Negative spin-orbit bowing in semiconductor alloys

Su-Huai Wei and Alex Zunger
Solar Energy Research Institute, Golden, Colorado 80401
(Received 5 October 1988)

Early measurements on many bulk III-V alloys showed that the spin-orbit splitting $\Delta_0$ at the valence-band maximum (VBM) was universally reduced relative to the average value of the endpoint 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 $\Delta_0$. Our self-consistent electronic-structure calculations for Ga(As,Sb) show very little $s$ mixing in the VBM and an enhancement of $\Delta_0$. Intraband $p$-$p$ coupling is shown to dominate the changes in $\Delta_0$.

The recognition$^{1,2}$ that the spin-orbit splitting $\Delta$ 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$^{3-7}$ through measurements of $\Delta$. Of the numerous chemical perturbations studied in this way, those associated with alloying two isovalent $AC$ and $BC$ semiconductors have received particular attention.$^{3,7}$ Here, physical properties $F(x)$ of such $A_xB_{1-x}C$ alloys$^5$ (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

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

where $\bar{F}(x)$ is the concentration-weighted average of the corresponding quantities for the endpoint constituents $F(x) \equiv xF(AC) + (1-x)F(BC)$. 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$^5,6,8$ $b(E) > 0$, the bowing $b(\Delta)$ of the spin-orbit splitting $\Delta$ shows unusual trends: early measurements on bulk ternary III-V alloys$^3,6,8$ showed negative (upward concave) bowing $b(\Delta_0) < 0$ for the spin-orbit splitting $\Delta_0$ near the L point, but positive$^9$ bowing $b(\Delta_0) > 0$ for the spin-orbit splitting $\Delta_0$ at the $\Gamma$ 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 $\Delta_0$ and $\Delta_1$.

The generally accepted$^{1,3,7,10-14}$ 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 $\Delta_0$) this will reduce $\Delta_0(x)$ from its average value $\bar{\Delta}_0(x)$ by a factor $1 - Q_s(x)$,

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

giving [from Eq. (1)] positive bowing

$$b(\Delta_0) = Q_s(x) \Delta_0(x)/x(1-x) > 0 .$$

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

$$b(\Delta_0) \approx b(E_0)/\bar{E}(x) ,$$

to deduce from Eq. (3)

$$Q_s(x) = x(1-x) b(E_0)/\bar{E}(x) .$$

Here, $\bar{E}(x)$ is an average effective band gap$^4$

$$3[2E_0^+ + (E_0 + \Delta_0)^-]^{-1} .$$

Taking from experiment$^3,4$

$$b(E_0)$$

and the linear averages $E_0$ and $\Delta_0$, one finds from Eq. (5) that the observed$^7$ $b(\Delta_0)$ in In$_x$As$_{1-x}$Sb, Ga$_x$,As$_{1-x}$Sb, and Ga$_x$,In$_{1-x}$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 our 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 $\Gamma$ is symmetry forbidden; hence $\Delta(x) \equiv \Delta(\Delta)$. However, in the mixed $C$-centered clusters, including the $AB_3$, $A_xB_x$, and $A_xB_y$ (n=1,2,3) 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 struc-
tique, 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 $X_n = \frac{1}{2}, \frac{1}{2}$, and $\frac{1}{4}$ and orientations as follows: For the 50%-50% composition ($n=2$) we use the layered tetragonal $P4m2$ ("CuAu-like," denoted CA), the chalcopyrite $I42d$ (denoted CH), and the layered trigonal $R3m$ ("CuPt-like," denoted CP) structures, having layers arranged periodically in the [001], [110], and [111] directions, respectively. For the 75%-25% (or 25%-75%) compositions ($n=1$ and 3) we use the "Luzonite" (L) $P43m$ and the Famatinite (F) $I42m$ structures [see Ref. 15(a) for pictures of these structures].

We use the first-principles semirelativistic linear augmented-plane-wave (LAPW) method to solve self-consistently the local-density band-structure equations for the seven periodic Ga$_2$As$_x$Sb$_{1-x}$ compounds 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 $\{u\}$ ($u = \frac{1}{2}$ gives the unrelaxed values where all bond lengths are equal, i.e., $R_A = R_B$). The spin-orbit splittings are then calculated through a second variational procedure. For the end-point compounds our first-principles calculation shows good agreement with the measured spin-orbit splittings (given in parentheses, notation of Ref. 18): for GaAs, we find $\Delta_0 = 0.34(0.34)$; $\Delta_0' (\Gamma_{15}) = 0.19(0.17)$; $\Delta_1 (\Gamma_{3v}) = 0.21(0.22)$; $\Delta_2 (\Gamma_{5v}) = 0.08(0.08)$; 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 $\Delta_0$, $\Delta_0'$, $\Delta_1$, $\Delta_2$, 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 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, spin-orbit splitting and their bowing parameters.

