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Electronic structure of ultrathin (GaAs), (AlAs), [001] superlattices and the $Ga_{0.5}AI_{0.5}As$ alloy

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Using self-consistent electronic structure calculations we contrast the energy levels of the ultrathin (GaAs)_n (AlAs)_n [001] superlattices (n = 1,2) with those of the disordered Ga_{0.5} Al_{0.5} As alloy and a long period ($n \to \infty$) superlattice. Conventional Kronig-Penney and effective mass models suggest that, because of the relatively light electron effective masses and small barrier heights, only delocalized superlattice conduction states would exist in the n = 1 limit. We find a number of such conventional "averaging states" (delocalized on both sublattices). In addition, we also find states localized on a single sublattice. For small n's, the latter are divided into two classes: (i) "repelling states" (distinct alloy states which fold in the superlattice into states of identical symmetry, which, in turn, repel each other and tend to localize), and (ii) "segregating states" (a pair of localized states Ψ^{α} and Ψ^{β} , where symmetry compels Ψ^{α} to have a vanishing angular momentum component I on a subset α of unit cell atoms, whereas the complementary state Ψ^{β} is localized on the other atoms β . These states are split by the potential difference $V_{I}^{\beta} - V_{I}^{\alpha}$). We analyze new luminescence, reflectance, and Raman data in light of our theoretical model. Studies of the II-VI superlattices (CdTe)₁(HgTe)₁ shows similar behavior.

I. INTRODUCTION

Recent advances in atomic-scale control over nucleation and growth made possible the synthesis of alternate ultrathin superlattices $(AC)_n (BC)_n$ with a substantial degree of crystallographic perfection.¹⁻³ This development, together with the recent predictions⁴ and observation⁵⁻⁸ of sponta*neous* ordering of an homogeneous $A_{0.5}B_{0.5}C$ semiconductor alloy, have raised the question of whether such ordered superlattice phases have a new electronic structure⁹ or are essentially identical to the alloy.¹⁰ Recent self-consistent electronic structure calculations on the (GaAs), (AlAs), superlattice¹¹⁻²⁴ and the Ga_{0.5}Al_{0.5}As alloy,^{18,25,26} coupled with experiments characterizing the superlattice^{10,23,24,27-30} and the alloy,³¹⁻³⁴ permit assessment of this issue. In this paper, we theoretically describe the way in which the energy levels of ultrathin superlattices differ from those of: (i) a disordered alloy of the same 50%-50% composition, (ii) the average energies of the binary constituents, and (iii) the energy levels of a thick, $n \rightarrow \infty$ superlattice, i.e., a single interface between two semi-infinite slabs of AC and BC. We then analyze the recent experimental data on (GaAs), (AlAs), in light of our predictions. Extension of our calculations to superlattices of II-VI compounds shows that the same theoretical principles apply.

II. METHOD OF CALCULATIONS

We have performed self-consistent band structure and total energy calculations for GaAs, AlAs, and the [001]oriented (GaAs)_n(AlAs)_n superlattice (n = 1,2) within the local density approximation (LDA),³⁵ using the first principles, all electron, general potential LAPW (linearized augmented plane wave) method.³⁶ Minimization of the total energy with respect to the unit cell volume yields for GaAs and AlAs equilibrium lattice parameters, bulk moduli, and cohesive energies in good accord with experiment (Table I), given that the only input was the atomic numbers. In contrast, excited-state properties, such as band gaps, are systematically underestimated^{37,38} by the LDA (Table I). Since we are interested in understanding the changes in the spectra of the superlattice and the alloy with respect to those of the constituent binary compounds, it is essential that all systems be treated on an equal footing. We have therefore identified, for each superlattice level, the proportion of GaAs and AlAs character in its wave function, and shifted the calculated superlattice energy level by the weighted average of the errors of the corresponding states in bulk GaAs and AlAs (Table I). Since LDA errors are rather similar for a given state in GaAs and AlAs (Table I), this procedure is expected to introduce only a small uncertainty in the LDA corrected energy levels. Throughout this work we use the measured low-temperature band gaps; extrapolation to room-temperature gaps can readily be performed using the measured temperature coefficients.³⁹ For the energy of the L_{1c} state of AlAs we use the recently revised value.³⁷

