Critical Analysis of the Virtual Crystal Approximation

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We investigate the validity and limitations of the Virtual Crystal Approximation (VCA), widely and successfully adopted to describe random semiconductor alloys. Calculations are performed within the tight-binding approximation using ensembles of supercells, each cell containing up to 4000 atoms with periodic boundary conditions. Two simple problems are studied in this context. First we consider a single quantum well of GaAs, with width W, confined by $Al_xGa_{1-x}As$ barriers. Calculation of electron energies shows quantitative discrepancies when compared to VCA results. The second problem regards bulk $Al_xGa_{1-x}As$. We perform a spectral decomposition of the main gap wavefunctions determined through tight-binding supercell calculations. The amount of zinc-blende symmetry character in the wavefunctions of direct and indirect gap structures is extracted and compared to the VCA predictions. In this case, a qualitative agreement is obtained.

I GaAlAs/GaAs/GaAlAs Quantum Wells

The recent progress in powerful crystal growth techniques, such as the molecular beam epitaxy (MBE) and the metal-organic chemical vapor deposition (MOCVD), has allowed the growth of semiconductors of different atomic compositions on top of other semiconductor substrates, with monolayer precision.

We consider a GaAs quantum well of width W between $Al_xGa_{1-x}As$ (for $x < 0.4$) barriers, grown along the z direction. This is an example of a system with only direct-band gap constituents. For the x-y plane there is no quantum confinement and the carriers can move freely. In this type of quantum well (type-I) the energy difference between the larger band gap of the barriers and the smaller band gap of the well material causes a confinement potential both for the electrons in the conduction band and for the holes in the valence band.

A powerful theoretical approach to determine the electronic structure of this system is the so called Envelope-Function Approximation (EFA), developed by Bastard and collaborators[1]. The energy of the electronic (conduction) states (E_C) may be obtained in a single band model which consists of solving a Schroedinger-like one-dimensional equation:

$$[-\frac{\hbar^2}{2}\frac{\partial}{\partial z}\frac{1}{m^*(z)}\frac{\partial}{\partial z} + V(z)]\Psi(z) = E_C\Psi(z) \qquad (1)$$

where $V(z)$ is the attractive quantum well potential:

$$V(z) = \begin{cases} 0 & for \quad |z| < W/2 \\ V_C & for \quad |z| > W/2, \end{cases} \qquad (2)$$

where V_C is the conduction-band offset. In eq.(1), $m^*(z)$ is an effective mass which characterizes the different materials, and is assumed to have the same value as the corresponding bulk materials, and $\Psi(z)$ is the envelope-function. The alloy region in the envelope function approach is treated within the Virtual Crystal Approximation (VCA). Though an alloy has no translational invariance, the VCA recovers it by replacing the potential by a periodic one which is produced by "average" atoms. For an alloy $Al_xGa_{1-x}As$ the potential is approximated by $U_{VCA}(\vec{r}) = xU_{AlAs}(\vec{r}) + (1-x)U_{GaAs}(\vec{r})$, which is periodic. The form of equation (1) implies that the adopted boundary condition at the GaAs/GaAlAs interface is the continuity of $\Psi(z)$ and of $\frac{1}{m^*}(\frac{\partial}{\partial z})\Psi(z)$. This point has been questioned in the literature [2].

Thus, in the envelope function scheme, the presence of different materials along the z direction reflects in the electrons as if they moved through a continuous medium with variable effective mass $m^*(z)$ and subject to an external potential $V(z)$.

An alternative approach, based on the tight-binding approximation, allows atomic-scale description of the different materials. We adopt a tight-binding supercell formalism. This formalism also allows a realistic treatment of the disorder in the alloy region [3]. We use tetragonal cells with dimensions $N_x = N_y (= N_{||})$ and N_z. Periodic boundary conditions are imposed and for each W the value of N_z is taken sufficiently large to guarantee convergence of the calculated electronic properties to the infinitely wide GaAlAs separators situations. Specific atomic configurations are generated numerically according to the occupational probabilities of the sites of the group-III: $P(Al) = 1 - P(Ga) = x$. A good description of the atomic distribution in the (001) planes is obtained for $N_{||}$=8 ML (1 ML = 2.85 Å, i.e., half of the conventional cubic lattice constant), and for the largest W value considered here, convergence requires N_z=70 ML, which corresponds to cells with 4480 atoms. The tight-binding parameters were taken from Ref.[4] with the zero energy level at E_C^Γ(GaAs) and a negative band offset correction to the diagonal matrix elements of AlAs of 0.47 eV. It should be noted that previous treatments of heterostructures using the tight-binding approximation [5] describe the alloy region in the VCA. In this case the Hamiltonian matrix elements are averaged according to the corresponding species composition.