From these results for Ga$_2$As$_x$Sb$_{1-x}$ 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 (Eq. (4)), we find that $b(\Delta_0)$ decreases as $E(\Omega)$ 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 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 Ga$_2$As$_x$Sb$_{1-x}$ a bowing of the direct gap of 0.9 eV, in reasonable accord with experiment (1-1.2 eV). However, for $\Delta_0$ 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 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 on high-quality epitaxial quaternary III-V alloys.

We have analyzed the origin of our predicted enhancement of $\Delta_0$ 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 $[\Gamma_{5v}, \Gamma_{5v}, \Gamma_{3v}]$ 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 $\Delta_0$ and their bowing parameters $b(E_0)$ and $b(\Delta_0)$, respectively, in ordered GaAs$_{1-x}$Sb$_x$ structures in the [001], [011], and [111] orientations. Theoretical equilibrium lattice constants are used throughout.

<table>
<thead>
<tr>
<th></th>
<th>$E_0$</th>
<th>$\Delta_0$</th>
<th>$b(E_0)$</th>
<th>$b(\Delta_0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[001]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GaAs$_4$(ZB)</td>
<td>1.52</td>
<td>0.338</td>
<td>$\cdots$</td>
<td>$\cdots$</td>
</tr>
<tr>
<td>GaAs$_4$Sb(L)</td>
<td>1.09</td>
<td>0.453</td>
<td>1.31</td>
<td>$-0.12$</td>
</tr>
<tr>
<td>GaAs$_4$Sb$_2$(CA)</td>
<td>0.86</td>
<td>0.549</td>
<td>1.23</td>
<td>$-0.10$</td>
</tr>
<tr>
<td>GaAs$_4$Sb$_3$(L)</td>
<td>0.79</td>
<td>0.630</td>
<td>1.09</td>
<td>$-0.08$</td>
</tr>
<tr>
<td>GaSb$_4$(ZB)</td>
<td>0.81</td>
<td>0.708</td>
<td>$\cdots$</td>
<td>$\cdots$</td>
</tr>
<tr>
<td>[011]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GaAs$_2$Sb$_2$(F)</td>
<td>1.22</td>
<td>0.441</td>
<td>0.67</td>
<td>$-0.06$</td>
</tr>
<tr>
<td>GaAs$_2$Sb$_2$(CH)</td>
<td>1.13</td>
<td>0.521</td>
<td>0.17</td>
<td>$-0.01$</td>
</tr>
<tr>
<td>GaAs$_2$Sb$_3$(F)</td>
<td>0.91</td>
<td>0.626</td>
<td>0.45</td>
<td>$-0.06$</td>
</tr>
<tr>
<td>[111]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GaAs$_2$Sb$_2$(CP)</td>
<td>0.37</td>
<td>0.605</td>
<td>3.18</td>
<td>$-0.33$</td>
</tr>
</tbody>
</table>

states$^{8,15}$ (e.g., $\Gamma_{5p}(X_{5p})$, $\Gamma_{5p}(W_{5p})$, and $\Gamma_{5p}(L_{5p})$) 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 $\Delta E_r$. We find that $\Delta E_r$ between GaAs and GaSb (indeed, between any common-cation CA, B$_{1-}$-type) system$^{15,20}$ has a maximum on the sublattice with the heavier atom (GaSb, here). We calculate for Ga$_2$As$_2$Sb $\Delta E_r = 0.65 \pm 0.10$ eV.) Since the potential at the VBM is higher on the Sb lattice, level repulsion increases with the wave function amplitude of VBM on this sublattice (see Fig. 1), enhancing $\Delta_0$ 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$_2$As$_2$Sb from GaAs + GaSb into three steps associated with physically recognizable states. First, compress (expand) bulk GaSb (GaAs) from their equilibrium lattice parameters $a$ to the intermediate lattice parameter of Ga$_2$As$_2$Sb at equilibrium. The bowing parameter associated with this volume deformation (VD) step is denoted $b_{VD}$. Second, bring together GaAs and GaSb, already prepared at their final volume, to form Ga$_2$As$_2$Sb in any of the three structures. The bowing parameter associated with this step is denoted $b_{CE}$; it reflects charge exchange (CE) contributions. Finally, relax Ga$_2$As$_2$Sb in any of its three structures from the ideal equal-bond length geometry ($u = \frac{1}{2}$) to the energy-minimizing geometry (where $R_{Ga-Sb} = R_{Ga-As}$). The bowing parameter associated with this structural (S) relaxation step is denoted $b_S$. Clearly by construction $b_{VD} + b_{CE} + b_S$ 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 $b_{VD}(\Delta_0) < 0$. (ii) For structure exhibiting weak intra-band mixing (e.g., CH, CA), charge-transfer effects give $b_{CE}(\Delta_0) > 0$, reflecting small $s$-$p$ mixing. Note that both $b_{VD}$ and $b_{CE}$ are small, and that the major contribution to $b(\Delta_0)$ comes from (iii) the structural relaxation term $b_S$. Structural relaxation enhances the interband 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$^8$ on bulk alloys. We address the former question first.

