Electronic Structure and Phase Stability of LiZnAs: A Half Ionic and Half Covalent Tetrahedral Semiconductor

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The first electronic structure calculation of the ordered α, β, and γ cubic phases of an "interstitially filled tetrahedral compound" $A^{\rm I}B^{\rm II}C^{\rm V}$ (where the $B^{\rm II}$ and $C^{\rm V}$ atoms occupy the normal zinc-blende sites and $A^{\rm I}$ occupies one of the empty zinc-blende tetrahedral interstitial sites) reveals strongly covalent ($B^{\rm II}$-$C^{\rm V}$) and strongly ionic ($A^{\rm I}$-$C^{\rm V}$) bonds in the *same structure*, superior cohesion relative to the III-V analog (GaAs), and semiconducting (α and β forms) as well as metallic (γ form) behavior.

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Most nonmetals constructed from interpenetrating face-centered-cubic sublattices have chemical bonds which can be characterized as ionic (I-VII compounds), covalent (the IV-IV diamondlike semiconductors), or intermediate (III-V and II-VI compounds). Among these compounds, the "normal octet tetrahedral semiconductors" (e.g., diamond, zinc-blende, and chalcopyrite structures) have traditionally taken a central role in establishing much of our current understanding of covalency in condensed matter.[1-3] These normal tetrahedral compounds can be characterized as "empty tetrahedral interstitial structures" in the sense that, in addition to the four tetrahedral nearest-neighbor atoms at a distance $d=\sqrt{3}a$ (where a is the lattice parameter), each atom is also surrounded by four *empty* tetrahedral interstitial sites at the same distance d from it. One can construct, however, a class of materials where these empty interstitial sites are stoichiometrically occupied: Whereas the zinc-blende structure of a $D^{\rm III}C^{\rm V}$ compound (e.g., GaAs) has the $D^{\rm III}$ atom at $\tau_1=(0,0,0)a$, the $C^{\rm V}$ atom at $\tau_2=(\frac{1}{4},\frac{1}{4},\frac{1}{4})a$, and two empty interstitial sites at $\tau_3=(\frac{1}{2},\frac{1}{2},\frac{1}{2})a$ (next to the anion) and $\tau_4=(\frac{3}{4},\frac{3}{4},\frac{3}{4})a$ (next to the cation), one could "transmute" $D^{\rm III}$ into its isovalent pair $B^{\rm II}+A^{\rm I}$ (e.g., Ga into Zn+Li) and distribute these atoms among the τ_1, τ_3, and τ_4 sites. There are three distinct ways of distributing periodically three atoms, A, B, and C, on the four sublattices τ_1, τ_2, τ_3, and τ_4. These are denoted in Fig. 1(a) as the α, β, and γ phases of the $A^{\rm I}B^{\rm II}C^{\rm V}$ compounds.[4] Of this general group of compounds $A^{\rm I}B^{\rm II}C^{\rm V}$, with $A^{\rm I}=$ Li, Na, Cu, Ag; $B^{\rm II}=$ Mg, Zn, Cd; and $C^{\rm V}$ = N, P, As, Sb, and Bi, about 25 members have been synthesized,[4-7] mostly in the 1940's, but to the best of the authors' knowledge they have been characterized only in terms of their crystal structures (mostly α, α', γ, and γ' forms) and colors.

In this paper we describe the results of the first electronic structure calculation of all ordered phases of a prototypical $A^{\rm I}B^{\rm II}C^{\rm V}$ compound (LiZnAs). We find that (i) despite a large electronegativity difference between their constituent atoms (leading normally to insulating behavior), the α and β phases are direct-band-gap semiconductors and the γ phase is metallic; (ii) the cohesion of the α phase is larger not only with respect to the β and γ structures, but also relative to its binary zinc-blende analog (GaAs); and (iii) despite the great resemblance of the band structures of the α and β phases to those of the conventional covalent zinc-blende semiconductors, the bonding in these systems can be remarkably characterized as *half ionic and half covalent*, with the $A^{\rm I}$-$C^{\rm V}$ and $B^{\rm II}$-$C^{\rm V}$ bonds being nearly *pure* ionic and covalent, respectively.

