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Negative spin-orbit bowing in semiconductor alloys

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Early measurements on many bulk III-V alloys showed that the spin-orbit splitting Δ_0 at the valence-band maximum (VBM) was universally *reduced* relative to the average value of the end-point constituents. This led to the assumption, guiding much of the subsequent data analysis, that such alloys universally mix some conduction-band s character into the VBM ("*interband* coupling"), suppressing Δ_0. Our self-consistent electronic-structure calculations for Ga(As,Sb) show very little s mixing in the VBM and an *enhancement* of Δ_0. *Intraband p-p* coupling is shown to dominate the changes in Δ_0.

The recoginition[1,2] that the spin-orbit splitting Δ reflects the way bonding in solids redistributes charge around the constituent atomic cores has long been used to gauge trends in the chemical environment in semiconductors[2-7] through measurements of Δ. Of the numerous chemical perturbations studied in this way, those associated with alloying two isovalent AC and BC semiconductors has received particular attention.[3-7] Here, physical properties $F(x)$ of such $A_xB_{1-x}C$ alloys[8] (lattice constants, bond lengths, mixing enthalpies, band gaps, effective masses, etc.) can often be measured as a continuous function of composition x and represented well by a parabolic dependence

$$F(x)=\bar{F}(x)-bx(1-x)\,, \tag{1}$$

where $\bar{F}(x)$ is the concentration-weighted average of the corresponding quantities for the end-point constituents $\bar{F}(x)\equiv xF(AC)+(1-x)F(BC)$. Central to the understanding of alloy properties has been the question whether (and why) the alloy environment acts to enhance ("negative bowing," $b<0$) or diminish ("positive bowing") the magnitude of $F(x)$ beyond the linear average $\bar{F}(x)$ of the constituents. Whereas virtually all low-lying direct band gaps E of any isovalent semiconductor alloy exhibit *positive* (downward concave) bowing[4,6,8] $b(E)>0$, the bowing $b(\Delta)$ of the spin-orbit splitting Δ shows unusual trends: early measurements on *bulk* ternary III-V alloys[3-6] showed *negative* (upward concave) bowing $b(\Delta_1)<0$ for the spin-orbit splitting Δ_1 near the L point, but *positive* bowing[9] $b(\Delta_0)>0$ for the spin-orbit splitting Δ_0 at the Γ point of the valence-band maximum (VBM). In contrast, more recent measurements[7] on *epitaxial* lattice-matched quaternary III-V alloys showed $b(\Delta)<0$ for both Δ_0 and Δ_1.

The generally accepted[3-7,10-14] idea explaining $b(\Delta_0)>0$ in $A_xB_{1-x}C$ alloys of tetrahedrally bonded semiconductors AC and BC is due to Van Vechten, Berolo, and Woolley.[4] They noted that alloy potential fluctuations resulting from deviations from tetrahedral local atomic geometries could mix some fractional conduction-band s character $Q_s(x)$ into the otherwise p-like wave function at the VBM ("interband coupling"); in displacing some p character (which gives rise to Δ_0) this will reduce $\Delta_0(x)$ from its average value $\bar{\Delta}_0(x)$ by a factor $1-Q_s(x)$,

$$\Delta_0(x)=\bar{\Delta}_0(x)-Q_s(x)\bar{\Delta}_0(x)\,, \tag{2}$$

giving [from Eq. (1)] *positive* bowing

$$b(\Delta_0)=Q_s(x)\bar{\Delta}_0(x)/x(1-x)>0\,. \tag{3}$$

The magnitude of this interband mixing $Q_s(x)$ was not calculated microscopically. However, it was argued by Van Vechten, Berolo, and Woolley[4] that since the potential fluctuation giving rise to it is also the likely cause of the bowing $b(E_0)$ of the direct band gap, one can use the scaling assumption

$$\frac{b(\Delta_0)}{\bar{\Delta}_0(x)}=\frac{b(E_0)}{\tilde{E}(x)}\,, \tag{4}$$

to deduce from Eq. (3)