The superlattice energy levels were calculated for n = 1in two geometries. First, given the small experimental difference between the lattice parameters of GaAs and AlAs (Table I), we computed the superlattice energy levels at the average of the two (experimental) lattice parameters of GaAs and AlAs, i.e., $\bar{a} = 5.6569$ Å, assuming an equal bond geometry $R(\text{Ga-As}) = R(\text{Al-As}) = (\sqrt{3}/4)\overline{a}$ length = 2.4495 Å. Second, to see how a tetragonal distortion affects the superlattice energy levels, we have minimized the elastic energy of the superlattice¹⁸ (using the LAPW calculated equilibrium bond lengths of AlAs and GaAs and experimental bond bending and bond stretching force constraints), finding at equilibrium a = 5.6569 Å, c = 5.6922Å, R(Ga-As) = 2.4590 Å, and R(Al-As) = 2.4502 Å. At this relaxed geometry, a LAPW calculation of the superlat-

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FIG. 1. Energy level diagram of GaAs-AlAs system: (a) states of buik GaAs and AlAs at the X and Γ point with respect to their respective valence-band maxima at Γ_{15v} ; (b) states of the Ga_{0.5} Al_{0.5} As alloy also with respect to Γ_{15v} ; (c) calculated states of the (GaAs)₁(AlAs)₁ superlattice; and (d) same as (a) but showing the bulk energy levels on an absolute energy scale obtained by shifting the GaAs levels upward by $\frac{1}{2}\Delta E_v$ and that of AlAs downwards by the same amount, where ΔE_v is the valence-band offset. Angular brackets in (d) denote the centers of the potential wells.

tice energy levels was performed. As we will see below (Table IV), the maximum difference in energy levels for n = 1 between these two geometries is 0.06 eV.

III. ALLOY ENERGY LEVELS

The energy gap $E_g^{(i)}(x)$ for state *i* of the $A_x B_{1-x} C$ alloy is related to the concentration (x) weighted average of the energies of the binary constituents $E_g^{(i)}(AC)$ and $E_g^{(i)}(BC)$ through the bowing parameter $b^{(i)}$

$$E_{g}^{(i)}(x) = x E_{g}^{(i)}(AC) + (1-x) E_{g}^{(i)}(BC) - b^{(i)} x (1-x).$$
(1)

We obtain $E_g^{(1)}(\text{Ga}_{0.5}\text{Al}_{0.5}\text{As})$ using the low-temperature data for $E_g^{(1)}(\text{AlAs})$ and $E_g^{(1)}(\text{GaAs})$ (Table I), and the measured bowing parameters³¹⁻³³ for the alloy (available at room temperature) $b(\Gamma_{1c}) = 0.37 \text{ eV}, b(X_{1c}) \simeq 0.1 \text{ eV}$, and $b(L_{1c}) = 0.055 \text{ eV}$. The bowing parameters for X_{1c} and L_{1c} agree well with our previously calculated parameters¹⁸ [also showing that $b(X_{3c}) \simeq 0$], whereas the experimental value of $b(\Gamma_{1c})$ we use here is larger than the previously calculated values^{18,25,26} for the disordered alloy. The resulting energy levels of the binary constituents and the Ga_{0.5}Al_{0.5}As alloy are shown in Figs. 1 (a) and 1 (b), respectively [see also Fig. 2(c)]. These show that at x = 0.5 the alloy conduction-band minimum is near X_{1c} , where X_{1c} is at an energy E_v $+ (2.10 \pm 0.05) \text{ eV}$, followed by the Γ_{1c} state at E_v $+ (2.22 \pm 0.02)$ and L_{1c} at $E_v + (2.40 \pm 0.1) \text{ eV}$, while X_{3c} is at a yet higher energy, at $\sim E_v + 2.65 \text{ eV}$.

The X_{1c} energy is close to the observed bound exciton emission energy near x = 0.5 (2.077 eV at^{30,34} 2 K). The long nonexponential decay lifetime and the occurrence of two (GaAs and AlAs) longitudinal optical (LO) phonon



FIG. 2. Energy level diagram of GaAs-AlAs system for the k points \overline{M} and \overline{R} away from the center of zone. (a) absolute energy levels of GaAs and AlAs; (b) (GaAs)₁(AlAs)₁; and (c) Ga_{0.5}Al_{0.5}As alloy.

S. -H. Wei and A. Zunger 5795

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side bands³⁴ substantiate the assignment of this emission to the vicinity of the X_{1c} level. The L_{1c} energy observed in reflectance and extrapolated to 0 K is at³¹ ~2.14 eV, significantly lower than our LDA corrected value¹⁸ at E_v + 2.40 eV. However, a new interpretation³⁷ suggests that the former value should be ~0.3 eV higher, in good agreement with our value.

