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Band structure of semiconductor alloys

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The band structures of several semiconductor alloys have been calculated by a method which takes into account the reduced local symmetry in the alloys. The alloy band structure is found from the weighted average of the band structures calculated for crystals formed from the different nearest-neighbor configurations that can occur in the alloys. In this way one avoids making the usual single-site approximation in which the effects of local atomic rearrangements on the alloy band structure are neglected. The results are compared with experiment in two ways. First the variation with composition of the splitting of the valence bands at Γ is found to be in excellent agreement with experiment for the three alloys $Al_xGa_{1-x}As$, $Ga_xIn_{1-x}As$, and $Ga_xIn_{1-x}P$ which were studied. In addition, the bowing of the Γ, L, and X band edges and the alloy composition at which the direct-to-indirect band-gap crossovers occur are in good agreement with experiment.

I. INTRODUCTION

The effect of local atomic rearrangements on the properties of semiconductor alloys has been emphasized recently on the basis of both experimental and theoretical results. Direct experimental evidence has come from extended x-ray-absorption fine-structure (EXAFS) measurements[1,2] which show that atoms relax from their ideal sites in such a way that the bond length between each type of nearest-neighbor (NN) pair in the alloy is kept nearly the same as in the respective parent crystal. Ultraviolet-photoelectron-spectroscopy[3,4] (UPS) and nuclear-magnetic-resonance[5] (NMR) results show that the atoms in the alloy retain their chemical identities and that chemical shifts depend on the local electronic arrangement. Theoretical input[6-11] has come from first-principles band-structure and total-energy minimization calculations on single-crystal analogs of certain configurations which may occur in alloys. These show that atomic relaxation has important consequences for both the electronic and total energies. For example, predictions[8] of new crystal structures made on the basis of the calculations incorporating the atomic relaxations have subsequently been observed.[12,13]

Most treatments of alloys have been based on the virtual-crystal approximation (VCA) in which the alloy is replaced by a hypothetical crystal composed of atoms occupying ideal, parent-crystal sites in a weighted-average crystal potential. The coherent-potential approximation (CPA) is a significant improvement on the VCA in that it takes into account some effects of disorder in a single-site approximation in which the remainder of the crystal is still treated as a mean environment.[14] Both methods are based on effective Hamiltonians which do not allow for local atomic rearrangement and which possess the full parent-crystal symmetry. In view of the above evidence, particularly that for atomic relaxations,[1,2] it is desirable to reexamine applications of the VCA and CPA to semiconductor alloys.[9] One approach is to consider perfect crystals formed from local configurations likely to occur in the alloys[6-11] and to draw conclusions about the alloys from these. However, it would be desirable to have a band-structure method for the alloys themselves which takes into account the reduced local symmetry. In this work we describe an extension of the energy average (EA) method[15] which allows this to be done. Results in good agreement with experiment are obtained for three different semiconductor alloys.

The EA method is an attempt to take into account local effects in the alloy more realistically while retaining the simulated long-range order and translational symmetry that are necessary to describe the alloy from a conventional band-structure point of view. The local effects include the reduced point-group symmetry, lattice distortions, and the identity of the different chemical species in the alloys. In principle the method is based on calculating the band structure of all the periodic crystals that can be formed by translational symmetry of the different possible local configurations that occur in the alloys. The band structure of the alloy is then taken to be the suitably weighted average of the band structures corresponding to these local configurations. In this way the mixing of certain band states due to the lowered symmetry in the alloy can be taken into account in a systematic way. This mixing has been taken into account previously by using a phenomenological expression for it[16,17] and by using perturbation theory.[18] The weighted-average contribution of several different configurations to the total energy has also been calculated using first-principles methods to predict the change in enthalpy with composition.[8] The EA method can be viewed as an extension of these ideas. The theory is a better approximation the larger the size of the configurations, but for practical reasons the following results are confined to the 16 NN configurations which can be accounted for in a unit cell four times as large as the unit cell in the parent semiconductors. Our previous results[15] showed that the reduced local symmetry due to differing site occupancy alone produced a relatively small effect, insufficient, for example, to account for the observed variation in the spin-orbit splitting of the valence band of several III-V semiconductor alloys. In this work we show that the inclusion of the atomic relaxations inferred from EXAFS measurements leads to much greater splittings in good agreement with experiment. We also examine the effect of the internal electric fields which are set up by differing site occupancy and atomic relaxation.