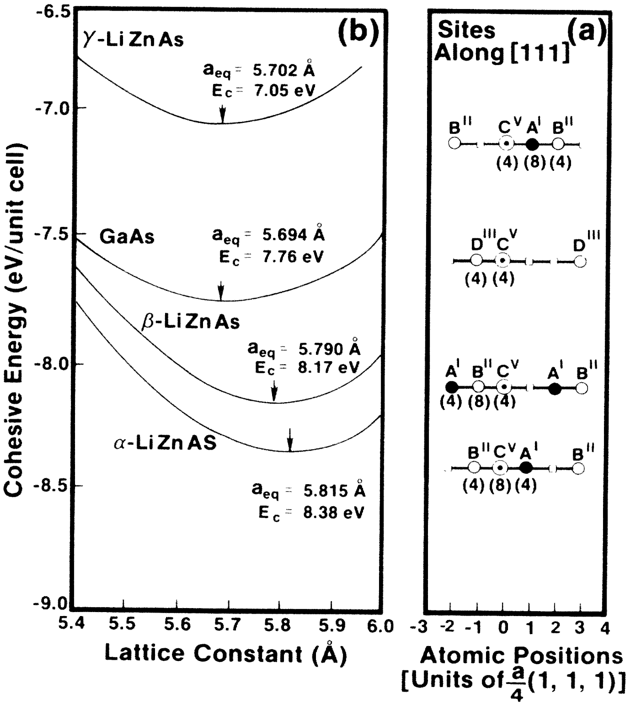

FIG. 1. (a) Atomic positions along the ⟨111⟩ crystal direction for the α, β, and γ phases and for GaAs. Numbers in parentheses denote coordination numbers. Open squares denote empty sites. (b) Cohesive energies E_c as a function of lattice constant.

We have used the general potential linear augmented plane-wave method.[8] Atomic radii of $R(\text{Li}) = R(\text{Zn}) = 2.30$ a.u. and $R(\text{As}) = 2.315$ a.u., two special **k** points, and the Hedin-Lundqvist exchange correlation were used. Figure 1(b) depicts, as a function of lattice parameter, the calculated cohesive energies[9] of the α, β, and γ forms [Fig. 1(a)] 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 and 5.69 Å (Ref. 8)] are close to the observed values [5.92 (Ref. 5) and 5.65 Å (Ref. 8), respectively], and so is the bulk modulus of GaAs [76.2 GPa (Ref. 8)] relative to its measured value [78.9 GPa (Ref. 8)].

We find the α phase to be the stablest among the α, β, and γ forms [Fig. 1(b)]. This can be understood semiclassically both in terms of the electrostatic configurational (Madelung) energies, and in terms of bond-strain-energy models.[10] 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 $d = \frac{1}{4}\sqrt{3}a$, we find

$$\begin{aligned} E_{\text{M}}^{(\alpha)} &= -d^{-1}[\alpha_{\text{ZB}}(q_A^2+q_B^2)+\alpha_{B2}q_Aq_B], \\ E_{\text{M}}^{(\beta)} &= -d^{-1}[\alpha_{\text{ZB}}q_B^2+\tfrac{1}{2}\sqrt{3}\alpha_{B1}q_A(q_A+q_B)], \quad (1) \\ E_{\text{M}}^{(\gamma)} &= -d^{-1}[\alpha_{\text{ZB}}q_A^2+\tfrac{1}{2}\sqrt{3}\alpha_{B1}q_B(q_A+q_B)]. \end{aligned}$$