IV. ESSENTIAL PHYSICS OF LOCALIZATION IN ULTRATHIN SUPERLATTICES

A. Potential wells

Ultrathin superlattices are not expected to follow the simple, particle-in-a-box scaling rules⁴⁰ pertinent to thicker superlattices, where confinement of a particle with effective mass m^* in an infinite well with width d raises its energy by $U_i = \pi^2 \hbar^2 / 2m_i^* d^2$. Nevertheless, it will be useful to assess actual confinement effects in thin superlattices (as obtained from our full band calculation) by contrasting our calculated energy levels with those expected for more conventional, thicker superlattices. These reference energies can be obtained by positioning the energy levels of bulk GaAs and AlAs [Fig. 1(a)] on an absolute energy scale [Fig. 1(d)], using either the recently measured⁴¹ or our calculated⁴² valence-band offset $\Delta E_v = 0.45 \pm 0.05$ eV. The valence-band maximum energy for the alloy [Fig. 1(b)] is taken at the center [denoted $\langle \Gamma_v \rangle$ in Fig. 1(d)] of Γ_{15v} (GaAs) and Γ_{15v} (AlAs). Using the conduction-band energies of Table I and ΔE_{ν} gives the conduction-band offsets $\Delta E_{c}(\Gamma_{1c})$ = 1.16 eV, $\Delta E_c(X_{3c}) = 0.24$ eV, and $\Delta E_c(L_{1c}) = 0.77$ eV (all three lower on the GaAs well), whereas for $\Delta E_c(X_{1c})$ we find an offset of 0.20 eV with minimum on the AlAs side. Figure 1(d) also indicates for Γ_{1c} , X_{1c} , and X_{3c} the centers of each potential well (in angular brackets); these are precisely the averages over the corresponding energies of the bulk constituents given in Figs. 1(a) and 2(a).

It is natural to think of the ultrathin superlattice states as resulting from folding the alloy states (in their fcc Brillouin zone) into the smaller superlattice Brillouin zone (BZ). Table II gives the folding relations for n = 1 and

TABLE I. Calculated and experimental data for conduction-band energies in eV (relative to the valence-band maximum), equilibrium lattice parameters a_{ec} (in Å), bulk moduli B (in GPa), and cohesive energy E_c (in eV) of GaAs and AlAs. The LDA energy levels are calculated at the lattice parameters 5.659 and 5.660 Å for GaAs and AlAs, respectively.

		GaAs		AlAs					
	LDA	Exptl. ^a (low T)	Diff.	Exptl. ^a LDA (low T) Diff.					
Γ_{1c}	0.241	1.52	1.28	1.838	3.13	1.29			
Xic	1.324	1.98	0.66	1.315	2.23	0.91			
X _{3c}	1.528	2.30 ^b	0.77	2.180	2.99 ^b	0.81			
L_{1c}	0.809	1.81	1.0	1.994	3.03 ^b	1.04			
a_{eq}	5.690	5.642	0.8%	5.661	5.652	0.2%			
B	76.2	75.4	1.1%	76.1	~77	-1.1%			
E_c	3.88 3.31 1		17.2%	4.33	3.81	13.6%			

* Data collected in Refs. 18 and 37.

^bCalculated in Ref. 37.

TABLE II. Folding relationships between wave vectors in the Brillouin zone of the zinc-blende (ZB) structure and the (1,1) and (2,2) superlattices⁴³ along the [001] direction (in units of $2\pi/a$).

	(1,1)	ZB
Ē	(0,0,0)	(0,0,0);(0,0,1) ΓX_z
M	(1,0,0)	(1,0,0); (1,0,1) $X_x \qquad X_y$
R	(1,1,2,2)	$(\frac{1}{2},\frac{1}{2},\frac{1}{2}); (\frac{1}{2},\frac{1}{2},\frac{3}{2})$ L L
Angeland States and A	(2,2)	ZB
Ē	(0,0,0)	$(0,0,0); (0,0,\pm\frac{1}{2}); (0,0,1)$ $\Gamma \qquad \Delta \qquad X_z$
\overline{M}	(1,0,0)	$ \begin{array}{c} (1,0,0); \ (1,0,1); \ (1,0,\pm\frac{1}{2}) \\ X_x & X_y & W \end{array} $
\overline{X}	$(\frac{1}{2},\frac{1}{2},0)$	$(\frac{1}{2},\frac{1}{2},0); (\frac{1}{2},\frac{1}{2},1); (\frac{1}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2})$

