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Modification of the virtual-crystal approximation for ternary III-V compounds

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We discuss a modification of the virtual-crystal approximation for alloys in the semiempirical tight-binding method of band-structure calculations, which explicitly includes the interactions between unlike second neighbors. The results are applied to the quaternary $Ga_yIn_{1-y}As_xP_{1-x}$ and its constituent ternary compounds.

It has been noted previously[1] that the virtual-crystal approximation (VCA) for semiconductor alloys leads to bowing parameters of the main gap that are too weak to account for experiment. This failure of the VCA is usually attributed to the fact that no interactions between unlike second neighbors are included. Van Vechten and Bergstresser[1] earlier incorporated a correction for this via the dielectric theory. Taking $Ga_xIn_{1-x}As$ as an example, the virtual-crystal approximation consists of the linear superposition of the GaAs and InAs Hamiltonians. Therefore only information on Ga-Ga and In-In second-neighbor interactions, but not on Ga-In second-neighbor interactions, is included. The purpose of this Communication is to propose an extension of the virtual-crystal approximation in the framework of the tight-binding method.[2] This extension consists of including interactions between unlike second neighbors which are not considered in the VCA. Results are applied to the band structures of the quaternary $Ga_yIn_{1-y}As_xP_{1-x}$ and its constituent ternary alloys. Special attention will be paid to the compound $Ga_xIn_{1-x}As$ where the present theory might provide an explanation for the unusually small saturated drift velocities found in recent experiments.[3]

In the Slater-Koster notation,[2] only three second-neighbor parameters exist because of symmetry: $E_{xx}(110)$, $E_{xx}(011)$, and $E_{xy}(110)$; second-neighbor interactions involving s orbitals are neglected. To these we add explicitly the interactions between unlike second neighbors with a composition dependence of $x(1-x)$. Thus our modification of the virtual-crystal second-neighbor parameters E^{VC} reads

$$E^{\text{ternary}} = E^{VC} + x(1-x)\,V \quad , \tag{1}$$

where E stands for any second-neighbor interaction and V is the interaction parameter between unlike second neighbors. It is understood that for alloying on the cation site, V is only added to the cation-cation second-neighbor interactions and, respectively, for alloying on the anion site. The experimentally determined bowing parameters of the main gaps are used to adjust V for a ternary compound. This has been done for the four ternaries building up the quaternary $Ga_7In_{1-y}As_xP_{1-x}$. In Table I, we list the parameters used for $Ga_xIn_{1-x}As$, which will be discussed in more detail below; the other parameters are compiled elsewhere.[4] One can now calculate the energy-gap variation of the quaternary since no new second-neighbor interactions have to be included. Considering that the interactions between P and As

TABLE I. Tight-binding parameters used for $Ga_xIn_{1-x}As$ in eV. The notation is that of Slater and Koster (Ref. 2). The corresponding conduction bands are shown in Fig. 2.

	GaAs	InAs
$E_{ss}^{a}(000)$	−14.537	−14.537
$E_{ss}^{c}(000)$	−7.137	−8.180
$E_{pp}^{a}(000)$	−5.900	−5.900
$E_{pp}^{c}(000)$	−0.720	−0.600
$E_{ss}^{ac}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	−1.405	−1.406
$E_{sp}^{ac}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	1.113	0.695
$E_{sp}^{ca}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	1.090	1.179
$E_{xx}^{ac}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	0.131	0.324
$E_{xy}^{ac}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	1.325	1.044
$E_{xx}^{aa}(110)$	0.040	0.105
$E_{xx}^{aa}(011)$	0.030	0.090
$E_{xy}^{aa}(110)$	0.125	0.125
$E_{xx}^{cc}(110)$	0.275	0.250
$E_{xx}^{cc}(011)$	−0.625	−0.450
$E_{xy}^{cc}(110)$	−0.050	−0.050
$V_{xx}^{cc}(110)$	0.7	
$V_{xx}^{cc}(011)$	1.17	
$V_{xy}^{cc}(110)$	0.2	

on the anion site will be different for Ga or In on the cation site, the modification of the virtual-crystal second-neighbor interactions reads, for the quaternary,

$$E^{\text{quater}} = E^{\text{VC}} + x(1-x)[yV_{\text{As-P}}^{\text{GaAsP}} + (1-y)V_{\text{As-P}}^{\text{InAsP}}] + y(1-y)[xV_{\text{Ga-In}}^{\text{GaInAs}} + (1-x)V_{\text{Ga-In}}^{\text{GaInP}}] \quad . \quad (2)$$

Figure 1 shows the variations of the lowest conduction band for $Ga_yIn_{1-y}As_xP_{1-x}$ lattice matched to InP. The effect of the inclusion of the additional second-neighbor interactions is shown and compared to experiment. No further adjustments have been made for the quaternary.