$$Q_s(x)=x(1-x)b(E_0)/\tilde{E}(x)\,. \tag{5}$$

Here, $\tilde{E}(x)$ is an average effective band gap[4] $3[2\bar{E}_0^{-1}+(\bar{E}_0+\bar{\Delta}_0)^{-1}]^{-1}$. Taking from experiment[3,4] $b(E_0)$ and the linear averages $\bar{E}_0$ and $\bar{\Delta}_0$, one finds from Eq. (5) that the observed[9] $b(\Delta_0)$ in $\mathrm{In}_x\mathrm{As}_{1-x}\mathrm{Sb}$, $\mathrm{Ga}_x\mathrm{As}_{1-x}\mathrm{Sb}$, and $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{As}$ at $x=0.5$ require interband mixing coefficients Q_s of 48%, 11%, and 10%, respectively. This model has been used extensively in data analysis[3,4,7,14] and theoretical calculations.[11-14]

To examine whether s-p interband coupling is the physical cause of Eq. (4), we calculated $Q_s(x)$ directly from self-consistent wave functions of structural models of AC-BC compounds. The relevant local geometries of substitutional $A_xB_{1-x}C$ alloys are C-centered tetrahedra with n A atoms and $(4-n)$ B atoms at its vertices $(0\leq n\leq 4)$. If all vertices are occupied by the same atom (i.e., if $n=0$ or $n=4$, as is the case in pure AC and BC zinc-blend compounds, respectively) s-p coupling at Γ is symmetry forbidden; hence $\Delta(x)\equiv\bar{\Delta}(x)$. However, in the mixed C-centered clusters, including the AB_3, A_2B_2, and A_3B ($n=1,2$, and 3, respectively) tetrahedra, s-p coupling is symmetry allowed. To estimate $Q_s(x)$ in an alloy, we have constructed *periodic* structures $A_nB_{4-n}C_4$ with $n=1$, 2, 3, exhibiting all local environments characteristics of an alloy. We then calculated their band structure, wave functions, and hence Q_s. The highly localized nature of the spin-orbit interactions suggests that our neglect of long-range-disorder effects present in a real alloy will not significantly modify our predictions. We cover a range of compositions $X_n = \frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ and orientations as follows: For the 50%-50% composition ($n=2$) we use the layered tetragonal $P\bar{4}m2$ ("CuAuI-like," denoted CA), the chalcopyrite $I\bar{4}2d$ (denoted CH), and the layered trigonal $R3m$ ("CuPt-like," denoted CP) structures, having layers arranged periodically in the [001], [201], and [111] directions, respectively. For the 75%-25% (or 25%-75%) compositions ($n=1$ and 3) we use the "Luzonite" (L) $P\bar{4}3m$ and the Famatinite (F) $I\bar{4}2m$ structures [see Ref. 15(a) for pictures of these structures].

We use the first-principles semirelativistic linear augmented-plane-wave (LAPW) method[16] to solve self-consistently the local-density band-structure equations for the seven periodic $Ga_4As_nSb_{4-n}$ structures indicated above ($1 \leq n < 3$), as well as for the binary end-point compounds ($n=0$ and 4). For each structure, we first minimize the total energy to find equilibrium lattice constants and the cell internal structural parameters[15] $\{u\}$ ($u = \frac{1}{4}$ gives the unrelaxed values where all bond lengths are equal, i.e., $R_{AC} = R_{BC}$). The spin-orbit splittings are then calculated through a second variational procedure.[17] For the end-point compounds our first-principles calculation shows good agreement with the measured spin-orbit splittings[18] (given in parentheses, notation of Ref. 18): for GaAs, we find $\Delta_0 = 0.34(0.34)$; $\Delta_0'(\Gamma_{15c}) = 0.19(0.17)$; $\Delta_1(L_{3v}) = 0.21(0.22)$; $\Delta_2(X_{5v}) = 0.08(0.08)$; and $\Delta_d(\Gamma_d) = 0.46(0.45)$. Similarly, for GaSb we find 0.708(0.75); 0.22(0.21); 0.40(0.43); 0.24(0.24); and 0.46(0.45) for Δ_0, Δ_0', Δ_1, Δ_2, and $\Delta_d(\Gamma_d)$, respectively (all energies are in eV).