n = 2 [001]-oriented superlattices⁴³; Table III provides the correspondence relationships between these states. Within simple confinement models one could classify all superlattice states as being either "mass-delocalized states" [if m_i^* is sufficiently light to make $U_i > \Delta E_c(i)$], or "mass-localized states" [when m_i^* is sufficiently heavy and $\Delta E_c(i)$ sufficiently small to make $U_i < \Delta E_c(i)$]. Given that the potential wells have a finite height, mass-delocalized states will then have their energies near the respective well centers (much like the equivalent bulk alloy); their wave functions will extend over both sublattices. In contrast, mass-localized states will have energies intermediate between the respective well center and well edge; their wave functions will then localize preferentially on a single sublattice. Superlattices with large repeat periods and finite band offsets show at CBM only mass-localized states whose energies lie close to the respective well bottoms.

The relevance of this simple model becomes clear when one realizes that in the particular case of $(GaAs)_1(AlAs)_1$ treated here, one finds that all conduction-band masses⁴⁴ are

TABLE III. Mapping of the zinc-blende (ZB) states into superlattice states for n = 1,2. The origin of the coordinate system is on the anion site.

ZB	(1,1)	(2,2)	
Γ _{1c}	$\overline{\Gamma}_{1c}$	$\overline{\Gamma}_{1c}$	
X _{te}	\overline{M}_{5c} $\overline{\Gamma}_{4c}$	$\begin{cases} M_{1c} \\ M_{2c} \\ \overline{\Gamma}_{1c} \end{cases}$	
X3c	$\begin{cases} \overline{M}_{1c} \\ \overline{M}_{2c} \\ \overline{\Gamma}_{1c} \end{cases}$	<i>Μ</i> _{sc} Γ _{4c}	
L_{1c}	$\frac{\overline{R}_{1c}}{\overline{R}_{4c}}$	$rac{\overline{X}_{1c}}{\overline{X}_{4c}}$	

S. -H. Wei and A. Zunger 5796

sufficiently light and all barrier heights $\Delta E_c(i)$ are sufficiently small that all states shown in Fig. 1 are predicted to be mass-delocalized within this simple model. This will serve as a useful reference statement to which our actual self-consistent calculations can be compared.

Our self-consistent calculations on ultrathin superlattices do not assume any simple potential well or wave function model. As we will see below, this leads to the prediction that localization can exist even in the limit of ultrathin superlattices (and even without the presence of strain⁴⁵), although simpler models would lead to the expectation of mass-delocalized states. Before discussing the details of our results, we first point to the two physical mechanisms which we find lead to localization of nominally mass-delocalized states.

B. Physics of repelling and segregating states

First, folding of two different alloy states (α, k_1) and (β, k_2) into a given point \overline{K} in the superlattice BZ may result in superlattice states $(\lambda_1, \overline{K})$ and $(\lambda_2, \overline{K})$ of the same symmetry λ (e.g., for n = 1, the zinc-blende states Γ_{1c} and X_{3c} each yield a $\overline{\Gamma}_{1c}$ state in the superlattice, see Table III). Such states of identical symmetry will then repel each other. While we will not use perturbation theory in our calculations, this repulsion can be simply portrayed in this language: the energy shift relative to the well center is

$$\Delta E^{(n)}(\lambda_1,\lambda_2) = \pm \frac{|\langle \alpha, k_1 | \Delta V^{(n)} | \beta, k_2 \rangle|^2}{\epsilon_{\alpha}(k_1) - \epsilon_{\beta}(k_2)}, \qquad (2)$$

where $\Delta V^{(n)}(\mathbf{r})$ is the ordering potential, i.e., the difference between the potential of the $(AC)_n (BC)_n$ superlattice and that of an alloy of the same composition (this ordering potential becomes stronger if the superlattice geometry is relaxed relative to the equal bond length structure). This repulsion lowers the energy of one of the two states. Hence, even if this state was mass-delocalized in the absence of level repulsion, it could become localized due to this energy lowering. We refer to this class of states as "repulsion localized states." As the repeat period n increases, the level repulsion energy $\Delta E^{(n)}(\lambda_1,\lambda_2)$ diminishes. The reduction in level repulsion energy shifts the lower level up, and the upper level down, both approaching their respective well-center energy. [Note that as the symmetry of these folding states also changes with *n* (see Table III), $\Delta E^{(n)}(\lambda_1, \lambda_2)$ may even change sign.] A further increase of n will eventually reduce the confinement energy U, hence lower the lowest energy at \overline{K} , approaching their respective well-bottom energies proportionally to $U_i \sim 1/d^2$. Hence, level repulsion can lead to a nonmonotonic change in the superlattice energy levels with n, whereas simple confinement models inevitably lead to a monotonic trend.