In order to compare the tight-binding results with those obtained within the envelope function approach, we use for m^* and V_C the values obtained in our tigth-binding parametrization for these quantities. The conduction band is nearly parabolic around the Γ point of the Brillouin zone ($\vec{k} = 0$), therefore the electrons are well described by a single effective mass m^*_Γ(GaAs). Furthermore, the barrier is determined by the conduction-band minimum in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$, which is also at the Γ point. Thus the tunneling states, through which electrons with energy E_C can traverse the barrier region, are characterized by an imaginary wave vector $k = i\kappa$, where κ is determined by the tunneling-barrier height $E_C^\Gamma(\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}) - E_C$. Following the VCA scheme:

$$\begin{aligned}
E_C^\Gamma(\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}) &= xE_C^\Gamma(\mathrm{AlAs}) + (1-x)E_C^\Gamma(\mathrm{GaAs}), \\
m^*_\Gamma(\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}) &= x\, m^*_\Gamma(\mathrm{AlAs}) + (1-x)\, m^*_\Gamma(\mathrm{GaAs}) \quad \text{and} \\
V_C = x\,[E_C^\Gamma(\mathrm{AlAs}) &- E_C^\Gamma(\mathrm{GaAs}) - \text{offset}] = 1.02\,x \text{ eV}.
\end{aligned}$$

Fig. 1 compares the electron energies of the single band envelope function model (hexagons) with those of the full tight-binding supercell method (squares), as a function of the GaAs well width when surrounded by barriers of $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ for $x = 0.2$ and 0.3 respectively. Tight-binding results with the alloy region treated within the VCA are given by the triangles.

The energy values for $W = 0$ represent V_C defined in (2) for the EFA, which is about 100 meV above the full tight-binding energy. For narrow wells the full tight-binding results for the energy are consistently lower than the envelope function ones, differing by about 80 meV for widths of 2 ML for x=0.2 and by about 100 meV for x=0.3, as we can see in Fig. 1. As W increases, the results from both methods approach, and they converge faster for the larger x. For $x = 0.2$, agreement within 5meV is obtained only for well widths W above 80 Å, while a similar agreement for $x = 0.3$ is already achieved for W =60 Å. So, as x increases, the narrow well region difference in energy increases while in the wide W region the agreement between the EFA and tight-binding results improves. This apparently contradictory result is attributed to the difference of barriers height in the two cases. The barrier height increases with x. Consequently, as illustrated in Fig. 2 for W = 40Å, the wave function is more localized in the well (GaAs) region for $x = 0.3$ than for $x = 0.2$. Therefore the effects of disorder in the alloy region become less relevant as x increases. Note that in Fig. 1 the agreement between the TB-VCA and the EFA covers essentially the whole range of W values. Also, in Fig. 2, the wavefunctions for EFA and tight-binding VCA are in excellent agreement and are both more localized in the well than the full tight-binding one. We conclude that, among the approximations underlying the envelope function approach, the treatment of the alloy disorder within the VCA is responsible for the largest discrepancy obtained in the narrow well limit. Barriers described within the VCA lead to higher energies, i.e., states more localized in the well region than when different atomic species are considered in the alloy region. This indicates that the VCA produces effectively higher barriers for the alloy than the actual disordered atomic potential. Another indication of this localization effect is the narrower superlattices mini-band widths obtained in the EFA. For a 40 Å(GaAs) /20 Å(AlGaAs) superlattice with $x = 0.3$, the band width calculated within the EFA is 32 meV, while the full tight-binding result is 55 meV.