Here, $\alpha_{\text{ZB}} = 1.6381$, $\alpha_{B1} = 1.7476$, and $\alpha_{B2} = 1.762$ are the Madelung constants for the zinc-blende, $B1$ (NaCl-type), and $B2$ (CsCl-type) structures, respectively, and E_{M} for the zinc-blende structure is $-\alpha_{\text{ZB}}q_C^2/d$. Assuming that the polarity of the atoms A, B, and C is approximately structure independent, we find from Eq. (1) $E_{\text{M}}^{(\alpha)} < E_{\text{M}}^{(\beta)} < E_{\text{M}}^{(\gamma)}$, i.e., the correct order of stability $\alpha > \beta > \gamma$. Second, semiclassical valence-force-field models[10] 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 $R_{\text{ZnAs}}^0 \cong 2.47$ Å (2.453, 2.489, and 2.471 Å in[11] ZnSiAs_2, ZnGeAs_2, and ZnSnAs_2, respectively) and $R_{\text{LiAs}}^0 \cong 2.53$–2.59 Å (in Li_3As[12]), the α phase has both Zn-As and Li-As bond lengths $[R_{\text{ZnAs}} = R_{\text{LiAs}} = \frac{1}{4}\sqrt{3}a = 2.56$ Å; see Fig. 1(a)] closer to the ideal values than does the β phase ($R_{\text{ZnAs}} = 2.56$ Å, $R_{\text{LiAs}} = a/2 = 2.96$ Å) or the γ phase ($R_{\text{ZnAs}} = a/2 = 2.96$ Å, $R_{\text{LiAs}} = 2.56$ Å). 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 ($R_{AC} \equiv R_{AC}^0$), and that its classical point-ion Madelung energy is considerably more negative (even at the same lattice constant) than that of the I-II-V structure,[13] we find that the cohesive energy of LiZnAs considerably exceeds that of GaAs [Fig. 1(b)]. (Contemporary models of covalency[2,3] suggest reduced cohesion with increased polarity.) 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 ($a_1 = 5.69$ Å) to that calculated for LiZnAs ($a_2 = 5.81$ Å). We find that this requires an investment of an elastic volume-deformation (VD) energy $\Delta E_{\text{VD}} = 0.04$ eV [Fig. 1(b)] [proportional to the strain $\sim B(a_2 - a_1)^2$]. Second, disproportionate the Ga nucleus into "Li+Zn," placing Li at its interstitial lattice site in LiZnAs. According to Fig. 1(b), this *releases* a chemical (C) energy $\Delta E_C = -0.68$ eV (partially[13] an electrostatic effect). The dominance of ΔE_C over ΔE_{VD} suggests that the excess stability of LiZnAs over GaAs is a chemical effect (i.e., bonding), not a bulk elastic effect. To clarify this behavior we show in Fig. 2 the calculated ground-state valence charge densities on the (110) plane of the different phases of LiZnAs and GaAs at the same lattice constant. Figure

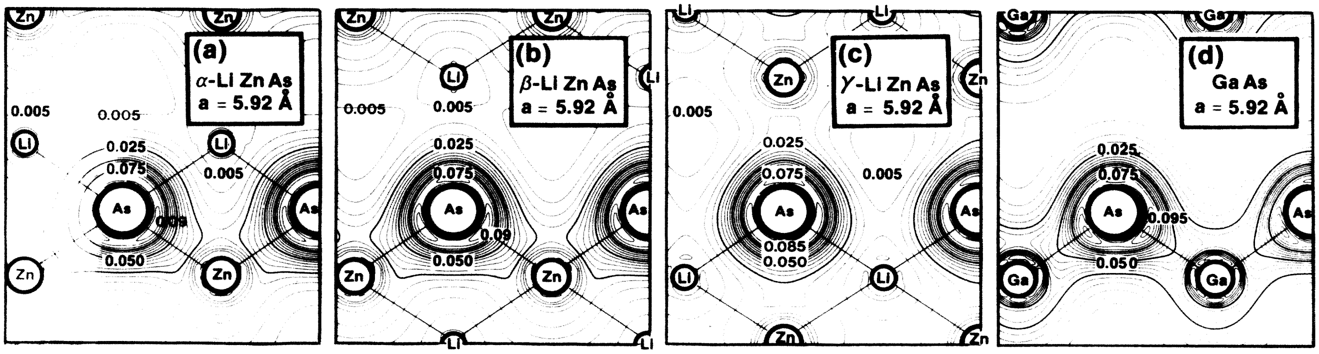

FIG. 2. Calculated valence charge densities (omitting the Zn $3d$ band) of α-, β-, and γ-LiZnAs and of GaAs. Contour steps are 0.005 e/a.u.^{3}

