Magnitude and size scaling of intervalley coupling in semiconductor alloys and superlattices

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Coupling between different G, X, and L band-structure valleys is responsible for ~a! level anticrossing in superlattices as a function of period, pressure, and electric field and for ~b! ''optical bowing'' of band gaps in random alloys. We investigate the symmetry, magnitude, and size scaling of intervalley coupling in semiconductor superlattices and alloys by direct supercell calculations, performed with screened pseudopotentials and a plane-wave basis, considering up to 10^6 atoms/supercell. Projecting the calculated electronic wave functions c_i of alloys or superlattices onto the bulk states of the constituent zinc-blende materials shows that c_i contain a ''majority representation'' from one or more zinc-blende states g. The intervalley coupling $E(i,j)$ between the alloy states c_i and c_j then includes a term $2F(g,g\delta)V(g,g\delta)$ due to the ''majority representations'' g and $g\delta$ of c_i and

was calculated via a plane-wave screened pseudopotential method using a ; 33 000 atom cubic supercell ~see Sec. III!. It is then projected onto a set of virtual-crystal-approximation ~VCA! zinc-blende Bloch functions $f_{m,k}^{\mathrm{VCA}}(r)$:

$$c^{\sim i!}\sim r!=\sum_{m,k} A_{m,k}^{\sim i!} f_{m,k}^{\mathrm{VCA}}\sim r!, \qquad \sim 1!$$

where k is the reciprocal vector of the supercell within the zinc-blende Brillouin zone and m is the band index. The amplitude $P_k^{\mathrm{CBM}}=(_m\Vert A_{m,k}^{\mathrm{CBM}}\Vert^2$ is shown in Fig. 2~a! vs the k points of the supercell. As we can see, a single zinc-blende component $k=\Gamma$ contributes 90% of the total weight of the alloy CBM wave function. Further analysis shows that the weight on $k=\Gamma$ comes mainly from a single zinc-blende VCA state Γ_{1c}. The 10% minority contribution of other k points @mostly from the L point in Fig. 2~a!# results from intervalley coupling. Although small, these minority P_k^{CBM} components contribute significantly to the optical bowing ~a nonlinear dependence of the alloy eigenvalues on composition! in this system.[8,9]

We are interested here in establishing ~i! the existence or absence of intervalley coupling $E(g,g\delta)$ between given states g and $g\delta$, ~ii! the magnitude of the coupling, and ~iii! its scaling with the systems size. Regarding item ~i!, i.e., the *existence or absence* of intervalley coupling, this is often discussed in the literature by considering the overall symmetry of the composite system.[10,11] This type of analysis can be used, for example, to explain[10] why the Γ_{1c}-X_{1c} anticrossing gap is zero for odd n ~Fig. 1!, while the anticrossing gap for Γ_{1c}-X_{3c} is zero for even n. But the applicability of the symmetry-based analysis is limited to highly symmetric composite systems. In many cases, such as the alloy system illustrated in Fig. 2~a!, the overall symmetry is too low to be useful in this respect. Regarding ~ii!, the *magnitude and scaling* of intervalley coupling is important for understanding optical bowing in alloys,[8,9] the indirect optical transition without phonon interaction,[1,12] the resonant intervalley tunneling in quantum well electron transmission,[13] and the characteristic pressure-induced changes of photoluminescence.[14,2] Regarding ~iii!, the size scaling of $E(g,g\delta)$ is related to the order of the transition from direct to indirect

The first term is limited to the neighborhood dk of k_0 and gives the ''majority representation.'' dk equals zero for alloys ~Fig. 2!, but includes a few points for superlattices ~Fig. 3!. We will use $g=(n_0,k_0)$ to denote the constituent basis function at the center of the majority representation.

The anticrossing gap $E(g,g8)$ between the states $c^{(i)}$ @with a majority contribution g

entire intervalley coupling between the states of Eq. ~10! originates from the minority representation of the wave functions. On the other hand, for other pairs of states, we have a nonzero majority contribution to the coupling @provided that the overlap factor $F(g,g8)$ is not zero#.