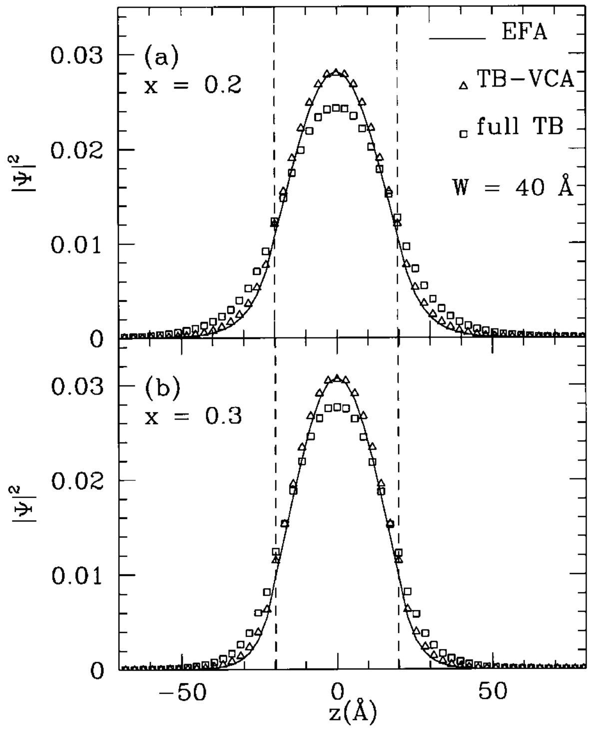

Figure 1. Energy of the first electron state in a GaAs quantum well confined between $Al_xGa_{1-x}As$ barriers as a function of the well width W for the indicated values of x. Results of calculations using the envelope function approximation.

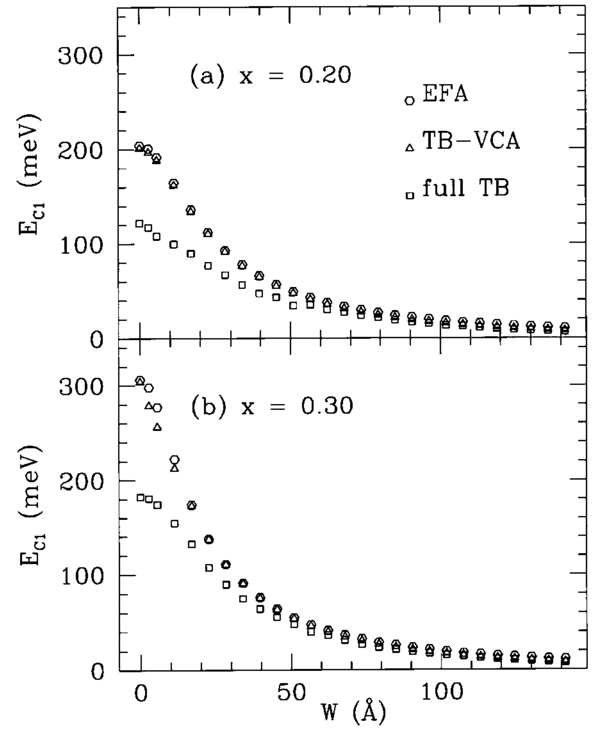

Figure 2. Envelope function squared of the first electron state in a GaAs quantum well confined between $Al_xGa_{1-x}As$ barriers for well width $W = 40$Åand for the indicated values of x. Results of calculations using the envelope function.

II Spectral decomposition of alloy wavefunctions

$Al_xGa_{1-x}As$ alloys are characterized by a critical concentration x_c that determines the crossover from a direct band-gap semiconductor ($x < x_c$) to an indirect band-gap semiconductor ($x > x_c$). The usual criterion for this transition described in the literature relies in the VCA: As discussed above, although an alloy has no translational invariance, zinc-blende symmetry is recovered within the VCA. In this approach the top of the valence band is always a Γ point and the direct-to-indirect crossover is identified with a Γ - X transition in the conduction band wavefunction symmetry. However, this rule is not strictly applicable to disordered alloys, since these systems do not have translational symmetry and therefore $\vec{k}$ is not a good quantum number.

Using finite-size scaling techniques in supercells, Koiller and Capaz [3] have recently shown that this crossover is analogous to a first-order phase transition, in the sense that it produces a discontinuous change in some "order parameter" [6]. This result, which was obtained using only real-space techniques, is consistent with a VCA-type of transition (Γ - X crossing in reciprocal space). We know, however, that disorder should prevent an alloy wavefunction to have *purely* Γ or X symmetry. Therefore, it should be interesting to understand the reciprocal-space meaning of Koiller and Capaz results.

We perform a Fourier analysis of the band-edge wavefunctions of both direct and indirect gap structures in a large (3456 atoms) fcc supercell. The supercell consists of 12 × 12 × 12 fcc primitive cells of the zinc-blende structure. The Fourier decomposition allows us to determine the amount of zinc-blende $\vec{k}$-symmetry in those wavefunctions. The real-space wavefunctions in the tight-binding approach are defined by their expansion coefficients $c_\alpha(\vec{R})$ in the atomic orbital α ($\alpha = s, p_x, p_y, p_z, s^*$) and zinc-blende site $\vec{R}$. These coefficients are periodic in the supercell and therefore can be expressed as Fourier sums

$$c_\alpha(\vec{R}) = \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{R}} c_\alpha(\vec{k}) \ , \qquad (3)$$

where the wavevectors in the sum are only those allowed by periodic boundary conditions in the supercell. These wavevectors define a 12 × 12 × 12 grid in the Brillouin Zone.