Figure 1 compares the calculated charge densities (averaged over the crystal-field split components[19]) at the VBM of the ternary ABC_2 compounds with those obtained for the binary end-point compounds AC and BC. It also gives the percentage s, p, and d character of these states inside the muffin-tin spheres. Table I gives our calculated direct band gaps,[20] spin-orbit splitting and their bowing parameters.

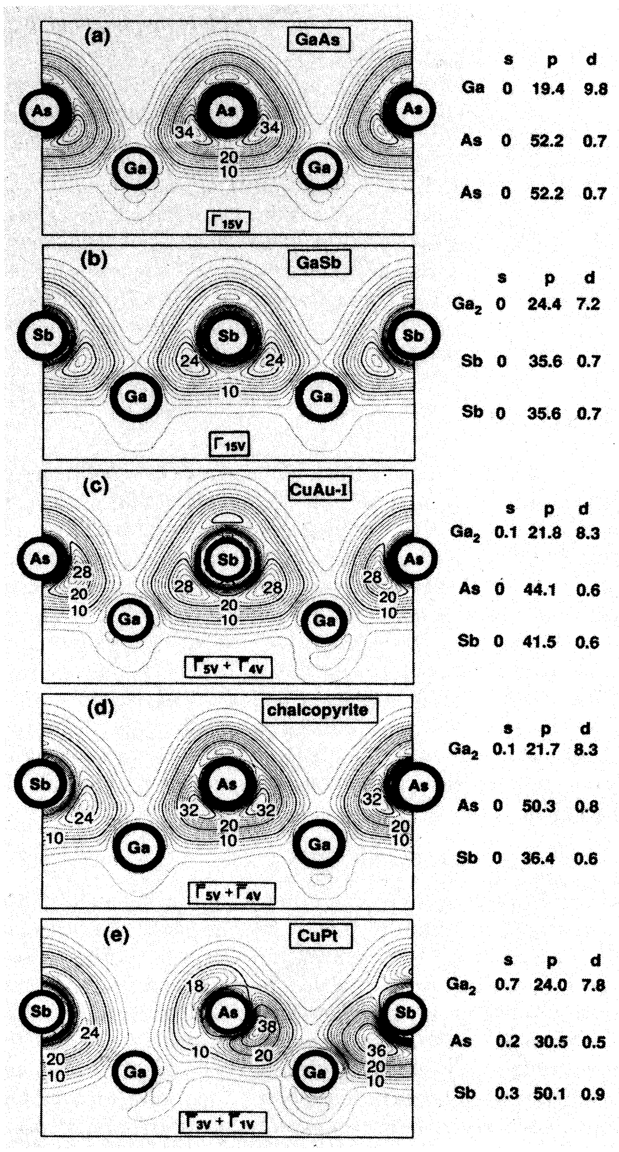

FIG. 1. Charge-density contours [in units of 5×10^{-4} $e/(\text{a.u.})^3$ and step size of 2] for the sum of the three highest valence-band states in Ga_2AsSb and their binary constituents. Also shown are the percentage s,p, and d character within atomic spheres of radii $R(\text{Ga}) = 2.3548$ a.u., $R(\text{As}) = R(\text{Sb}) = 2.2741$ a.u. Charge has been normalized to 2 electrons per 4-atom cell.