Neglecting the intraband $p$-$p$ coupling, Chadi$^{12}$ calculated the shift $\delta \Delta_0 = \Delta_0 - \Delta_0$ induced by interband $s$-$p$ coupling of strength $\Delta V$. 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 $\Gamma_{6c}$ (the conduction band minimum, or CBM), $\Gamma_{8c}$ (the doubly degenerate VBM) and $\Gamma_{7c}$ (the spin split-off band), and considering the lowest nonvanishing (second order) perturbation in $\Delta V$.

![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).](image-url)
Clearly, for the perturbation theory to be valid, the perturbation $\Delta V/\bar{E}_0$ must be $13 < 1$. 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 $4 \times 4$ $s$-$p$ coupling problem. The comparison shows that: (i) while second-order perturbation indeed gives $b(\Delta_0) > 0$, it deviates from the exact solution past $\Delta_0/\bar{E}_0 = 0.3$; the values of $\Delta V/\bar{E}_0$ needed to fit the experimental value of $b(\Delta_0)$ in InAs$_{1-x}$Sb$_x$ is considerably larger ($\approx 1.2$ 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 $\Delta V/\bar{E}_0 = 1.2$ used to fit the observed $b(\Delta_0)$ yields an $s$-$p$ mixing coefficient $\bar{Q}_s = 25\% \,[\text{Fig. 2(b)}]$ 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.\textsuperscript{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 $21$ Cd$_x$Hg$_{1-x}$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\textsuperscript{1,4,6,9} 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 \textit{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., InAs$_{1-x}$Sb$_x$) also have in bulk form a large miscibility gap, such samples are generally inhomogeneous. Experiments on recently grown \textit{homogeneous} GaAs$_x$Sb$_{1-x}$ epitaxial samples\textsuperscript{22} should provide a better test to our theory.

We thank Sverre Frost for useful discussion. One of us (A. Z.) wishes to thank F. H. Pollak for attracting his attention to this problem and for helpful discussions. This work was supported by the U.S. Department of Energy under Grant No. DE-AC02-77-CH00178.

\textsuperscript{4} J. A. Van Vechten, O. Berolo, and J. C. Woolley, Phys. Rev. Lett. 29, 1400 (1972), and reference therein.
\textsuperscript{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).
\textsuperscript{7} P. Parayananth 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.
\textsuperscript{9} In an early study (Ref. 3), a number of bulk alloys were said to show $b(\Delta_0) \approx 0.1$ eV, e.g., GaAs$_{1-x}$P$_x$ (0.175), InAs$_{1-x}$P$_x$ (0.357), InAs$_{1-x}$Sb$_x$ (1.17), Ga$_x$In$_{1-x}$P (0.101), and Ga$_{1-x}$In$_x$As (0.144). Later on (Ref. 4) these authors have revised these values, i.e., GaAs$_{1-x}$P$_x$ (0.02 $\pm$ 0.04) and InAs$_{1-x}$P$_x$ (0.08). Negative or zero bowing was found, however, for Ga$_x$In$_{1-x}$P [0.05, Ref. 5(a)]; 0.0, Ref. 5(b), GaAs$_{1-x}$P$_x$ ($-0.03$, Ref. 6), and ZnSe$_{1-x}$Te$_x$ [0.6585; A. Ebina, Y. Sato, and T. Takuhashi, Phys. Rev. Lett. 32, 1366 (1974)].
\textsuperscript{12} D. J. Chadi, Phys. Rev. B 16, 790 (1977). In Eqs. (24) and (25) of this paper, $a_2$ should be $\frac{1}{2}$, not $\frac{3}{2}$. Also, $\delta V$ of Eq. (23) should be reduced by a factor of $-2$ due to the omitted normalization of the wave functions of the bonding and anti-bonding states. These corrections (a total of factor $-2\sqrt{2}$) give $\Delta V/\bar{E}_0$ values of 0.62 and 0.18, for InAs$_{1-x}$Sb$_x$ and GaAs$_{1-x}$Sb$_x$, respectively, instead of 1.79 and 0.52.
\textsuperscript{13} M. F. Ling and D. J. Miller, Phys. Rev. B 34, 7388 (1986).
\textsuperscript{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).
\textsuperscript{19} The fourfold degenerate $\Gamma_5$ states of the zinc-blend structure is split in the ternary phase by a small crystal-field interaction; see Ref. 15(b). Our calculated $\Delta_0$ values represent an average over these states. The $\Gamma_5$ and $\Gamma_7$ components in the CA and CP structures, respectively, have no $s$-$p$ mixing, by symmetry.
\textsuperscript{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). $\Delta_0$ 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).
\textsuperscript{21} S.-H. Wei and A. Zunger, Phys. Rev. B 37, 8958 (1988), and references therein.
FIG. 1. Charge-density contours [in units of $5 \times 10^{-4}$ e/ (a.u.)$^3$ and step size of 2] for the sum of the three highest valence-band states in Ga$_2$AsSb and their binary constituents. Also shown are the percentage $s$, $p$, and $d$ character within atomic spheres of radii $R$(Ga) = 2.3548 a.u., $R$(As) = $R$(Sb) = 2.2741 a.u. Charge has been normalized to 2 electrons per 4-atom cell.