II. THEORY

A. Justification of the EA method

In the first part of this section, we give a derivation of the EA approach and show its relationship to the VCA. This is done in the context of the semiempirical tight-binding (SETB) method, which is the band-structure method used in this work, but the discussion could be easily extended to other band-structure approaches. In the SETB VCA method the matrix elements which determine the band structure are usually interpolated between the parent-crystal values, according to the alloy composition, without further justification. It is useful to consider the theoretical framework and assumptions which this procedure requires. The first step in the calculation of the conventional band structure of an alloy must be the replacement of the real alloy with a crystal form or forms which have translational symmetry. This is done by assuming the Hamiltonian $H^{AB}(x,\mathbf{r})$ of the alloy A_xB_{1-x} [for example, $(\mathrm{AlAs})_x(\mathrm{GaAs})_{1-x}$, which is also written $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$] is of the form

$$H^{AB}(x,\mathbf{r})=xH_A(\mathbf{r})+(1-x)H_B(\mathbf{r}) \tag{1}$$

where $H_I(\mathbf{r})$ with $I=A,B$ are the Hamiltonians for the pure crystal forms A and B, respectively. Thus the alloy is incorrectly assumed to have not only the translation symmetry but also the point-group symmetry of the parent crystals A and B. In the SETB form of the theory, the Hamiltonian is written

$$H_I(\mathbf{r})=\sum_{\mathbf{R}_i}[H_I^{\mathrm{at}}(\mathbf{r}-\mathbf{R}_i)+\Delta V_I(\mathbf{r}-\mathbf{R}_i)] \tag{2}$$

where $H_I^{\mathrm{at}}(\mathbf{r}-\mathbf{R}_i)$ is the Hamiltonian of the free atoms comprising species I in the unit cell located at $\mathbf{R}_i$ and $\Delta V_I(\mathbf{r}-\mathbf{R}_i)$ is the difference between the free-atom potential and crystal potential in the unit cell.

The eigenfunctions $\Phi^{AB}(x,\mathbf{r})$ of $H^{AB}(x,\mathbf{r})$, where $\mathbf{k}$ is the wave vector based on the alloy unit-cell size, are expanded in terms of Bloch sums of basis states $\Phi_n(\mathbf{r})$ which must be assumed to have two properties. The first is that they be simultaneous eigenfunctions of $H_A^{\mathrm{at}}(\mathbf{r})$ and $H_B^{\mathrm{at}}(\mathbf{r})$ with eigenvalues E_A and E_B, respectively. This requirement is equivalent to the assumption that $H_A^{\mathrm{at}}(\mathbf{r})$ and $H_B^{\mathrm{at}}(\mathbf{r})$ commute. The second assumption is that the matrix elements of these simultaneous eigenfunctions are the same in the alloy as the matrix elements in the respective parent crystals.

The energies of the alloy band structure can be found from the secular determinant whose elements are

$$H_{mn}^{AB}(\mathbf{k})=[xE_A+(1-x)E_B]\delta_{mn} + \sum_{\mathbf{R}_i}[xH_{mn}^{A}(\mathbf{R}_i)+(1-x)H_{mn}^{B}(\mathbf{R}_i)]e^{i\mathbf{k}\cdot\mathbf{R}_i} \tag{3}$$

where $H_{mn}^{I}(\mathbf{R}_i)=\langle\Phi_m(\mathbf{r})\,|\,\Delta V\,|\,\Phi_n(\mathbf{r}+\mathbf{R}_i)\rangle$ and $\mathbf{R}_i$ are the vectors to the NN and possibly the next NN if the latter are included as well. The values of $\Delta H_{mn}^{I}(\mathbf{R}_i)$ and E_I are taken as adjustable constants to fit the band structure of the parent crystals, $I=A$ or B.