From these results for $Ga_4As_nSb_{4-n}$ we conclude that: (i) the s character found at the VBM ($Q_s < 3\%$) is too small to explain within the s-p model the observed $b(\Delta_0)$ values. (ii) Unlike the scaling assumption used in the s-p model[4] [Eq. (4)], we find that $b(\Delta_0)$ *decreases* as $b(E_0)$ increases. (iii) The main change in wave functions in the ternary structures relative to the binary constituents is in their *p-character* and degree of spatial localization, not in s-p mixing. (iv) We have previously shown[8] that alloy properties can be approximated well by taking the average over the five [001] clusters (with weights reflecting their statistical occurrences at x). This predicts for $GaAs_xSb_{1-x}$ a bowing of the direct gap of 0.9 eV, in reasonable accord with experiment[18] (1-1.2 eV). However, for Δ_0 the same calculation predicts $b(\Delta_0) < 0$. While we are unaware of experimental $\Delta_0(x)$ data for this system, our result conflicts with $b(\Delta_0) > 0$ measured by Woolley and co-workers[9] for a number of other bulk III-V alloys. The sign (and magnitude) of our calculated $b(\Delta_0)$ agrees, however, with more recent measurements[7] on high-quality epitaxial quaternary III-V alloys.

We have analyzed the origin of our predicted *enhancement* of Δ_0 by the alloy environment and found it to reflect predominantly the increased wave function localization on the Sb sublattice relative to that in the binary constituents (Fig. 1). The mechanism for this intra-valence-band coupling is as follows: In the ternary structure, the wave functions at the VBM [$\bar{\Gamma}_{5v}$, $\bar{\Gamma}_{5v}$, and $\bar{\Gamma}_{3v}$ in CA, CH, and CP, respectively, using the nonrelativistic notation] have the same symmetries as those of *lower-lying* folded-in

TABLE I. Calculated (Ref. 20) (in eV) direct band gaps E_0, spin-orbit splitting Δ_0 and their bowing parameters $b(E_0)$ and $b(\Delta_0)$, respectively, in ordered $Ga_4As_nSb_{4-n}$ structures in the [001], [201], and [111] orientations. Theoretical equilibrium lattice constants are used throughout.

	E_0	Δ_0	$b(E_0)$	$b(\Delta_0)$
		[001]		
Ga_4As_4(ZB)	1.52	0.338	···	···
Ga_4As_3Sb(L)	1.09	0.453	1.31	−0.12
$Ga_4As_2Sb_2$(CA)	0.86	0.549	1.23	−0.10
Ga_4AsSb_3(L)	0.79	0.630	1.09	−0.08
Ga_4Sb_4(ZB)	0.81	0.708	···	···
		[201]		
Ga_4As_3Sb(F)	1.22	0.441	0.67	−0.06
$Ga_4As_2Sb_2$(CH)	1.13	0.521	0.17	−0.01
Ga_4AsSb_3(F)	0.91	0.626	0.45	−0.06
		[111]		
$Ga_4As_2Sb_2$(CP)	0.37	0.605	3.18	−0.33

TABLE II. Decomposition of the total bowing parameters of Ga_2AsSb into volume deformation (VD), charge exchange (CE), and structural (S) contributions (in eV), see text.

	$b_{\rm VD}$	$b_{\rm CE}$	b_S	$b_{\rm tot}$
		band gap		
CuAuI	−0.02	0.31	0.94	1.23
Chalcopyrite	−0.02	−0.03	0.22	0.17
CuPt	−0.02	1.60	1.60	3.18
		Δ_0		
CuAuI	−0.04	0.08	−0.14	−0.10
Chalcopyrite	−0.04	0.07	−0.04	−0.01
CuPt	−0.04	0.00	−0.29	−0.33

states[8,15] [e.g., $\bar{\Gamma}_{5v}(X_{5v})$, $\bar{\Gamma}_{5v}(W_{4v})$, and $\bar{\Gamma}_{3v}(L_{3v})$ in CA, CH, and CP, respectively]. Such equal-symmetry pairs interact, repelling the upper level to higher energy. This leads to a charge redistribution. The *direction* of this redistribution is decided by the relative potential energies of the two sublattices, i.e., the band offset ΔE_v. We find that ΔE_v between GaAs and GaSb (indeed, between any common-cation CA_xB_{1-x}) system[15(b),21] has a maximum on the sublattice with the *heavier* atom (GaSb, here). (We calculate for Ga_2AsSb $\Delta E_v = 0.65 \pm 0.10$ eV.) Since the potential at the VBM is higher on the Sb lattice, level repulsion increases the wave function amplitude of VBM on this sublattice (see Fig. 1), enhancing Δ_0 in the alloy, thus yielding $b(\Delta_0) < 0$. Similar coupling between conduction bands of the same symmetry repel the CBM *downwards* leading to $b(E_0) > 0$.

