Reduced symmetry and the band structure of semiconductor alloys

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It is suggested that the neglect of the reduced local symmetry at some sites in alloys can be a serious shortcoming in the calculation of alloy band structures. A phenomenological scheme which takes account of the reduced local symmetry while preserving long-range order through the virtual-crystal approximation is described for calculating the band structure of alloys. It is shown that the method leads to an overall band structure similar to the corresponding virtual-crystal approximation but gives better agreement with experiment for the splitting of the valence bands at Γ.

I. INTRODUCTION

Semiconductor alloys like $Hg_{1-x}Cd_xTe$, or the dilute magnetic semiconductors like $Cd_{1-x}Mn_xTe$, have properties intermediate between their pure compound constituents and thereby have important practical applications. Many of the applications, or potential applications, rely on a knowledge of the band structure which has usually been approached from a theoretical point of view using the virtual-crystal approximation (VCA) or the coherent-potential approximation (CPA). Recent applications of these methods to alloys have attempted to account for the compositional and positional disorder in the alloy.[1-8] In the VCA, the alloy is represented by a hypothetical crystal in which every site of the disordered lattice or sublattice is replaced by an imaginary atom whose properties are the weighted average of the atoms occupying those sites in the alloy. This is obviously a rather drastic approximation, and it is known from ultraviolet photoelectron spectroscopy (UPS), for example, that the two species on the disordered sites retain their own character to a large extent.[9] The CPA represents an improvement because it takes into account the disorder resulting from the occupancies of some sites by different chemical species. One of the most significant consequences of either approach is that although disorder may be taken into account, the model alloy retains the full local symmetry of the pure forms of either of its compound constituents. For example, according to either model, $Cd_{1-x}Zn_xTe$ possesses the cubic zinc-blende symmetry of CdTe. Recent x-ray-absorption fine-structure (EXAFS) measurements of $Cd_{1-x}Zn_xTe$ and other alloys confirm that the local symmetry is quite different from cubic in the real alloys, not only because of the random occupancies of the sites, but also because of lattice distortions.[10-13] For the special case of an equimolar alloy, for example, $In_{0.5}Ga_{0.5}P$, it has been possible to investigate some consequences of the lattice distortion by assuming the alloy had the chalcopyrite structure.[8] It was suggested that structural distortion explained most of the optical bowing in semiconductor alloys.[8]

One effect of the lower symmetry which exists in the real alloy is the removal of the degeneracy of certain states in the crystal. For example, the degeneracy of the two p-like bands at Γ in the zinc-blende structure would be removed in real alloys. This effect has been pointed out by Chadi,[14] who attempted to account for it by a perturbation calculation, which the following results suggest was in error because the effect is too large to treat by perturbation theory.

Since the symmetry of a crystal has a great influence on the band structure, it would seem desirable to incorporate the lower symmetry and not just the disorder to be found in the alloy into the calculation of the band structure at a fundamental level. The correction introduced by Chadi[14] suggests a way of doing this.

If the alloy is of the type $U_{1-x}V_xW$, for example, $In_{1-x}Ga_xAs$, there are 16 possible nearest-neighbor configurations of the atom W. Each of these configurations can be represented in unit cells which are four times as large as the primitive unit cell of the zinc-blende structure. The band structure of hypothetical crystals corresponding to each of the unit cells can be calculated using the semiempirical tight-binding (SETB) method.[15] Fourteen of the sixteen different configurations have lower symmetry than the zinc-blende structure (and the alloy in the VCA method) and the lower symmetry is incorporated into the band structure corresponding to each. The band structure of the alloy as a whole is then found by calculating the average of these 16 band structures. Thus the effects of lower symmetry are included by taking the average band structure of different lattices rather than calculating the band structure of the average lattice as in the VCA method.

II. THEORETICAL MODEL

The Slater-Koster SETB scheme[15] was used to calculate the band structure. The model was based on nearest-neighbor interactions between the s, p_x, p_y, p_z basis states used for each of the two atoms in the unit cell, and included the spin-orbit (SO) interaction. To calculate the band energies $E(\mathbf{k})$ corresponding to wave vector $\mathbf{k}$, it is necessary to diagonalize a 64×64 secular determinant. If we consider an alloy of the form $U_{1-x}V_xW$ (e.g., $In_{1-x}Ga_xAs$) or $WU_{1-x}V_x$ (e.g., $InSb_{1-x}As_x$), the elements of the determinant can be written

$$H^{XX'}_{\alpha\alpha',\sigma\sigma'}(\mathbf{k}) = \sum_{X'} \langle \phi^X_{\alpha,\sigma}(0) \mid \mathscr{H} \mid \phi^{X'}_{\alpha',\sigma'}(\mathbf{R}_{XX'}) \rangle$$

$$\times \exp(i\mathbf{k}\cdot\mathbf{R}_{XX'}) , \qquad (1)$$

where $\alpha = s,x,y,z$ specifies the orbital symmetry s,p_x,p_y,p_z, respectively, $\sigma = \uparrow,\downarrow$ is the spin index, and $X,X' = U,V,W$ represents the type of atom. The Hamiltonian of the crystal, $\mathscr{H}$, need not be specified because the matrix elements are used as adjustable parameters in the SETB scheme. Since only interactions up to nearest neighbor are included, $\mathbf{R}_{XX'} = 0$ for $X = X$ and $\mathbf{R}_{XX'} = (a/2)(l\hat{x} + m\hat{y} + n\hat{z})$ for $X' \neq X$, where a is the side of the cubic unit cell and l,m,n are the direction cosines to the nearest neighbors of X.