In the EA approach on the other hand, translational symmetry is imposed on the alloy problem by considering the alloy as the weighted average of the periodic crystals which can be formed from the different local configurations which occur in the alloy. Thus the alloy A_xB_{1-x} is described by the Hamiltonian

$$H^{AB}(x,\mathbf{r})=\sum_i W_i(x)H_i(\mathbf{r}) \tag{4}$$

where $W_i(x)$ is the probability of local configuration i and $H_i(\mathbf{r})$ is the Hamiltonian corresponding to the crystal formed from configuration i by translational symmetry. The advantage of Eq. (4) over Eq. (1) is that in the former the point-group symmetry of the parent crystals, A and B, is not imposed on the alloy Hamiltonian $H^{AB}(x,\mathbf{r})$. Thus the effects of the lower symmetry of the local configurations, for example in the removal of the degeneracy of certain levels, can be incorporated into the alloy calculation in the EA approach. The next step in the EA approach is to assume that the Hamiltonians $H_i(r)$ in Eq. (4) commute with one another. This is to be compared with the corresponding assumption in the VCA that the atomic parts of the Hamiltonians, $H_I^{\mathrm{at}}(r)$ commute with one another. This step in the EA approach is equivalent to the assumption that the electrons remain in states defined by a certain configuration and are not scattered into other configuration states as they pass through the alloy. It follows that the wave function for the alloy $\varphi_{\mathbf{k}}^{AB}(x,r)$ can be written as the product of the eigenfunctions $\chi_{\mathbf{k}}^{i}(r)$ of the Hamiltonians $H_i(r)$ and thus, from Eq. (4), the band energies of the alloy can be obtained from

$$E_{\mathbf{k}}(x)=\sum_i W_i(x)E^i(\mathbf{k}) \tag{5}$$

where the $E^i(\mathbf{k})$ are the band energies of a crystal formed from configuration i. Thus in the EA approach the band structure of the alloy is obtained from the weighted averages of the band structures of crystals corresponding to the different local configurations in the alloy.

The real alloy has no repeating unit and therefore it should be better to use as large a repeating unit as possible to impose the translational symmetry which is required to treat the alloy in the band picture. Thus it is reasonable to assume that the extended states of each of the configurations that are considered must be involved in the extended states of the alloy. On a very simple picture, the latter must be formed as the electrons encounter the different configurations as they move from one unit cell to the next in the alloy. In the EA approximation the actual extended states are found from the weighted averages of the extended states for each configuration without taking the scattering among the states into account explicitly.

It is reasonable to neglect the scatterings between different configurations because this type of correction which is accounted for by the CPA method should become less important as the unit cell for which the band structure is obtained becomes larger. For example, the CPA correction due to the variation in potential in going from each normal-sized unit cell to the adjoining cells is taken into account in the EA method because the rapid fluctuation in potential on the smaller scale has been removed. It would of course still be very useful to include this correction in the calculation. However, even without it, it is expected that the EA will give much better results than the normal VCA.

B. Band-structure calculations

The 16 configurations involving the possible arrangements of NN's were considered and the band structure of each configuration was calculated using the SETB method as described previously. For an alloy of the type $A_xB_{1-x}C$, the probabilities in Eqs. (4) and (5) are given by $W_i(x)=\binom{4}{n_i}(1-x)^{4-n_i}x^{n_i}$ where n_i is the number of cations of type A in configuration i. We have found that it is important to take into account the changes of atom positions that are known from EXAFS results to occur in the various local configurations. The new atom positions in the unit cell were calculated using Eq. (9) of Ref. 2 which was shown to lead to interatomic distances in good agreement with EXAFS data for $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$ and other crystals[2] and which is here assumed to apply to $\mathrm{Ga}_x\mathrm{Al}_{1-x}\mathrm{As}$ as well. The new atom positions were incorporated into the SETB calculation by expressing the matrix element which occurs in the secular determinant in Eq. (3) as

$$H^I_{mn}(\mathbf{R}_i)=H^I_{mn}(\mathbf{R}_0)e^{-\beta\Delta a}\ . \tag{6}$$

Here the matrix elements $H^I_{mn}(\mathbf{R}_0)$ between the basis states m and n in an undistorted crystal have been modified by the changes $\Delta a = |\mathbf{R}_i| - |\mathbf{R}_0|$ in NN vectors in the exponential term. The main effect of the new atom positions is the changed directions of bonds which enter via the exponential term in Eq. (3). The parameter β in Eq. (6) can be determined from the measured change in band gaps of the parent crystals as a function of pressure which also changes the bond lengths in crystals.

