II}B^{III}C^V$ compound, LiZnP, Wood, Zunger and de Groot[7] found the ternary compound to be a direct band gap semiconductor despite the fact that its parent zincblende compound $(ZnP)^-$ and its "binary analog" (GaP) were strongly indirect-gap materials! The moral of this observation is that "weak" perturbations can have profound effects on the electronic structure since, e.g., the direct vs. indirect nature of a semiconductor is a delicate matter which nonetheless has important technological consequences.

How should we understand the small but potentially important perturbations in the conduction bands of $(B^{III}C^V)^-$ or other zincblende-like compound when $(A^I)^+$ or another interstitial atom is inserted to make a real ternary compound? The ground state charge density of the binary analog (e.g., GaAs for LiZnAs) or the parent $(B^{III}C^V)^-$ compound provides no clue to band modifications upon interstitial insertion since interstitial ground state charge densities are very low; see Fig. 3. We wish to emphasize that conduction band states of both real zincblende semiconductors and those of hypothetical $(B^{III}C^V)^-$ are classified most naturally according to the wavefunction 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[7,17]. In Figure 6 (from Ref. [18]) we display for GaP the partial (pseudo) charge density $\rho_{n\mathbf{k}}(\vec{r}) = |\psi_{n\mathbf{k}}(\vec{r})|^2$ (band index n, wavevector \mathbf{k} in the Brillouin zone) in the zincblende (110) plane for the lowest conduction bands at the X point of the face-centered cubic Brillouin zone (X_{3c} and X_{1c} for GaP, taking the origin

"ZINCBLLENDE" COMPOUNDS

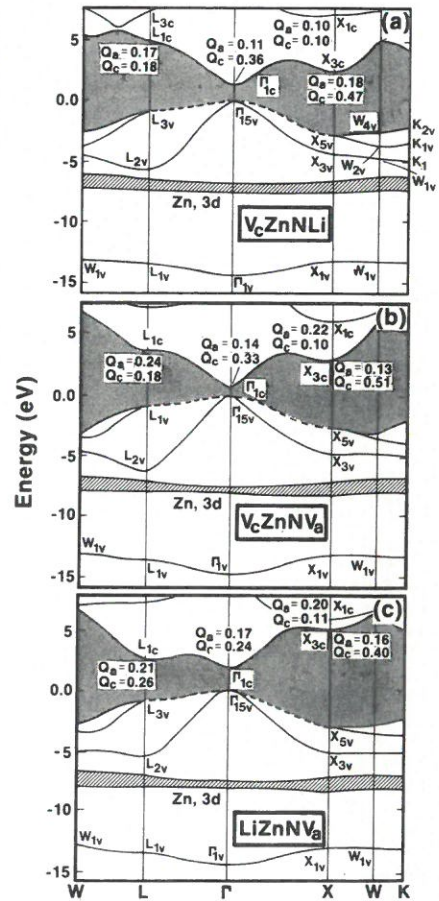
ter of α and β LiZnAs (or, spatially separated from the [9] predict these phases to the α and β phases (Fig. As (Fig. 4e), whereas the γ The heteropolar $L_{IV}-L_{IV}$ and valence bands are, substantively, for the α -phase eV and 3.67 eV, respective-

on the cation site [and hence interchanging X_3 and X_1 labels with respect to Fig. 4]). In all cases regions of high charge density are indicated by dot shading; diagonal shading indicates low charge density. This figure suggests the lowest conduction bands will show extreme selectivity with respect to insertion of closed-shell atoms: the X_{3c} (X_{1c}) band density has maxima (minima) at or near V_C and minima (maxima) at or near V_A , whereas the Γ_{1c} band (not shown) has a much smaller V_A-V_C charge density disparity. This emphasis on the interstitial sites 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

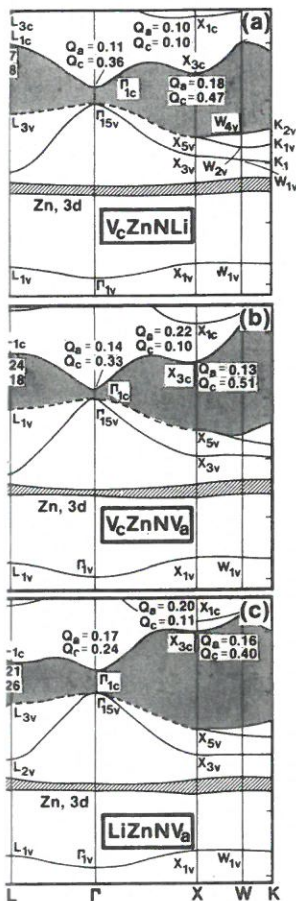
useful for the more atomic-like valence band states. For example, whereas the lowest conduction band at X for GaP (X_3 , if the origin is on the cation[19]) has most of its amplitude on V_C and is said, in analogy to the behavior of atomic wavefunctions about their origin, to be s-like around V_C (p, d-like, etc., around V_A), 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, classified from the traditional substitutional sites \ddot{t}_1 and \ddot{t}_2 , $X_3(X_1)$ is formally characterized as cation-(anion)-like[19], although little amplitude actually resides on these substitutional sites. In contrast, the conduction band state Γ_1 is anti-bonding 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[20]). 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 electrons² and an upward shift of the energy of the conduction band having largest s amplitude on that site. Insertion of He into the interstitial sites of GaP or Si was shown by Wood et al. to have profound effects on the electronic structure of the resulting compounds; the same principle was applied to LiZnP, where it was shown[7] that it is a direct gap material since insertion of Li^+

(isoelectronic with He) into the interstitial site of $(ZnP)^-$ (isoelectronic and (c), β phases of LiZnN; fictitious zincblende $(ZnN)^-$ phase, all pushes upward the conduction bands at X more than Γ_1 .