The spin-orbit interaction in $\mathscr{H}$ is taken to be the same as for isolated atoms and it is therefore only nonzero for $X' = X$. The effect of the remainder of the Hamiltonian is parametrized according to the Slater-Koster scheme

$$\langle \phi^X_{\alpha,\sigma}(0) \mid \mathscr{H} \mid \Phi^{X'}_{\alpha',\sigma'}(\mathbf{R}_{XX'}) \rangle = \delta_{\sigma\sigma'} E_{\alpha\alpha'}(lmn)_{XX'} .$$

We use the form of the E's in the two-center approximation, for example,

$$E_{xx}(lmn)_{UW} = l^2(pp\sigma)_{UW} + (1 - l^2)(pp\pi)_{UW}$$

where $(pp\sigma)_{UW}$ and $(pp\pi)_{UW}$ are the appropriate parameters for the pure compound UW (InAs, in our example).

The final band energies are obtained from the weighted average of the band energies corresponding to the 16 possible configurations. The band energies $E(\mathbf{k},n)$ depend only on the number n of nearest-neighbor atoms of type U or V, and not on their arrangement; thus the final energies, $E(k)$, for each band are given by

$$E(\mathbf{k}) = \sum_{n=1}^{4} (1-x)^n x^{4-n} E(\mathbf{k},n) P(n) ,$$

where $P(0) = P(4) = 1$, $P(1) = P(3) = 4$, and $P(2) = 6$ are the weighting factors corresponding to arrangements with n nearest-neighbor atoms U around a W atom in the alloy $U_{1-x}V_x W$. We have used the SETB parameters given by Chadi[14] in the calculations below.
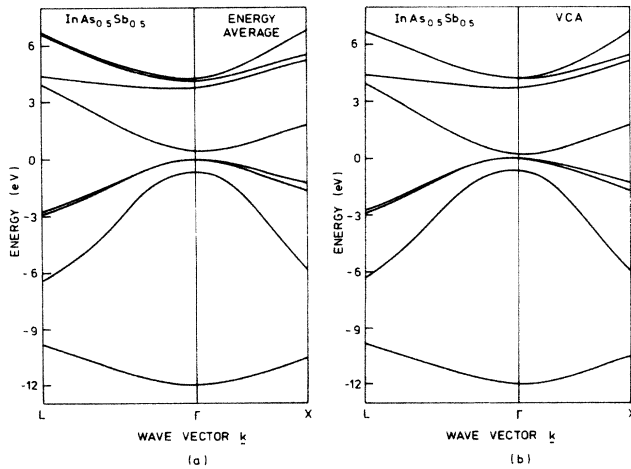

FIG. 1. A section of the band structure for the alloy InSb$_{0.5}$As$_{0.5}$. (a) Method described in this work. (b) Virtual-crystal approximation (VCA).
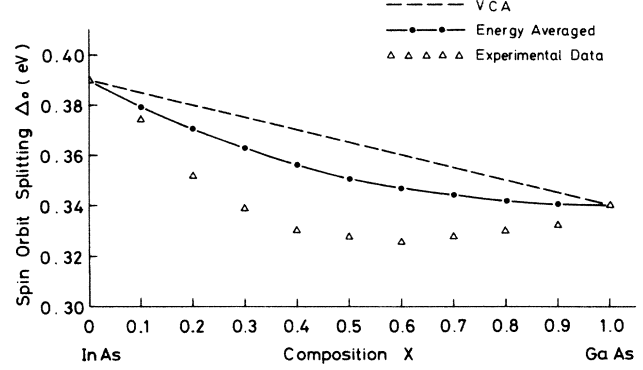

FIG. 2. Variation of the energy splitting Δ_0 of the upper valence bands of the alloy In$_{1-x}$Ga$_x$As as function of the composition x. Theoretical results are given for the virtual-crystal approximation (VCA), and the method described in this work. The experimental results are taken from Ref. 16.

