Gap Variation in Semiconductor Alloys and the Coherent-Potential Approximation

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The well-known results of the coherent-potential–approximation (CPA) alloy theory are useful for understanding the energy-gap variation in semiconductor alloys. A CPA theory of the valence bands in III-V compounds demonstrates that alloy disorder can contribute significantly to the band-gap bowing parameter, while causing very little broadening of the E_0 spectra. We conclude that the CPA should replace the earlier theories for studying the electronic structure in semiconductor alloys.

Because of its importance in applications and to the fundamentals, the energy-gap variation in semiconductor alloys has been the subject of many experimental and theoretical studies.[1-8] The difference between the measured gaps in a binary alloy and the concentration-weighted average of the gaps of the consituent compounds, e.g., $Ga_xIn_{1-x}As$, is found[1] to be reasonably well described as a quadratic function of the concentration x,

$$\delta E = bx(x-1). \qquad (1)$$

The constant b in Eq. (1) is called the bowing parameter; it is found to be positive for low-lying transitions such as E_0, E_1, and E_2. However, the theoretical interpretation of this result is still laced with controversy. The main issue centers around the contribution of alloy disorder. In one popular theory, the virtual-crystal approximation (VCA), the disorder is completely neglected and the band energies are determined from averaged, renormalized, periodic potentials. If the alloy potential were merely taken to be the average of the two constituent potentials, the concentration variation of the energy gap would be linear. The bowing effect in VCA arises from the renormalization procedure that accounts for modifications of the screening, and for scaling with the lattice constant.[2,3] This procedure does not guarantee that b will be positive.[4] For this reason, Van Vechten and Bergstresser[3] proposed a dielectric model (DM) in which b contains two terms, $b = b_i + b_e$. The parameter b_i (intrinsic) is the VCA contribution to the bowing, and b_e (extrinsic) is a contribution attributed to alloy disorder. The parameter b_e was assigned a simple form,

$$b_e = \delta^2/A, \qquad (2)$$

where δ is the rms fluctuation in the potentials, and A is an adjustable bandwidth parameter. Objection to the alloy-disorder contribution was raised[2] on the grounds that, experimentally, alloying has very little broadening effect on the E_0 spectra.[2,5,6] A theoretical objection to some alloy-disorder calculations was further raised by Van Vechten[9] himself on the basis of a thermal equilibrium screening consideration. This argument was subsequently expanded beyond its original intent[2] to conclude that VCA is not just an approximation but rather an accurate representation of the potentials in an alloy so that the DM disorder contribution to b vanishes. However, while charge shifts do tend to smooth the potentials, it is evident from the potentials found in self-constant band theories of compounds that this last conclusion is unjustified.

In the process of studying the valence-band structure of the III-V compound zinc-blende alloys[10] using the coherent-potential approximation (CPA),[11,12] we found that CPA is useful in resolving some of the controversy just mentioned. We shall show that the variation of the gap E_0 can be readily understood in terms of a well-established CPA model.[12] A similar conclusion based on a specialized band model has been drawn by Siggia.[8] It should be emphasized that CPA is a more complete, systematic theory than either VCA or DM and should replace them in studies of semiconductor alloys.

Let us start by examining the CPA equation for the self-energy in a single-band model[13] for a binary alloy A_xB_{1-x} (for III-V compounds A and B each represent a compound designation, e.g., $A = \mathrm{GaAs}$, $B = \mathrm{InAs}$),

$$\Sigma = \epsilon - (\epsilon_A - \Sigma)F(\epsilon_B - \Sigma), \qquad (3)$$

where ϵ is the VCA potential, $\epsilon = x\epsilon_A + (1-x)\epsilon_B$, and F is a Green's function. The function F is related to the alloys density of states $\rho(E)$ through the dispersion relation,

$$F(E+i0) = \int dE'\rho(E')/(E+i0-E'). \tag{4}$$

If a lower-order approximation is made by letting $\Sigma = \epsilon$ on the right-hand side of Eq. (3), then the difference $\Sigma - \epsilon = \eta - i\Delta$ is given by

$$\eta = x(1-x)\delta^2 \operatorname{Re}F, \tag{5}$$

and

$$\Delta(E) = -x(1-x)\delta^2 \operatorname{Im}F = \pi x(1-x)\delta^2\rho(E), \tag{6}$$

where the scattering strength is defined as $\delta \equiv \epsilon_A - \epsilon_B$. It is easy to see from Eq. (4) that the real part of F, and thus η, is positive at the top of a band and negative at the bottom.

If Eq. (5) is applied independently to the valence band and the conduction band with scattering strengths δ_v and δ_c, respectively, then the alloy-disorder contribution to the bowing constant be comes

$$b_e = \delta_v^2 \operatorname{Re}F_v - \delta_c^2 \operatorname{Re}F_c. \tag{7}$$

Since $\operatorname{Re}F_v$ at the top of the valence band is positive and $\operatorname{Re}F_c$ at the bottom of the conduction band is negative, the bowing parameter b_e is guaranteed to be positive. This is a direct result of a behavior of the dispersion relation, Eq. (4), introduced by disorder. Similarly, the broadening paramater Δ in Eq. (6) vanishes at band edges, so that Δ is zero for both levels assoicated with the E_0 transition. Thus, the lack of alloy broadening in E_0 cannot be adduced as evidence against the existence of an alloy-disorder contribution to the bowing parameter. The full CPA self-energy Σ in Eq. (3) slightly modifies the above results (see Fig. 1), but the essential conclusions are not altered.