To further analyze the physical content of $b(\Delta_0)$, we have decomposed the process of formation of Ga_2AsSb from GaAs+GaSb into three steps associated with physically recognizable factors.[8] First, compress (expand) bulk GaSb (GaAs) from their equilibrium lattice parameters a to the intermediate lattice parameter of Ga_2AsSb at equilibrium. The bowing parameter associated with this volume deformation (VD) step is denoted $b_{\rm VD}$. Second, bring together GaAs and GaSb, already prepared at their final volume, to form Ga_2AsSb in any of the three structures. The bowing parameter associated with this step is denoted as $b_{\rm CE}$; it reflects charge exchange (CE) contributions. Finally, relax Ga_2AsSb in any of its three structures from the ideal equal-bond length geometry ($u = \frac{1}{4}$) to the energy-minimizing geometry (where $R_{\text{Ga-Sb}} \neq R_{\text{Ga-As}}$). The bowing parameter associated with this structural (S) relaxation step is denoted b_S. Clearly by construction $b_{\rm VD} + b_{\rm CE} + b_S$ is the total bowing b; each term is calculated separately from the corresponding band structure. Table II gives this decomposition for the $b(E_0)$ and $b(\Delta_0)$. This shows (i) volume-renormalization effects give $b_{\rm VD}(\Delta_0) < 0$. (ii) For structure exhibiting weak intraband mixing (e.g., CH, CA), charge-transfer effects give $b_{\rm CE}(\Delta_0) > 0$, reflecting small s-p mixing. Note that both $b_{\rm VD}(\Delta_0)$ and $b_{\rm CE}(\Delta_0)$ are small, and that the major contribution to $b(\Delta_0)$ comes from (iii) the structural relaxation term b_S. Structural relaxation enhances the intraband mixing, increasing $b(E_0)$ and decreasing $b(\Delta_0)$ proportionately.

Our results $b(\Delta_0) < 0$ for all ordered intersemiconductor phases of GaAs-GaSb conflict with (i) Chadi's[12] perturbative treatment of s-p mixing, and (ii) the early experiments[9] on bulk alloys. We address the former question first.

Neglecting the intraband p-p coupling, Chadi[12] calculated the shift $\delta\Delta_0 = \Delta_0 - \bar{\Delta}_0$ induced by interband s-p coupling of strength ΔV. The dashed lines in Fig. 2 show the results obtained for the closely related $InAs_{1-x}Sb_x$ by using the four unperturbed states Γ_{6c} (the conduction band minimum, or CBM), Γ_{8v} (the doubly degenerate VBM) and Γ_{7v} (the spin split-off band), and considering the lowest nonvanishing (second order) perturbation in ΔV.

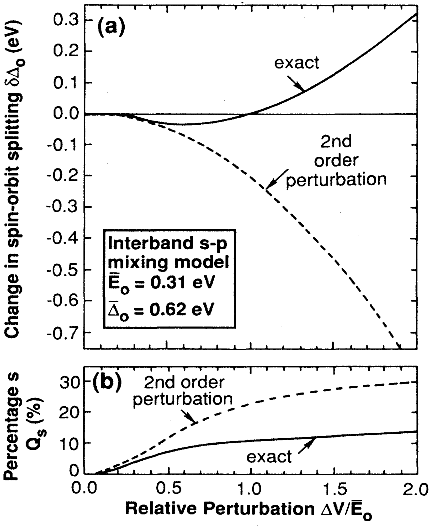

FIG. 2. Calculated (a) change in spin-orbit splitting and (b) percentage of s character at VBM from the interband s-p mixing model. Solid lines give the exact solutions and the dashed lines are obtained from second-order perturbation theory. Parameters taken for In(As,Sb).