In the remainder of this paper, we will show that we can distinguish two main types of intervalley couplings:

~i! *Large majority contribution in alloy (''strong coupling''):* This is the coupling between the ''VCA-allowed pairs'' @e.g., Γ_{1c}-X_{3c}, Γ_{1c}-L_{1c}, X_{1c}-L_{1c}, X_{1c}-L_{3c}, and X^{x}_{3c}-X^{y}_{3c} which are not in Eq. ~10!#. We will see that, in alloys, where the coupling states are extended and have a large overlap $F(g,g8)$, the majority term alone, using the model potential, can explain the full coupling quantitatively. The full coupling will be calculated by a direct diagonalization technique ~see Sec. III!, while the model coupling will be represented by the leading terms of Eqs. ~5!–~10!. Evaluating the structure factor $S(k_0-k8)$ using the random distribution of A atoms in Eq. ~7!, we have

$$E^{\text{alloy}}_{\text{maj}}(g,g8) = 2F(g,g8)V(g,g8) > 2S(k_0-k8)V(g,g8) = A\sqrt{\frac{8x(1-x)}{N}}\,V(g,g8)$$

We use

where $V(r,nk)$ is just the $V(g,g\delta)$ of Eq. ~8!. This second-order perturbation in eigenenergy corresponds to the first-order perturbation in wave function of Eq. ~15!. If we neglect the intervalley coupling, i.e., if we use only the majority representation state g as the alloy wave function, we obtain $b_{\mathrm{tot}}=b_{\mathrm{VCA}}$. In the case of $\mathrm{Ga}_x\mathrm{Al}_{1-x}\mathrm{As}$, we find that $b_{\mathrm{VCA}}=-0.38$ eV for the G_{1c}-G_{15v} energy gap, while the experimental result is $b_{\mathrm{tot}}^{\mathrm{expt}}=0.37$ eV.[26] This large discrepancy is due to $b_{\mathrm{coupl}}=b_{\mathrm{tot}}-b_{\mathrm{VCA}}$. In our current supercell calculation, $b_{\mathrm{tot}}=0.45$ eV,[20] which is close to the experimental result. The large difference $b_{\mathrm{VCA}}-b_{\mathrm{tot}}$ comes mainly from intervalley couplings in the conduction band. If we separate the band gap b_{tot} into $b_{\mathrm{CBM}}-b_{\mathrm{VBM}}$, we find that

$$b_{\mathrm{VBM}}=-0.05, \quad b_{\mathrm{CBM}}=-0.43: \ \text{VCA},$$

b

contribution, we compare in Fig. 5 the directly calculated Γ_{1c}-X_{3c} anticrossing gap with the results obtained using the single-k-point coupling of Eq. ~9!. In the alloy, this single-k-point coupling represented the majority contribution term, and thus agreed well with the directly calculated results ~Fig. 4!. But in superlattices, the single-k-point result is much larger ~5–100 times! than the directly calculated results. Furthermore, while the results of the single-k-point coupling scale in superlattice as $1/n$, where n is the superlattice period, our directly calculated Γ_{1c}-X_{3c} and Γ_{1c}-X_{1c} couplings scale as $1/n^3$. We find that these differences are due to the localization of the superlattice states $c^{(i)}$ and $c^{(j)}$. As a result, the extended single-k-point VCA states f_g^{VCA} and

square ~rms! value for the LDA results is 0.11 meV. On the other hand, the values at the lower half of Table I ~case II! are not predicted to be zero by symmetry; they have a rms value of 84 meV, about 1000 times larger than the values of case I. So, the violation of the superposition assumption @Eq. ~4!# due to the self-consistent potential is very small, only 0.1% as measured by the $\Delta f_g^{\mathrm{VCA}} V f_g^{\mathrm{VCA}}$ values.

B. Effects of atomic relaxation on superposition assumption

As we see above, the self-consistent LDA potential does not violate Eq. ~4! very much. Thus, here we will use the EPM to generate the total potential $V(\mathbf{r};N_A,N_B)$. We calculated an $In_{0.5}Ga_{0.5}As$ 64-atom supercell with the same substitutional configuration as the above $Ga_{0.5}Al_{0.5}As$ system (Ga→In, Al→Ga!. We used valence-force-field ~VFF! ~Ref. 28! method to relax the atomic positions. The fully relaxed atomic positions have average displacements of 0.13 Å for anions, and 0.05 Å for cations. Note that although the total potential can be written as a summation of the atomic screened potentials as in Eq. ~13!, Eq. ~4! which uses unrelaxed ideal position $\mathbf{R}_\mathbf{A}^\mathbf{0}$ @instead of the relaxed position

the selection rule of Eq.