With this background we may return to Fig. 5 to understand the electronic structure of the α and β phases of LiZnN. Note that in Fig. 5 we indicate the total charges Q_a and Q_c (including s, p, and d components) en-



X_1 labels with respect to sity are indicated by dot nsity. This figure sug- : selectivity with respect band density has maxima near V_A , whereas the Γ_{1c} density disparity. This he more traditional prac- states according to their lght-binding viewpoint



closed 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 zincblende compound $(ZnN)^-$ (Fig. 5b) to be a direct band gap semi-

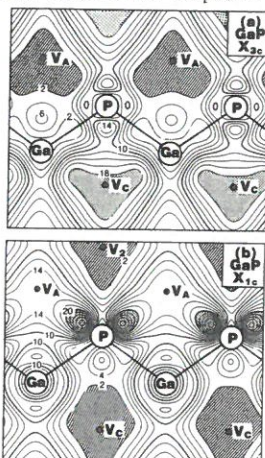


Fig. 6. Partial band pseudo charge densities (electrons/primitive cell, normalized to 8) for GaP, for (a) lowest and (b) next conduction band at X point of Brillouin zone.

conductor, in analogy with its binary compound GaN. Inspection of the charges Q_a and Q_c for the conduction bands of $(ZnN)^-$ at high symmetry points (Fig. 5b) 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. 5a) hence raises the energy of X_1 ; insertion at V_C (Fig. 5c) 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 zincblende compounds have relatively much more interstitial charge than do those at Γ , the former are more strongly perturbed by interstitial substitution 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.

INTERSTITIAL INSERTION RULE

The rule governing the distortion of the conduction bands of a zincblende system through interstitial substitution of a closed shell species can be further refined by considering the angular momentum 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. The results can be summarized in the form of a rule: "substitution of the tetrahedral interstitial sites in a zincblende semiconductor by He or Li^+ -like species (i.e., repulsive s core potentials, attractive non-s core potentials---see Ref. 21 for trends) raises (lowers) the energy of the conduction bands that have s (non-s) character on these sites". For example, referring to Fig. 7, one notes that 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 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 Wood et al. (using the self-consistent pseudopotential method as described in Ref. 18) for $HeGaPV_A$ and V_CGaPHe : they observed 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-

ted bands of (a), α ses of $LiZnN$; () of ficende $(ZnN)^-$ phase, all u.

to understand the elec- Note that in Fig. 5 we in- p, and d components) en-

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 about the interstitial

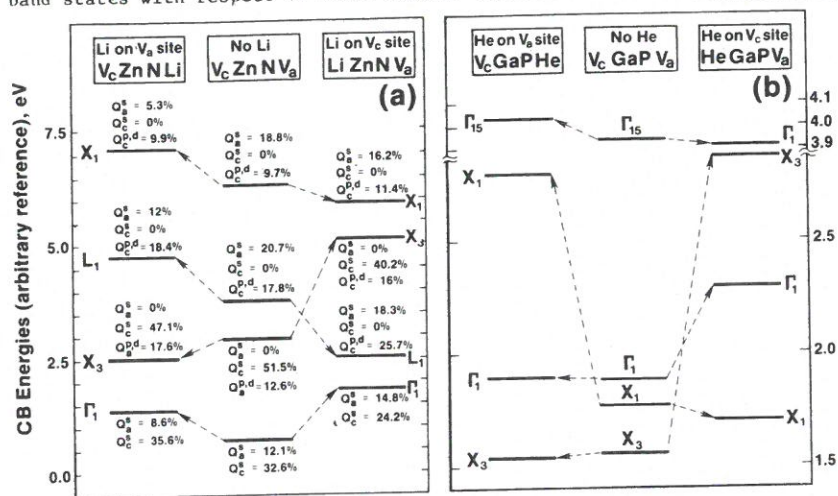


Fig. 7 Variation of energies of conduction-band states of (a) $(\text{ZnN})^-$ and (b) GaP, upon insertion of Li^+ and He, respectively; band and site charges for $\alpha=a,c$ and $l=s,p,d$ are also indicated.

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., non-local pseudopotentials) and the angular momentum-resolved electron density [18] $n_{l,\alpha}^{(i)}(r) \equiv \psi^{(i)} P_l(R_\alpha) \psi^{(i)}$ of a given band state i around the interstitial site $\alpha = V_a$ or V_c [22]. [Here $\psi^{(i)}$ is a band wavefunction and $P_l(R_\alpha)$ is the angular momentum projection operator with respect to $\hat{R}_\alpha = \hat{r}_3$ or $\hat{R}_\alpha = \hat{r}_4$; note the difference from the non-projected quantity $\rho_{nR}(\hat{r})$.] 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 [21] (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 be hence be raised in energy by an amount $\Delta\epsilon^{(i)} \propto \int dr v_0(r) n_{0,\alpha}^{(i)}(r)$ (and resulting in a reduction in their s content when non-linear effects are taken into account; see Ref. 8, Fig. 3), 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 $\Delta\epsilon^{(i)} \propto \int d^3r v_{l \neq 0}(r) n_{l \neq 0,\alpha}^{(i)}(r)$ (resulting in an enhancement of their non- s character [8]). This suggests that as we move to heavier group IA alkali atoms, having more repulsive s and p potentials than does Li (c.f. 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 [17]. 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, the latter are lowered (raised) by H (He) insertion.

For the ordered phases of LiZnAs this simple but powerful perturbative

laboration in part of the work described in this paper.

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