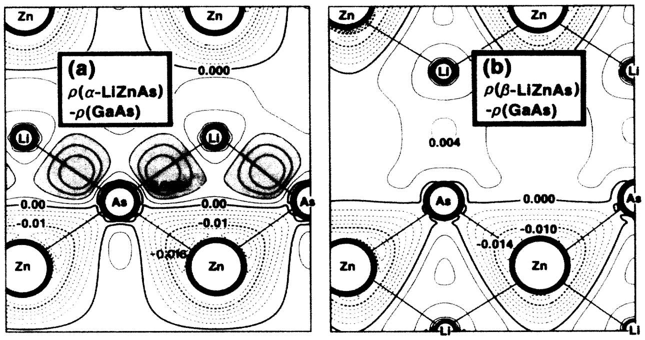

FIG. 3. Differences in valence charge densities at $a = 5.92$ Å of (a) α-LiZnAs and GaAs and of (b) β-LiZnAs and GaAs. Contour steps are 0.002 e/a.u.^{3} Dashed contours indicate negative values. The Li-As bonds are highlighted by shading.

3 depicts the *differences* in charge densities $\Delta\rho^{(i)}(\mathbf{r}) = \rho^{(i)}(\text{LiZnAs}) - \rho(\text{GaAs})$ for $i = \alpha$ and β, and $a = 5.92$ Å. Notice the following features: (i) The Zn-As bond in the α and β phases of LiZnAs [Figs 2(a) and 2(b)] is remarkably similar to the *covalent* Ga-As bond in GaAs [Fig. 2(d); both 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 zinc-blende structure. (ii) Examination of the charge-density differences in Fig. 3 reveals a small *directional accumulation* of charge ("residual covalency," depicted as shaded areas) on the Li-As bond in the α phase (far weaker in the β phase), indicative of additional stabilization of this structure. In addition, we see a global depletion of charge on the Zn-As bond, in both the α and β phases. The stability of the α over the β phase is hence a consequence of both 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 revealed 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. 2(c)]; its eightfold-coordinated Li sublattice gives rise to a charge distribution which can be best characterized as *metallic.*

Despite the substantial partial ionic character of α- and β-LiZnAs, we predict these phases to be semiconducting. The calculated band structures of the α and β phases [Figs. 4(a) and 4(b)] show great overall similarity to that of GaAs [Fig. 4(e)], whereas the γ phase as indicated above is metallic [Fig. 4(c)]. The heteropolar L_{1v}-L_{1v} and X_{1v}-X_{3v} gaps separating the lower valence band from the higher valence band are substantially larger in LiZnAs (5.30 and 5.34 eV, respectively, for the α phase) than in GaAs at the same lattice constant (4.52 and 3.67 eV, respectively) testifying to the larger polarity of LiZnAs. The conduction-band structure of LiZnAs [Figs. 4(a) and 4(b)] can also be related to that of GaAs [Figs. 4(d) and 4(e)] by the "interstitial insertion rule"[14,15] stating that substitution of the tetrahedral interstitial sites in normal tetrahedral semiconductors by atoms with repulsive s and attractive non-s effective potentials (e.g., Li^+) raises (lowers) the energy of the conduction bands that have s (non-s) character on these sites. We can therefore classify the conduction-band states in the III-V