The relations between the CPA, VCA, and DM results are easily deduced. VCA corresponds to neglecting the whole second term on the right-hand side of Eq. (3). The DM result for b_e in Eq. (2) can be obtained from Eq. (7) by setting $\delta_v^2 = \delta_c^2 = \delta^2$, and $\operatorname{Re}F_v = -\operatorname{Re}F_c = 1/2A$. Thus, the more complete CPA expressions contain the VCA and DM results as special cases.

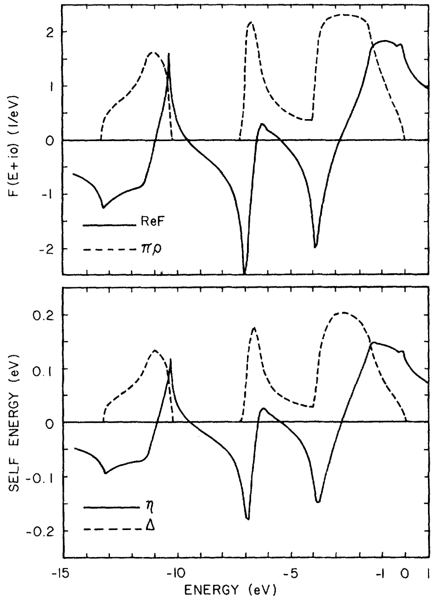

FIG. 1. The CPA alloy Green's function $F(E+i0) \equiv \operatorname{Re}F - i\pi\rho(E)$ (top panel) and the self-energy $\Sigma(E+i0) - \epsilon \equiv \eta(E) - i\Delta(E)$ (lower panel) as a function of energy E (in eV relative to the top of the valence band of InAs) for the $\mathrm{Ga_{0.5}In_{0.5}As}$ alloy obtained in Ref. 10.

As a first step toward numerical prediction of the properties of the semiconductor alloys we carried out a CPA calculation for the valence bands of the III-V compound alloys starting from the bond-orbital model (BOM).[14-16] The details will be presented elsewhere.[10] Here we describe only those results that are related to the present discussion. The BOM calculation is a tight-binding method in which the effect of the potentials is contained in a few energies characterizing the electron bonding states and the hopping among these states. For this kind of calculation, the main advantage of the BOM compared to usual tight-binding calculations based on atomic states is that in the BOM there is a natural division between large and small terms. The most important effect of disorder in a III-V compound alloy like $\mathrm{Ga_xIn_{1-x}As}$ is found to arise from the difference between the bond energies of the constituents (i.e., the energy difference between Ga-As and In-As bonds). The difference between the corresponding hopping energies of the constituents is much smaller in most cases. If the bond energies are treated in CPA, while VCA is used for the rest of the BOM parameters, then the 4×4 matrix equation for the self-energy reduces to a scalar equation like Eq. (3). In the modified equation F is replaced by $F/4$, and $\rho(E)$ in Eq. (4) is the total density of states of the four valence bands. To examine the validity of the expressions in Eqs. (5) and (6), we plot in Fig. 1 on the same energy scale the F function (the tope panel), and the difference $\Sigma - \epsilon \equiv \eta - i\Delta$ for the $\mathrm{Ga_{0.5}In_{0.5}As}$ alloy. This is the system with the largest scattering strength among the six III-V compound alloys studied. The fact that the signs and shapes of η and ReF and of Δ and ρ are in reasonable agreement shows that expressions like Eqs. (5) and (6) are good approximations for the III-V compound alloys. Note that the broadening Δ at the top of the valence band becomes negligible as we mentioned earlier.

Since the broadening energy Δ is small compared to the bandwidth throughout the entire valence band, the CPA band energies E corresponding to the VCA band energies $\epsilon_n(\vec{k})$ can be found by solving the equation $E - \epsilon_n(\vec{k}) - n(k) = 0$. Figure 2 shows the concentration dependence of the photoelectric thresholds,[17] i.e., the energy difference between the vacuum level and Γ_{15} for the six III-V alloys studied. All the CPA values, denoted by crosses, fall below the average values. Since the VCA in our calculation uses the average Hamiltonian, the bowing shown in the figure results entirely from the disorder contribution to the Γ_{15} level. This bowing alone contributes a b value of 0.48 eV for the total bowing constant quoted[2] for E_0. Since the BOM parameters in our study were deduced by fitting the broadened density of states of the pure compounds to x-ray valence-band spectra,[18] they suffer some uncertainties. Also, if potential renormalization to account for charge redistribution among the ions and lattice-constant changes in the alloy relative to the pure materials are included in the VCA averaging procedure then there are some nonlinear contributions to the gap variation even in VCA.[2,3] Thus the Γ_{15} levels shown in Fig. 2 are only qualitatively correct. Nevertheless, the indication here is that alloy disorder can contribute significantly to the bowing effect. In this connection, work by Berolo *et al.*[19] and the recent work by Chadi[20] also show that disorder is the dominant mechanism causing the bowing of the spin-orbiting splittings.