C. Crystal fields

Further correction to SETB matrix elements must be made for the alloy case as a result of the rearrangement of the atoms. The matrix elements are initially derived from a fit to the band structure of the parent crystals and therefore account for a crystal potential with space-group symmetry $T_d^2(F\bar{4}3m)$. Modifications to the matrix elements which occur in this symmetry, due to the altered atom positions in the unit cell of the alloys, have been described above but account needs also to be taken of the entirely new components of the crystal potential which occur as a result of the lower symmetry in the alloy. As a first approximation for the inclusion of these terms we have used the point-charge model of the crystal field[19] involving NN atoms only. It is not suggested that this model is adequate in the semiconductor alloys but it is used to give an order-of-magnitude estimate of the size of the entire term in the crystal potential. The covalent model of the crystal potential is not qualitatively different because terms with the same symmetry also arise from it.

To take the crystal fields into account, we add to the matrix elements of the alloy Hamiltonian, as calculated in Sec. II B above, the crystal-field term $\langle \varphi_m(\mathbf{r}) \,|\, V_{\mathrm{CR}}(\mathbf{r}) \,|\, \varphi_n(\mathbf{r}) \rangle$ where $V_{\mathrm{CR}}(\mathbf{r})$ is the Hamiltonian representing the perturbation due to that part of the crystal field which was not taken into account in the higher-symmetry parent crystals. We take $V_{\mathrm{CR}}(\mathbf{r})$ to be due to a discrete set of charges with charge e^* on the four NN cations around each anion. The cation sites require no correction as they have the same NN symmetry in the alloys and the parent crystals. The charge e^* is taken to be the Szigeti charge e_s in units of the electronic charge e given[20] by $e^*=e_s/e=m(r_a/d)+b$ where r_a is the ionic radius of the anion and d is the NN distance in the parent crystal. In the expansion of $V_{\mathrm{CR}}(\mathbf{r})$ for the point-charge model,[19] all terms up to order 2 are included because of the lower symmetry but higher-order terms can be neglected because only s and p electrons are involved in our calculations.

III. RESULTS

Calculations were performed for three alloys: $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$, $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{As}$, and $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$. There are three important inputs to the calculation of the band structure of the alloys using the EA approach. The first of these are the values of the SETB matrix elements for the parent III-V compound semiconductors. The values used were based on those in Ref. 18 with some adjustments in the cases of GaAs, AlAs, GaP, and InP to comply with more recent experimental data. The values for the different materials are given in Table I in the same nomenclature as Ref. 18. The second input to the calculation is the variation of these matrix elements with the small variation of NN distances which occur in the alloys. This was obtained by calculating the band gap of the parent crystals for different lattice constants with the SETB matrix elements adjusted according to Eq. (6) using different values of β. The experimental value of the band gap as function of the lattice spacing can be obtained from the pressure dependence of the band gap and the variation of the lattice constant with the pressure.[21] The most suitable values of β that were obtained are given in Table I and with them the pressure dependence of the band gap is reproduced to high precision over a pressure range up to 6 kbar. The changes in interatomic distances corresponding to those pressure ranges encompass the changes in interatomic distances that are encountered in the alloy calculations. Typical agreement between theory (this work and Ref. 22) and experiment is given in Fig. 1.

Finally the NN vectors in the alloys are required for all compositions. As explained above these were calculated

TABLE I. Parameters used in the calculation of the alloy band structure. The first eight rows give the SETB parameters in eV in the nomenclature of Ref. 18. The bond-stretching parameter α used in the calculation of atom positions is expressed in N m^{-1}. The parameter β used to modify the matrix elements due to the new atom positions is expressed in (nm)$^{-1}$.

	$Ga_xIn_{1-x}As$				$Al_xGa_{1-x}As$				$Ga_xIn_{1-x}P$			
	Ga	As	In	As	Al	As	Ga	As	Ga	P	P	In
E_p	3.35	1.16	3.35	1.03	2.83	1.379	3.60	0.949	4.35	0.89	3.679	0.96
E_s	−3.19	−8.21	−2.45	−9.51	−4.01	−5.05	−4.45	−6.95	−3.47	−7.35	−2.94	−7.75
$V_{s_a p_c \sigma}$	2.06		1.33		1.397		1.353		1.200		1.615	
$V_{s_c p_a \sigma}$	2.37		2.31		3.353		3.355		1.543		1.327	
$V_{ss\sigma}$	−1.69		−1.31		−1.831		−1.754		−2.025		−1.581	
$V_{pp\pi}$	−0.96		−0.71		−0.768		−0.733		−0.195		−0.280	
$V_{pp\sigma}$	3.51		2.93		2.96		2.853		1.868		1.970	
SO	0.131	0.14	0.058	0.14	0.008	0.14	0.058	0.14	0.058	0.022	0.131	0.022
α	41.19		35.18		42.92		41.19		47.32		43.04	
β	1.30		1.30		1.75		1.35		1.35		1.35	

by the method of Ref. 2 which requires a knowledge of the Keating bond-stretching parameters which were obtained from Ref. 23 or in the case of AlAs were calculated from the elastic constants.[21] The values used are also given in Table I.