We now discuss in some detail the effect of changing the various second-neighbor interactions, taking $Ga_xIn_{1-x}As$ as an example. The variation of the direct gap E_0 is strongly affected by $E_{xx}(110)$ and this parameter is used to set the bowing of this gap. In Fig. 2, the variation of the principal gaps across the alloy is shown both with and without the unlike second-neighbor interaction. The bowing of the principal gap E_0 has been adjusted to the experimental results of Cheng *et al.*[7] The situation is not so clear for the higher conduction bands, however. No experimental determinations of the bowing parameters

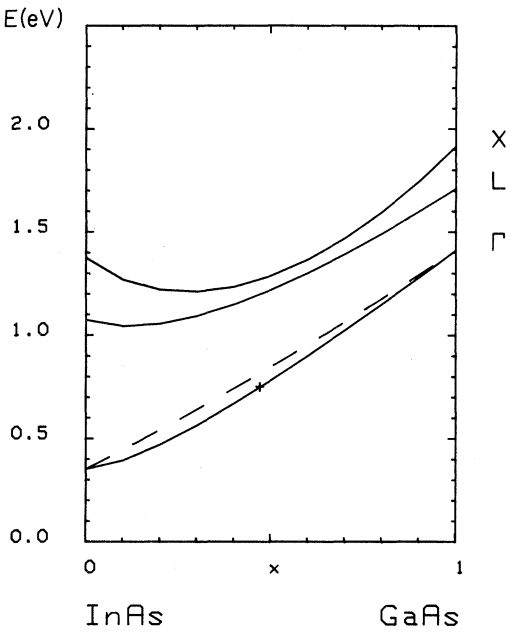

FIG. 2. Lowest conduction bands are shown for $Ga_xIn_{1-x}As$ as obtained from the parameters of Table I. Note the nearness of the L and X bands. The dashed curve is the principal gap with unlike second-neighbor interactions omitted. The cross is representative of experimental data.[7]

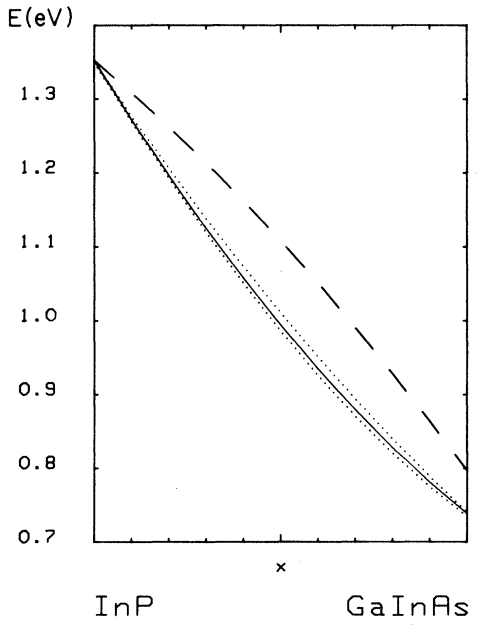

FIG. 1. Variation of the lowest Γ conduction band with composition is shown for the quaternary $Ga_yIn_{1-y}As_xP_{1-x}$ lattice matched to InP. The dotted lines show the range of experimental uncertainty; upper curve after Ref. 5, lower curve after Ref. 6. The dashed line gives the energy-gap variation in the VCA; note the wrong sign of the bowing parameter. The results for interactions between unlike second neighbors included are shown by the solid line.

of the L and X conduction bands are available. There exist only experiments for the bowing parameters of the E_1 and E_2 signals.[8] $E_{xx}(011)$ strongly influences E_2 where E_1 is solely determined by $E_{xy}(110)$. Again, the additional second-neighbor parameters have been adjusted to produce the experimentally observed bowing. It is interesting to note that, in keeping the bowing fixed, the separation between the L

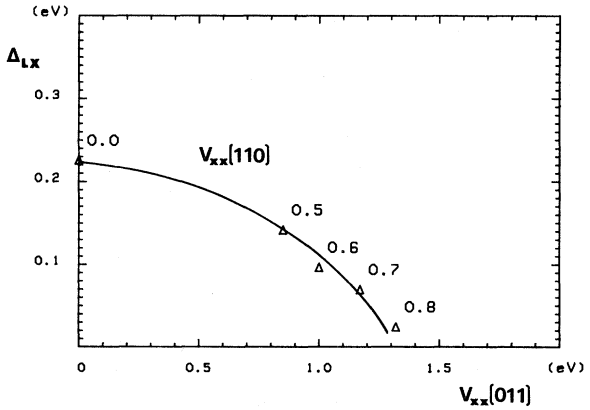

FIG. 3. Separation of L and X conduction bands Δ_{LX} is plotted vs $V_{xx}(011)$ for different values of $V_{xx}(110)$. The line corresponds to the experimentally observed bowing in the main gap and the E_1 and E_2 signals. The parameters adopted in Table I, which give the best overall fit, place $\Delta_{LX} \approx 70$ meV.

and X conduction bands, Δ_{LX} may become very small and eventually even negative. This is shown in Fig. 3. While a near-degeneracy ($\Delta_{LX} \sim 0$) of these valleys has not heretofore been expected, the anomalously low value of the saturated drift velocity found recently[3] in $Ga_{0.47}In_{0.53}As$ might be explained by this occurrence. In this case, enhanced intervalley scattering due to the nearness of the X band would effectively reduce the drift velocity. We suggest this thesis be tested experimentally.

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