We define an orbital-averaged "spectral weight" as

$$W(\vec{k}) = \sum_\alpha |c_\alpha(\vec{k})|^2 = \frac{1}{N} \sum_{\alpha,\vec{R},\vec{R}'} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')} c_\alpha(\vec{R}) c^*_\alpha(\vec{R}') \qquad (4)$$

which quantifies the amount of zinc-blende $\vec{k}$-symmetry character in the wavefunctions.

In Fig. 3 we plot $W(\vec{k})$ in a logarithmic scale in the plane $k_z = 0$ for different eigenstates. Fig. 3.a represents the spectral weight of the wavefunction in the top of the valence band for a direct-gap structure with x slightly below x_c. Notice that $W(\vec{k})$ is strongly concentrated at the Γ-point. In fact, 92% of the spectral weight is at $\vec{k} = 0$. The results for an indirect-gap structure with x slightly above x_c (Fig. 3.b) are practically identical. This is in surprising agreement with effective-potential predictions, i.e., the Γ symmetry of the valence-band top is almost unaffected by the disordered potential.

Fig. 3.c shows the results for the state in the bottom of the condution band for a direct-gap structure. In this case, the effect of disorder is bigger, but the Γ-point still retains most of the spectral weight (49%). The remaining weight spreads over the whole Brillouin Zone, particularly at the edges. This decrease in Γ-symmetry character is responsible for a decrease in the emission intensity of optical transitions with increasing Al concentration, although still in the direct-gap regime. This is a disorder effect that cannot be obtained within VCA. For the indirect-gap structure (Fig. 3.d), the situation changes drastically and the conduction-band wavefunction has less then 0.1% at Γ. Most of the weight spreads between the X and W points at the Brillouin Zone edges, which agrees qualitatively with VCA predictions [7].

These results, together with the finite-size scaling calculations of Koiller and Capaz, suggest the following picture for the direct-to-indirect gap transition in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$. For $x = 0$, we have pure GaAs, and the strong intensity in optical transitions is due to the perfect Γ-symmetry of both valence and conduction band edge wavefunctions. Increasing x up to x very near but below x_c will decrease the Γ character of the wavefunctions, specially for the conduction band. The wavefunctions will, however, retain a significant amount of Γ-symmetry that will provide a strong dipole moment for the band-to-band transition. When x is increased beyond the critical composition x_c, the spectral weight at Γ for the conduction-band state suddenly drops to zero, and the gap will become indirect.