The calculated band structures of the alloys are similar overall to the normal VCA results throughout the Brillouin zone.[15] The effects of the lower symmetry in the real alloy are more significant at the higher-symmetry points in the zone and thus the results at Γ, L, and X were chosen to be compared in detail with experimental results. This was done in two ways. The first involves the variation with alloy composition of the splitting Δ_0 of the upper valence bands at Γ and is shown in Fig. 2, together with experimental results.[24] Although there is a wide variation in the dependence of Δ_0 on composition among the different alloys, excellent agreement is obtained for all the alloys studied. A second comparison with experiment involved the variation with alloy composition of the energy of the conduction-band edges at Γ, L, and X measured with respect to the top of the valence band Γ_{15v}. Results for $Al_xGa_{1-x}As$ and $Ga_xIn_{1-x}P$ are shown in Figs. 3 and 4 and compared with some experi-

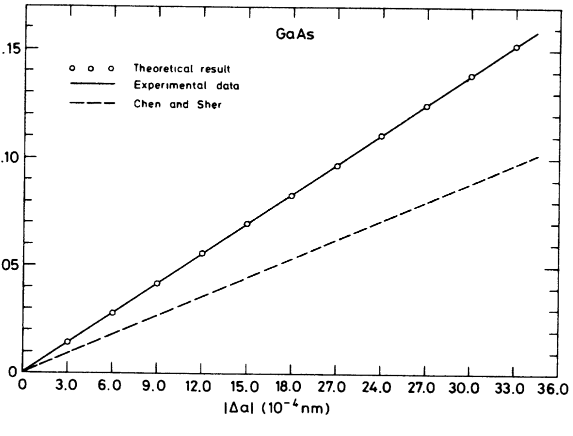

FIG. 1. Variation of the band gap of GaAs with the change Δa in the interatomic spacing. The theoretical result is from the band structure calculated with $\beta = 1.3$ nm^{-1} (Table I) used in Eq. (6). The experimental data is obtained by combining the dependence of the band gap on pressure and the lattice constant on pressure. The results marked Chen and Sher are obtained from Eq. (6) of Ref. 22.

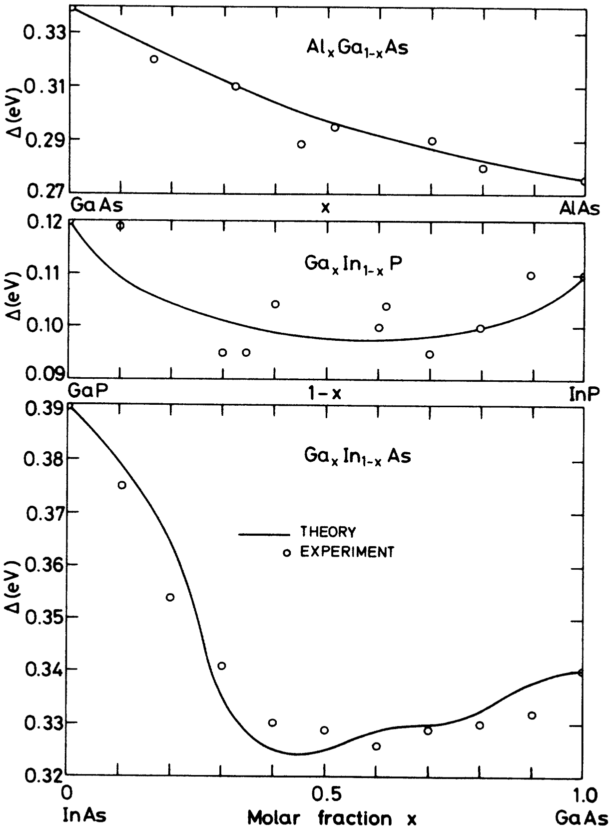

FIG. 2. Variation of the energy difference Δ_0 between the two uppermost valence bands at Γ with alloy composition x from the present calculations for the alloys shown. The results are compared with experimental values from Ref. 24.

mental results.[25–28] Once again good agreement between the EA approach and the experimental results is obtained.