We note that while Δ at the band edges is small, it is not small inside the band (it can be as large as 0.2 eV in Fig. 1), so these states are short lived. This will have a profound effect on hot-electron and hole transport phenomena. In particular, it can be expected to have an adverse effect on the efficiency of solar cells constructed from alloys and operated under high-concentration conditions. To access the seriousness of these effects, a more detailed calculation is needed that includes the conduction bands and phonon scattering.

In summary, the present CPA valence-band calculation using BOM shows that alloy disorder makes an important contribution to the energy-gap variation. However, our conclusion that disorder produces a positive bowing parameter of the gap E_0, but causes very little broadening, is a general CPA result and is independent of the band model used. We emphasize that CPA is a more complete theory than those used previously. The earlier theories such as VCA,[2] DM,[3] and other perturbation approaches[19,20] are lower-order approximations to CPA. While the present work provides a qualitative understanding of the gap E_0, we believe that a systematic CPA study using a better band model[21] which properly deals with both conduction and valence bands and the spin-orbit interaction will result in a qualitative description of the electronic structure of semiconductor alloys.

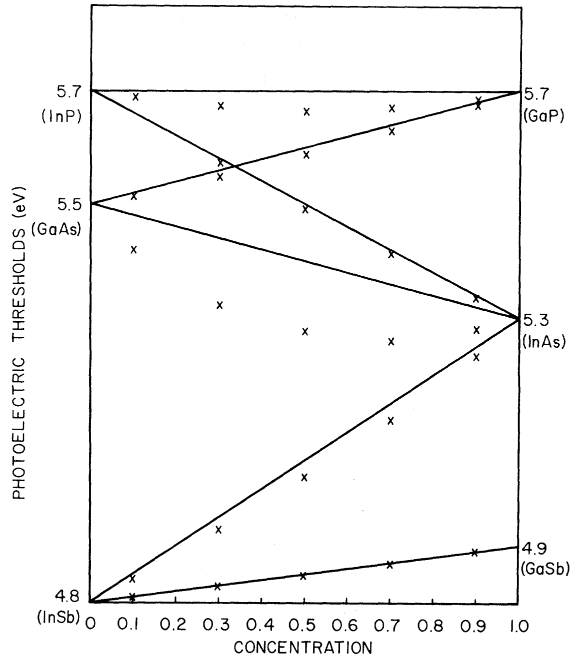

FIG. 2. The photoelectric thresholds (in eV) for the III-V compound alloys as a function of concentration. The crosses are the CPA results from Ref. 10 and the straight lines are the linear interpolations between the values of the pure crystals (Ref. 16).

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Anomalous Dimensionalities in the Spin-Glass Problem

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Arguments are given that the spin-glass problem has lower critical dimensionalities (below which no transition takes place) of 3 for vector spin-glasses and $\geqslant 2$ for Ising spin-glasses. Thus for vector spin-glasses, the physical case is also at lower critical dimensionality, which is relevant to the peculiar behavior observed in classical spin-glass alloys.

The treatment by Harris, Lubensky, and Chen[1] of the Edwards-Anderson[2] replica theory suggests that the upper critical dimensionality of the spin-glass system (the dimensionality at which mean-field theory fails) is 6, not 4 as it is in most conventional phase transitions. Young[3] has, by real-space renormalization methods, suggested a lower critical dimensionality (lcd, below which order disappears) of around 2 for the Ising spin-glass, and one of the present authors has adapted the Harris-Lubensky-Chen treatment to suggest an lcd of 3 for the vector-spin-glass case.[4] In our opinion, the experimental data[5] on Heisenberg glasses in three dimensions strongly suggests that this system is at, or close to, lcd, and may even have a line of critical points ending at $T=0$ like the 2D (two-dimensional) XY model and the 1D r^{-2} Ising model. (The evidence for this is the so-called "clustering" phenomena, clearly involving the weak dipolar anisotropy, which should not strongly affect an ordered system far from criticality and yet does so nonetheless over a wide range of temperature. A second point is that a magnetic field destroys the critical point as it does in a ferromagnet; yet at $H=0$ there is no evidence of a true two-phase region —rather the line $H=0$, $T<T_c$ seems more like a region of anomalous fluctuations.)

We try first to give strong plausibility arguments based on a version of real-space scaling that the lower critical dimensionality is 3 for the vector spin-glass.

First, let us define the order parameter we shall use for a vector spin-glass. While it is not certain, especially at low dimensionality, that a spin-glass has a unique ground-state configuration, Walker and Walstedt[6] have noted that, according to their computations, in local regions