Clearly, for the perturbation theory to be valid, the perturbation $\Delta V/\bar{E}_0$ must be[13] $\ll 1$. The solid lines in Fig. 2 show, as a function of the relative magnitude of the perturbation $\Delta V/\bar{E}_0$, the results we obtained by an exact diagonalization of this 4×4 s-p coupling problem. The comparison shows that: (i) while second-order perturbation indeed[12] gives $b(\Delta_0)>0$, it deviates from the exact solution past $\Delta v/\bar{E}_0 \simeq 0.3$; the values of $\Delta V/\bar{E}_0$ needed to fit the experimental value of $b(\Delta_0)$ in $\mathrm{InAs}_{1-x}\mathrm{Sb}_x$ is considerably larger (~ 1.2 was used in Ref. 12). For such large perturbations, the exact treatment of the s-p model gives $b(\Delta_0)<0$. (ii) The value $\Delta V/\bar{E}_0 \simeq 1.2$ used to fit the observed $b(\Delta_0)$ yields an s-p mixing coefficient $Q_s \simeq 25\%$ [Fig. 2(b)] which is considerably larger than what a self-consistent calculation would grant ($Q_s < 3\%$). (iii) Either exact or perturbative interband s-p mixing leads to an *increase* in the direct gap, or $b(E_0)<0$ (since the coupling pushes the VBM down and the CBM up), in conflict with all experiments on isovalent alloys.[4,10] Hence, this mechanism alone cannot represent the actual physical situation; inclusion of s-s, s-p, and p-p coupling through a full self-consistent calculation is needed. This (Table I) correctly leads to $b(E_0)>0$. (iv) The s-p mixing mechanism implies that $b(\Delta_0)$ will be large for systems with small band gaps. This is not observed for small gap materials such as[21] $\mathrm{Cd}_x\mathrm{Hg}_{1-x}\mathrm{Te}$.

The conflict between $b(\Delta_0)<0$, found theoretically here for ordered common-cation ternary phases, and $b(\Delta_0)>0$ measured by Woolley and co-workers[3,4,6,9] for similar systems, remains a puzzle and a challenge. Our discussion above shows that none of the available theories can explain the large positive bowing $b(\Delta_0)$ observed by Woolley *et al.* On the theoretical side, it is possible that long-range fluctuations neglected here might contribute to $b(\Delta_0)$. On the experimental side, it is possible that sample inhomogeneity and internal strains could have obscured the interpretation of the data. Since the systems which showed the largest positive $b(\Delta_0)$ values (e.g., $\mathrm{InAs}_{1-x}\mathrm{Sb}_x$) also have in bulk form a large miscibility gap, such samples are generally inhomogeneous. Experiments on recently grown *homogeneous* $\mathrm{GaAs}_x\mathrm{Sb}_{1-x}$ epitaxial samples[22] should provide a better test to our theory.

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[1] J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic, New York, 1973).

[2] M. Cardona, in *Solid State Physics,* edited by F. Seitz, D. Turnbull, and E. Ehrenreich (Academic, New York, 1969), Vol. 11.

[3] O. Berolo and J. C. Woolley, in *Proceedings of the Eleventh International Conference on the Physics of Semiconductors* (PWN Polish Scientific, Warsaw, 1972), p. 1420.

[4] J. A. Van Vechten, O. Berolo, and J. C. Woolley, Phys. Rev. Lett. **29**, 1400 (1972), and reference therein.

[5] (a) H. Lange, J. Donecker, and M. Friedrich, Phys. Status Solidi (b) **73**, 633 (1976); (b) C. Albert, G. Bordure, A. Laugier, and J. Chevallier, Phys. Rev. B **6**, 1301 (1972).

[6] A. C. Thompson, M. Cardona, K. L. Shaklee, and J. C. Woolley, Phys. Rev. **146**, 601 (1966).