IV. DISCUSSION

One of the fundamental questions with respect to semiconductor alloys is the origin of the nonlinear variation of the band energies with alloy composition, that is, band "bowing." The most important manifestations are the bowing of the valence- and conduction-band edges and the valence-band splitting Δ_0, which have been considered in the preceding section. A number of different origins of the band bowing have been suggested.[16–18,29] For the simple application of the VCA, the inputs to the calculation, in the form of the matrix elements or pseudopotentials of the theory being used, are linearly interpolated between the corresponding parent-crystal values. Some authors have suggested that the parameters entering into the VCA should not be interpolated linearly and then a greater nonlinear bowing of the bands can be obtained.[28,29] When the CPA is used to deal with the alloys, bowing can result, even when the parameters are linearly interpolated purely as a result of the inclusion of the site disorder by the CPA method, for example in $Cd_xHg_{1-x}Te$.[30] In applications of the CPA method to III-V compound semiconductor alloys, the bowing has been calculated with both a linear interpolation of the band parameters[31] and a nonlinear one.[28] The former[31] was based on an elliptical-band fit to the parent band structures and gave good agreement with experiment for $Ga_xIn_{1-x}P$ and $Ga_xIn_{1-x}As$. The second[28] was based on a SETB fit to the parent band structures but in this case the quantity which was linearly interpolated was the product of the SETB parameters and the square of the alloy lattice parameter with the lattice parameter itself assumed to follow Vegard's rule. This method of interpolation automatically[22] ensures a bowing of the form $-bx(1-x)$ even in the VCA without the refinement of the CPA which was used to obtain the final results. The justification of this interpolation method was that the SETB matrix elements scaled as $1/a^2$ in different III-V semiconductors, where a is the lattice constant. It should be pointed out that this form of scaling does not fit the dependence of the band-gap energy on pressure, and therefore lattice spacing, as well as the exponential-based interpolation used in this work, see Fig. 1. More impor-

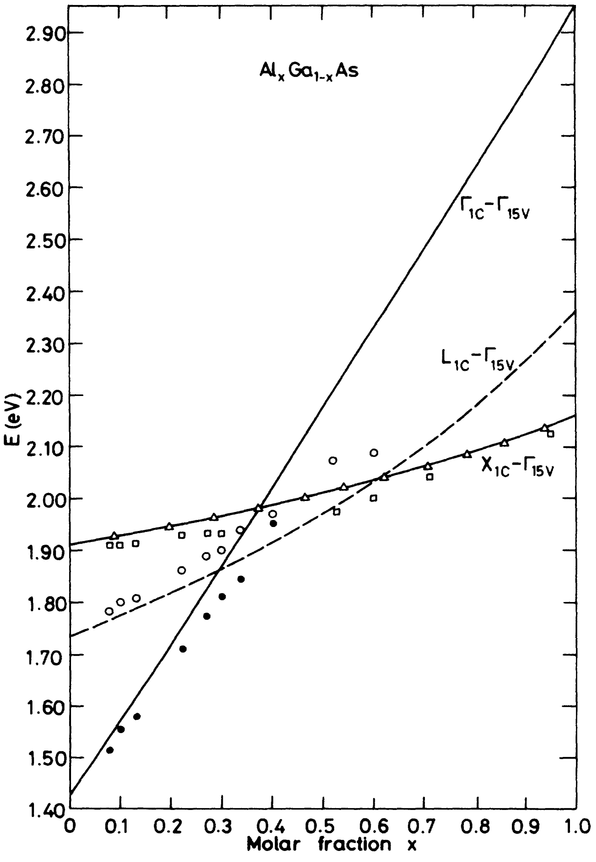

FIG. 3. Variation with alloy composition x of the energy of the conduction-band edges at Γ, L, and X measured with respect to the top of the valence band Γ_{15v} for $Al_xGa_{1-x}As$. Experimental values are from Ref. 28.