III. RESULTS AND CONCLUSION

The results of the VCA and energy average (EA) calculations for InSb$_{1-x}$As$_x$ are shown in Fig. 1. There is very little difference between the two methods in the overall band structure. The same comment applies to other alloys we have investigated. However, the details of the band structure are affected. In particular, the splitting of the p-like states in the valence band at Γ is changed. The composition dependence of the splitting Δ_0 between the Γ_8 and Γ_7 states is shown in Figs. 2 and 3 for two alloys. The results of the present method show some of the "bowing" which is apparent in the experimental spectrum to a much greater extent. The variation shown is caused by the lower symmetry experienced by the W atoms in the two alloys. In the VCA, for example, a matrix element like $H^{XX'}_{sx,\sigma\sigma'}(\mathbf{k})$ is zero at $\mathbf{k} = (0,0,0)$ while it is nonzero in 14 of the configurations which are averaged in the present approach. Therefore the present approach gives better agreement with experiment.
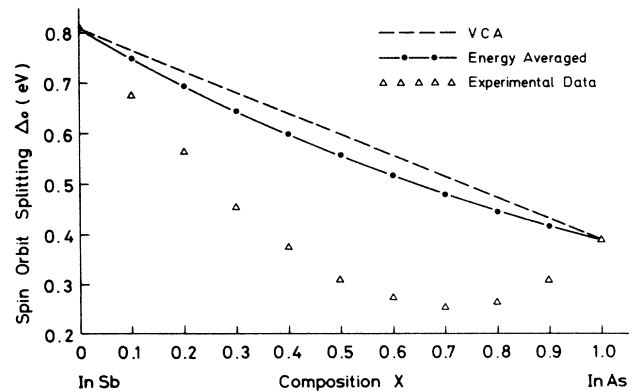

FIG. 3. Variation of the energy splitting Δ_0 of the upper valence bands of the alloy InSb$_{1-x}$As$_x$. Details of the theoretical and experimental results are given in the caption Fig. 2.

Chadi attempted to take the lower symmetry into account by applying first-order perturbation theory to the band structure calculated to zero order by the VCA method. That approach appeared to give much better agreement with experiment than the present method. We suggest that the two attempts differ because the effect of the lower symmetry due to the $E_{sx}(lmn)_{WX'}$ interaction is too large to be accounted for using perturbation theory. For example, the perturbation correction factor is of the order

$$[E_{sx}(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})_{UW} - E_{xz}(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})_{VW}]$$

$$- [E_{xs}(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})_{UW} - E_{xs}(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})_{VW}]/\Delta E$$

where ΔE is the band gap of the alloy corresponding to each local configuration. This fraction varies from about 1.4 to 1 as x varies from 0 to 1 for the case of $InSb_{1-x}As_x$ and from about 0.25 to 1 for the case of $In_{1-x}Ga_xAs$. In order for perturbation theory to be appropriate, the correction factor must be much less than unity, and therefore it is not appropriate to use a perturbation calculation in these cases.

There are only five nonequivalent local configurations in the alloy $InSb_{1-x}As_x$, and the splitting Δ_0 between the Γ_7 and Γ_8 states for each configuration is summarized in Table I. The change in Δ_0 in the VCA method is solely due to the change in the weighted average of the SO parameters used in that method. The changes in the perturbation method due to Chadi is in addition partly due to the reduced local symmetry as it is also for the EA approach. The results in Table I demonstrate that the reduced symmetry has a significant effect on the energy splitting of the energy levels indicated. However, Figs. 2 and 3 show that the predicted splitting of the averaged bands does not depart sufficiently from the linear variation to agree well with experiment. The full explanation for the variation of Δ_0 with composition may be due to the lattice distortion recently suggested by EXAFS results.[11-13] Lattice distortions of the nature suggested can

TABLE I. Compositional dependence of Δ_0(eV) for the possible local configurations in $InSb_{1-x}As_x$ in the virtual-crystal approximation (VCA), the perturbation approach of Chadi (Ref. 14) and the diagonalization of the secular determinant (this work).

Configuration	VCA	Perturbation theory	This work
InSb	0.81	0.81	0.81
$InSb_{0.75}As_{0.25}$	0.71	0.50	0.69
$InS_{0.5}As_{0.5}$	0.60	0.04	0.58
$InSb_{0.25}As_{0.75}$	0.50	0.32	0.48
InAs	0.39	0.39	0.39

be readily incorporated into the band-structure calculation method described in the present work, but not into other band-structure calculation methods for alloys.

It is suggested that a serious shortcoming in the calculation of alloy band structure is the neglect of the reduced local symmetry at some or all sites. The difficulty of overcoming this shortcoming is well known and is intimately related to the lack of long-range order in alloys. The CPA approach includes the effects of scattering due to local disorder but does not include the effect of the reduction of symmetry in the alloy. The approach described herein is a new attempt to account for the reduced local symmetry while retaining the simulated long-range order and translational symmetry through the VCA. Although the approach used has not been justified formally, it has been shown that it leads to an alloy band structure in substantial agreement with VCA, but with differences in detail which agree slightly better with experiment than the VCA itself.

ACKNOWLEDGMENT

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