[7] P. Parayananthal and F. H. Pollak, Phys. Rev. B **28**, 3632 (1983), and references 5–9 therein find $b(\Delta_0)$ of order -0.1 eV for a range of epitaxial III-V alloys.

[8] J. E. Bernard and A. Zunger, Phys. Rev. B **36**, 3199 (1987).

[9] In an early study (Ref. 3), a number of bulk alloys were said to show $b(\Delta_0)\gtrsim 0.1$ eV, e.g., $\mathrm{GaA}_{1-x}\mathrm{P}_x$ (0.175), $\mathrm{InAs}_{1-x}\mathrm{P}_x$ (0.357), $\mathrm{InAs}_{1-x}\mathrm{Sb}_x$ (1.17), $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$ (0.101), and $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{As}$ (0.144). Later on (Ref. 4) these authors have revised two values, i.e., $\mathrm{GaAs}_{1-x}\mathrm{P}_x$ (0.02 ± 0.04) and $\mathrm{InAs}_{1-x}\mathrm{P}_x$ (0.08). Negative or zero bowing was found, however, for $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$ [-0.05, Ref. 5(a); 0.0, Ref. 5(b)], $\mathrm{GaAs}_{1-x}\mathrm{P}_x$ (-0.03, Ref. 6), and $\mathrm{ZnSe}_{1-x}\mathrm{Te}_x$ [-0.585, A. Ebina, Y. Sato, and T. Takuhashi, Phys. Rev. Lett. **32**, 1366 (1974)].

[10] O. Berolo, J. C. Woolley, and J. A. Van Vechten, Phys. Rev. B **8**, 3794 (1973).

[11] R. Hill, J. Phys. C **7**, 516 (1974).

[12] D. J. Chadi, Phys. Rev. B **16**, 790 (1977). In Eqs. (24) and (25) of this paper, α_2 should be $\frac{4}{3}$, not $\frac{8}{3}$. Also, δV of Eq. (23) should be reduced by a factor of ~ 2 due to the omitted normalization of the wave functions of the bonding and antibonding states. These corrections (a total of factor $\sim 2\sqrt{2}$) give $\Delta V/\bar{E}_0$ values of 0.62 and 0.18, for $\mathrm{InAs}_{1-x}\mathrm{Sb}_x$ and $\mathrm{GaAs}_{1-x}\mathrm{Sb}_x$, respectively, instead of 1.79 and 0.52.

[13] M. F. Ling and D. J. Miller, Phys. Rev. B **34**, 7388 (1986).

[14] T. P. Pearsall, in *GaInAsP Alloy Semiconductors,* edited by T. P. Pearsall (Wiley, New York, 1982), p. 295.

[15] (a) J. L. Martins and A. Zunger, J. Mater. Res. **1**, 523 (1986); (b) S.-H. Wei and A. Zunger, J. Appl. Phys. **63**, 5794 (1988).

[16] S.-H. Wei and H. Krakauer, Phys. Rev. Lett. **55**, 1200 (1985), and references therein.

[17] A. H. MacDonald, W. E. Pickett, and D. D. Koelling, J. Phys. C **13**, 2675 (1980).