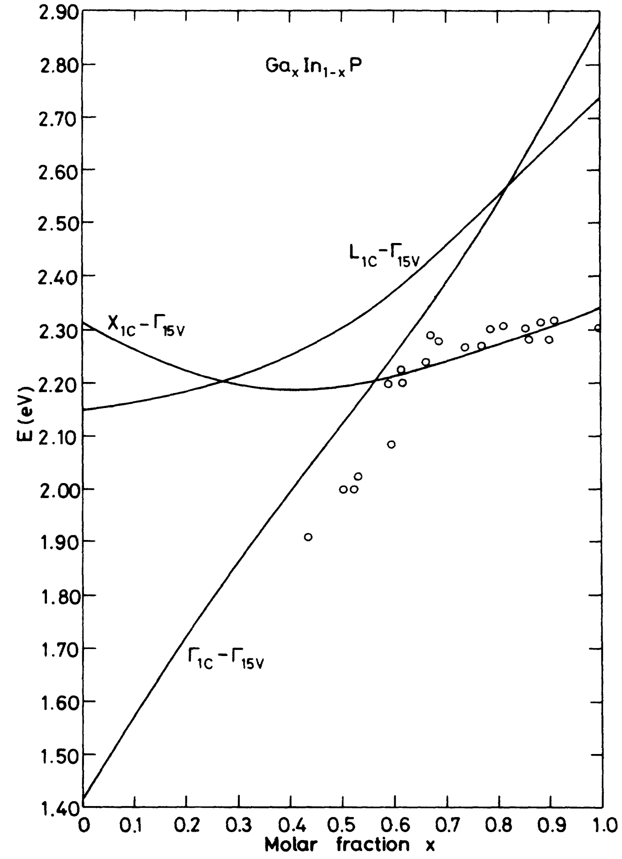

FIG. 4. Variation with alloy composition x of the energy of the conduction-band edges at Γ, L, and X measured with respect to the top of the valence band Γ_{15v} for $Ga_xIn_{1-x}P$. Experimental values are from Ref. 28.

tantly, the interatomic distances in the alloy do *not* change in the same way as the alloy lattice parameter. In fact, the EXAFS results[2] show that they stay nearly constant. Therefore the form of interpolation used in Ref. 28 and the resulting bowing parameters may not be justified.

The foregoing methods are essentially single-site theories in which all lattice sites are occupied by some averaged species, even if the properties of the averaged species are determined self-consistently as in the CPA. As mentioned in the Introduction, recent experimental results throw doubt on single-site theories. One approach to a multisite theory for alloys is to calculate the properties of a single crystal formed from the most likely configuration of atoms which can occur in the alloy and infer the properties of the alloy from calculations on that material.[9] As a result of calculations for a possible configuration likely to occur in 50%-50% alloys, bowing parameters and chemical trends were predicted and the physical origins of the contributions to the bowing parameters were identified. Further, the enthalpies of alloys have been calculated from weighted averages of the total energy of several configurations which occur in the alloy.[8] We now assess the results of the EA approach in which the band structure of the alloy is obtained from the weighted average of the various configurations which occur in the alloy.

The first point to notice is that the EA approach produces an alloy band structure which is a regular interpolation of the parent-crystal bands. Note that this result is obtained without an interpolation of the properties of the atoms in the alloy which is assumed in other approaches. In fact the parameters characterizing the atoms and interactions in the alloy for the SETB calculations are the same as the parent crystals except (1) the free-atom energies of the common cation species are linearly interpolated between the values of the two parent crystals and (2) the matrix elements are adjusted to take into account the slightly changed interatomic spacing between NN atoms in the alloy compared with the parent crystals.

Second, the splitting Δ_0 of the valence bands at Γ is a sensitive test of a theory of semiconductor alloys because its dependence on alloy composition departs significantly from a linear interpolation between the values of the parent crystals. Spin-orbit effects have not been included in the CPA calculations of the III-V semiconductor alloys[28,31] so a zero value would have been obtained because the lower symmetry which also contributes to the value of Δ_0 is also not included in the CPA. The value of Δ_0 has been calculated using the empirical pseudopotential method for the band structure.[29] However, in that case the bowing parameter that was found was based on the assumption that the NN distance was a constant for all neighbors in the alloy and varied as Vegard's law.[22] In view of the EXAFS data[1,2] this does not appear to be justified. A more likely explanation for the bowing in the variation of Δ_0 is the mixing of band states due to the reduced symmetry in the alloy.[16–18] The variation of Δ_0 with alloy composition has been fitted before using a phenomenological model for the mixing of conduction- and valence-band states due to the reduced symmetry.[16,17] Although the assumed form for the expression led to agreement with experiment for a number of alloys, no *a priori* justification for the form could be given.[16] The magnitude of the mixing between the valence- and conduction-band states was put on a more quantitative basis by Chadi,[18] who used perturbation theory within a VCA SETB model of the alloys. The value of Δ_0 was taken to be the weighted average of the values in the 16 possible local configurations in the alloy.