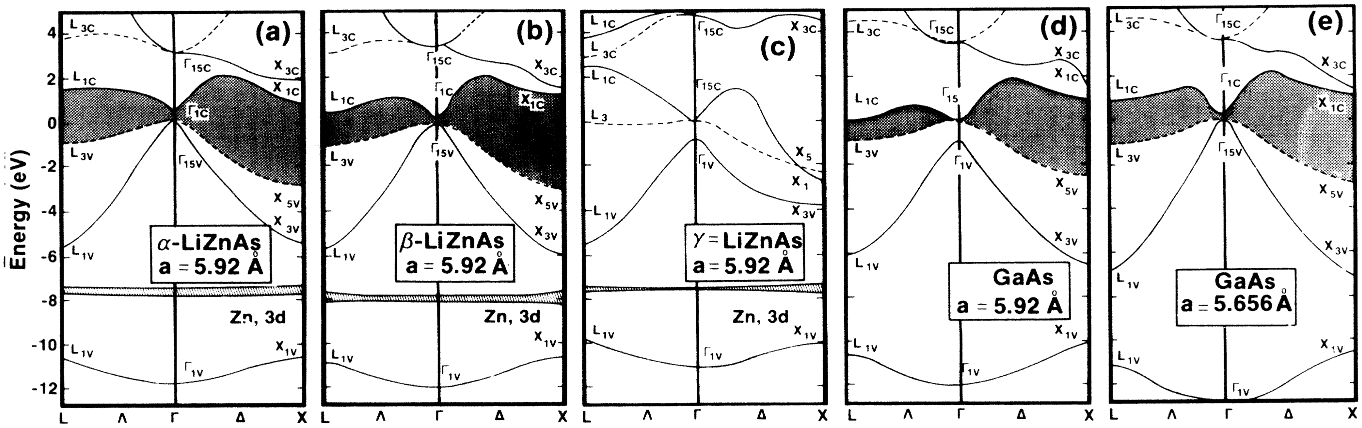

FIG. 4. Calculated band structures of (a) α, (b) β, and (c) γ phases of LiZnAs at $a = 5.92$ Å (the volume derivatives $a\,\partial F_g/\partial a$ of the band gaps of the α phase are -15.5, 4.5, and 10.1 eV, respectively, for Γ_c, X_c, and L_c), and of (d) GaAs at the same lattice constant and (e) GaAs at its equilibrium lattice constant $a = 5.656$ Å. Origin at As. The band-gap region is shaded.

system into four classes according to the angular momentum decomposition of their *interstitial charge*, and use this classification to deduce the energy shifts relative to $A^{\mathrm{I}}B^{\mathrm{II}}C^{\mathrm{V}}$. These are as follows: (i) States with *s character* on the interstitial site next to the *cation* (e.g.,[16] X_{1c}). These states will *move up in the* β *phase*, where this site is occupied. (ii) States with *s character* on the intersititial site next to the *anion* (e.g.,[16] X_{3c} and L_{1c}). These states *move up in the* α *phase*, where this site is occupied. (iii) States with *non-s character* on the interstitial site next to the *cation* (e.g., L_{1c} and L_{3c}). These states *move down in the* β *phase.* (iv) States with *non-s character* on the interstitial site next to the *anion* (e.g.,[16] X_{1c}). These states *move down in the* α *phase.* States with similar charge on *both* types of interstitial sites (e.g., Γ_{1c} with s charge and Γ_{15c} with non-s charge) move in the same direction upon occupying either sites (Γ_{1c} up, Γ_{15c} down). All of the expectations suggested by the interstitial insertion rule[14,15] are met by our calculated results (Fig. 4). This simple but powerful perturbative rule suggests that the stable α phase will have larger $\Gamma_{15v} \to \Gamma_{1c}$, $\Gamma_{15v} \to L_{1c}$, and $\Gamma_{15v} \to X_{3c}$ band gaps than the GaAs analog,[17] but a lower indirect $\Gamma_{15v} \to X_{1c}$ band gap. This prediction suggests that LiZnAs has a novel type of conduction-band structure, not encountered in any cubic III-V material: Among cubic III-V's, only BP, AlP, AlAs, and GaP have larger band gaps than GaAs; however, all are *indirect.*