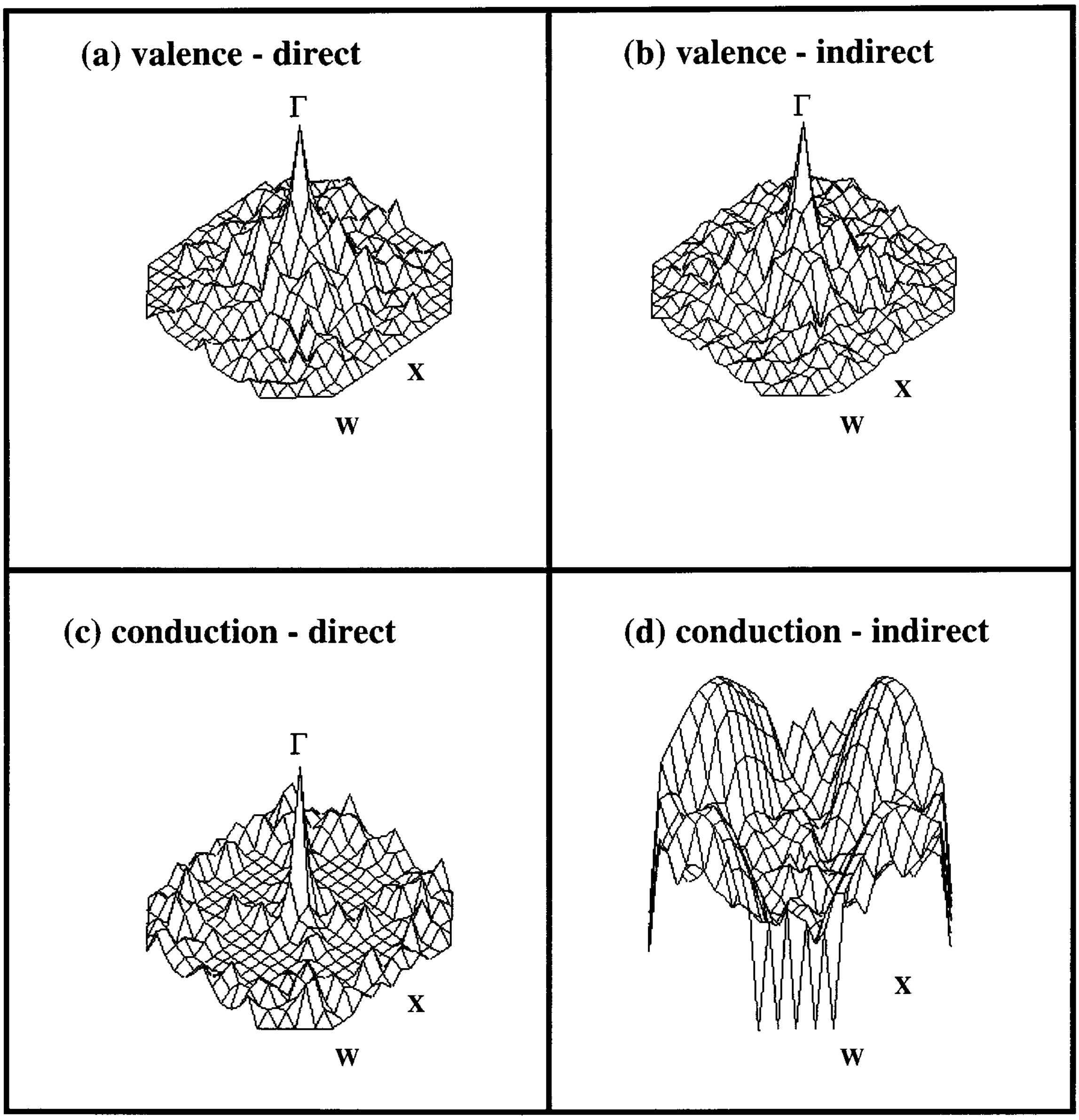

Figure 3. Logarithm of the spectral weight ln $W(\vec{k})$ in the plane $k_z = 0$ for the indicated states. The plot scales vary from: (a) a minimum of -16.0 to a maximum of -0.07. (b) a minimum of -16.0 to a maximum of -0.09. (c) a minimum of -11.0 to a maximum of -0.64.(d) a minimum of -18.0 to a maximum of -5.4.

III Conclusions

We have addressed two problems that show some of the limitations of VCA in describing electronic properties of disordered semiconductor alloys. First, we used a tight-binding supercell approach for describing the energy spectrum and wavefunctions of first electron state in narrow quantum wells. The calculation in the tight-binding model and in the envelope-function model were compared using as an example the $Al_xGa_{1-x}As/GaAs/Al_xGa_{1-x}As$ quantum wells. A good agreement between the models was found for wells whose width is larger than 80 Å(x=0.2) and larger than 60 Å(x=0.3). We observe that the discrepancy between the theories increases for decreasing well width. This is attributed to a steady decrease of the applicability of VCA in the alloy region of narrow quantum well structures.

In the second problem, we investigated the nature of the band-edge wavefunctions in $Al_xGa_{1-x}As$. Our results suggest that the symmetry of the wavefunctions is, to a good approximation, preserved in these disordered alloys. This result is qualitatively the same as the VCA prediction. From this point of view, the effective-potential picture remains valid for understanding the nature of the transition, even though certain details (such as the decrease of Γ character by increasing x in the direct-gap regime) cannot be described by VCA. Moreover, the value of x_c obtained in VCA is also in discrepancy with calculations involving a more realistic treatment of disorder [3], which suggests that VCA should be used with care when a quantitative description of the electronic properties of semiconductor alloys is desired.

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[6] The order parameter was conveniently chosen to be the dipole moment squared of the optical transition between band edges. When properly normalized, this quantity varies from 1 (order) for direct-gap GaAs to 0 (disorder) for indirect-gap AlAs.

[7] The tight-binding parametrization adopted produces a degeneracy along the X-W line for both GaAs and AlAs.