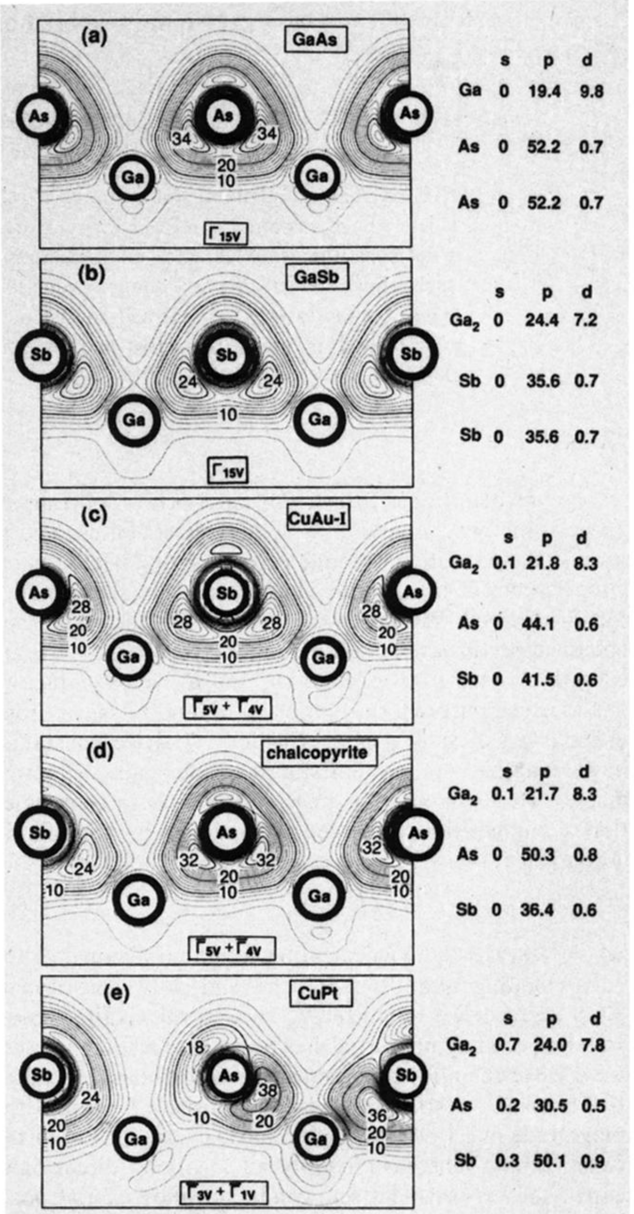
[18] *Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology,* edited by O. Madelung, M. Schulz, and H. Weiss (Springer-Verlag, Berlin, 1982), Group 3, Vol. 17, Pt. a.

[19] The fourfold degenerate Γ_8 states of the zinc-blend structure is split in the ternary phase by a small crystal-field interaction, see Ref. 15(b). Our calculated Δ_0 values represent an average over these states. The Γ_5 and Γ_3 components in the CA and CP structures, respectively, have no s-p mixing, by symmetry.

[20] The band gaps obtained by the local density approximation (LDA) are corrected by the wave function amplitude weighted average of the corrections appropriate to the end-point compounds, described in detail in Ref. 15(b). Δ_0 values are given directly from the LDA which correctly accounts for them, see M. Cardona, N. E. Christensen, and G. Fasol, Phys. Rev. B **38**, 1806 (1988).

[21] S.-H. Wei and A. Zunger, Phys. Rev. B **37**, 8958 (1988), and references therein.

[22] H. R. Jen, Y. T. Cherng, and B. G. Stringfellow, Appl. Phys. Lett. **48**, 1603 (1986); Y. E. Ihm, N. Otsuka, J. Klein, and H. Morkoc, Appl. Phys. Lett. **51**, 2013 (1987).



	s	p	d
Ga	0	19.4	9.8
As	0	52.2	0.7
As	0	52.2	0.7

	s	p	d
Ga_2	0	24.4	7.2
Sb	0	35.6	0.7
Sb	0	35.6	0.7

	s	p	d
Ga_2	0.1	21.8	8.3
As	0	44.1	0.6
Sb	0	41.5	0.6

	s	p	d
Ga_2	0.1	21.7	8.3
As	0	50.3	0.8
Sb	0	36.4	0.6

	s	p	d
Ga_2	0.7	24.0	7.8
As	0.2	30.5	0.5
Sb	0.3	50.1	0.9

FIG. 1. Charge-density contours [in units of 5×10^{-4} $e/(\text{a.u.})^3$ and step size of 2] for the sum of the three highest valence-band states in Ga_2AsSb and their binary constituents. Also shown are the percentage s,p, and d character within atomic spheres of radii $R(\text{Ga})=2.3548$ a.u., $R(\text{As})=R(\text{Sb})=2.2741$ a.u. Charge has been normalized to 2 electrons per 4-atom cell.