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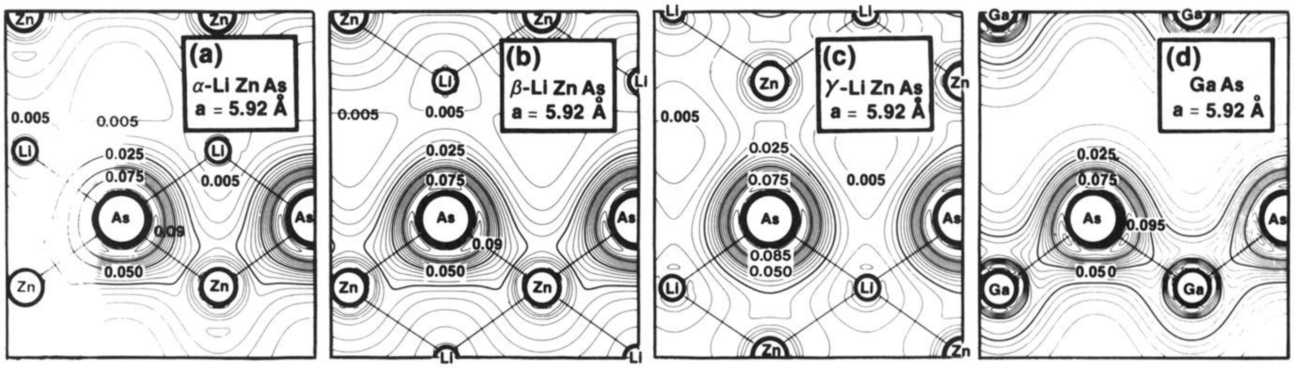
[17] The calculated band gaps show the usual underestimation due to the use of a local-density approximation. On the basis of the known underestimation in GaAs, we extrapolate a probable band gap of about 2.1 eV in LiZnAs. Self-energy corrections are unlikely to make the γ phase (band overlap of -2.55 eV) semiconducting.



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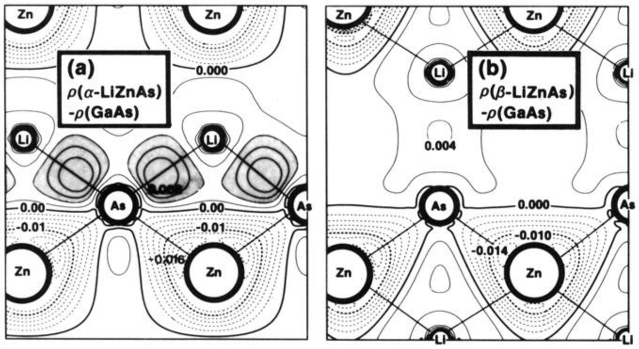

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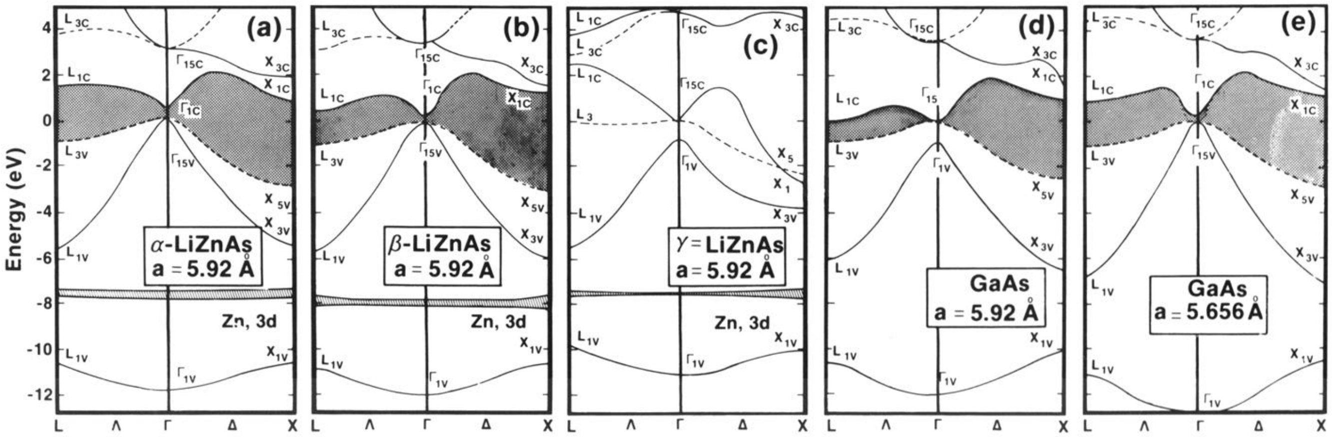

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