Although good agreement with experiment was obtained for several alloys, we have suggested[15] that the magnitude of the effect is so large that it is inappropriate to use perturbation theory to account for it. In the energy average approach the band energies are obtained by diagonalizing the secular determinant for each configuration directly without relying on perturbation theory. We showed that in that case the predicted variation of Δ_0 due to the combined effects of the lowered symmetry and the spin-orbit interaction was not in agreement with experiment. We therefore concluded that the previous good agreement was due to the use of perturbation theory to account for the interband mixing. In our previous calculations, the mixing was assumed to be entirely due to the differing site occupancy of the cation sites in the alloys with the consequent nonequivalence of one or more of the NN SETB matrix elements. In the present calculation we have included two further effects. First, the movement of the atoms in the alloy to preserve NN bond distances means the interband mixing is considerably enhanced because the atoms are no longer symmetrically arranged in the enlarged unit cell. Second, a crude estimate of the changes in the electrostatic potential due to the asymmetrical arrangements of atoms has been included. These changes are not included in the SETB parameters of the parent crystals because they are zero by symmetry in those cases. The comparison in Fig. 2 shows that the variation of Δ_0 with composition is well described by the present theory.

The final means of comparing theory with experiment involves the variation of the direct and indirect band gaps with alloy composition. This is a less sensitive test of the method chosen to represent the alloy than the calculation of Δ_0 referred to above. This is because the band bowing and cross-over concentrations depend to a significant extent on the values chosen for the energies of the band edges in the parent crystals. Although the latter values can be adjusted almost at will in the CPA (Refs. 28 and 31) theories and the present SETB theory which are being considered, there is considerable disagreement among the experimental results and consequently different authors have chosen to fit their parent-crystal results to different data. As an example, consider the case of $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$ in Fig. 4. Our results suggest that the gap is direct (Γ_{1c}-Γ_{15v}) for $x \leq 0.55$ and indirect (x_{1c}-Γ_{15v}) for $x > 0.55$ in approximate agreement with Ref. 28. However, had we chosen the L_{1c}-Γ_{15v} gap for $x = 0$, i.e., InP, to be 1.9 eV as in Ref. 31 we would have predicted in addition an L_{1c}-Γ_{15v} indirect gap over a small range of x as in Ref. 31. Values of the band bending coefficients also depend sensitively on the parameters used to represent the parent band structures and the experimental estimates of them also cover a wide range. Therefore it does not appear to be very meaningful to make a quantitative comparison of results for the alloys considered here. Qualitatively the experimental data, particularly for the concentration at which the direct gap to indirect gap transition occurs does indicate that positive band bowing does take place in the alloys and this type of bowing is predicted by all the theories considered which are therefore in better agreement with experiment than the conventional VCA results.

V. CONCLUSION

A method has been described for calculating the band structure of semiconductor alloys which takes into account the reduced local point-group symmetry in the alloys. The results are in good agreement with experiment, particularly for the valence-band splitting Δ_0 at Γ, if local rearrangements of atoms predicted by EXAFS results are taken into account. The results confirm previous suggestions about the importance of the reduced symmetry in alloys[16,17] in which the reduced symmetry was taken into account phenomenologically. In the present work, a semiempirical method has been used to calculate the band structures, as in nearly all previous alloy calculations, and consequently the theoretical predictions of quantities other than Δ_0 depend somewhat on the values for the semiempirical parameters. However, the present results are in good qualitative agreement with other experimental results for the alloys considered. It would be interesting to apply the EA method to the calculation of other properties of the alloys, for example, the density of states and carrier transport properties such as the lifetime of the alloy and mobilities. It would also be interesting to apply the EA method with first-principles band-structure calculations and hence eliminate the reliance on the semiempirical parameters.

ACKNOWLEDGMENT

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