Second, symmetry compatibility relationships (mapping alloy states into superlattice states, see Table III) can restrict certain wave functions to experience but a *portion* of the superlattice potential, hence induce a *symmetry enforced splitting*. A familiar example from crystal physics is the pair of zinc-blende states X_1 and X_3 , where (assuming that the origin of the coordinate system is on the anion site) the X_1 wave function has s character on the anion sublattice and p character on the cation sublattice, whereas the complementary state X_3 has p character on the anion and s character on the cation sublattice. By symmetry, X_1 has a vanishing s component on the cation sublattice and p component on the anion sublattice, whereas X_3 has a vanishing p component on the cation lattice and s component on the anion lattice. Since X_1 experiences the potential $V_s^a + V_p^c$, whereas X_3 experi-



5797 J. Appl. Phys., Vol. 63, No. 12, 15 June 1988

FIG. 3. Diagram of the evolution of the energy levels of the (GaAs)_n (AlAs)_n superlattice for n = 1, n = 2, and $n = \infty$.

ences $V_s^c + V_p^a$ (where c and a denote cation and anion, respectively), these states are split in proportion to

$$(V_s^a + V_p^c) - (V_s^c + V_p^a) = (V_s^a - V_s^c) + (V_p^c - V_p^a).$$

In elemental semiconductors (where $a \equiv c$) the two states are degenerate. The analogous example in [001] superlattices is the pair of states $\overline{R}_{1c}(L_{1c})$ and $\overline{R}_{4c}(L_{1c})$ originating from the GaAs and AlAs states L_{1c} (Table III). We refer to such a pair of states as "segregating states." One member, Ψ^{α} , of this pair has, by symmetry, a vanishing angular momentum (1) component on a subset α of unit cell atoms, whereas the second member Ψ^{β} has a zero l component on the complementary set of atoms β . The splitting between these states is proportional to $V_1^{\beta} - V_1^{\alpha}$ and depends on the superlattice period n. Segregating states could show localization (on lattices α and β) even if the effective masses and barrier heights would suggest them to be delocalized.

The significant distinction between repelling states and segregating states is that the former have the same symmetry (hence they repel), whereas the latter have different symmetries (hence, they are localized on different sublattices). Both types of states can show localization. In the absence of symmetry-induced repulsion or segregation effects we expect simple mass-delocalized ("averaging") or mass-localized behavior. Figure 1(c) shows the LDA corrected energy levels of the (1,1) superlattice at the zone center $\overline{\Gamma}$. Figure 2(b) shows the results away from $\overline{\Gamma}$ (at the \overline{M} and \overline{R} points). Figure 3 compares the results for (1,1) and (2,2) superlattices and indicates the limiting energies for a (∞, ∞) superlattice. We will next examine the nature of repelling states (Sec. V), segregating states (Sec. VI), and averaging states (Sec. VII) in $(GaAs)_n (AlAs)_n$. Overall trends are discussed in Sec. VIII, whereas Sec. IX gives extension to other superlattices.

V. SUPERLATTICE STATES AT THE ZONE CENTER: REPELLING STATES

The trends in the energies at the zone center $\overline{\Gamma}$ for $(GaAs)_n (AlAs)_n$ (n = 1,2) can be analyzed in terms of folding the Ga_{0.5}Al_{0.5}As alloy states as follows.

A. $\overline{\Gamma}_{1c}(X_c)$ and $\overline{\Gamma}_{1c}(\Gamma_{1c})$

In the (1,1) superlattice, the alloy X_{3c} state folds by symmetry into the superlattice state $\overline{\Gamma}_{1c}(X_{3c})$, while the alloy Γ_{1c} state folds into itself and becomes the superlattice $\overline{\Gamma}_{1c}(\Gamma_{1c})$ state (Table III). (We denote superlattice states by a bar and indicate in parenthesis the corresponding zincblende alloy state mapped into it.) Since these two states have the same Γ_1 symmetry, they will repel, as shown in Fig. 1(c). This repulsion lowers the energy of $\overline{\Gamma}_{1c}(\Gamma_{1c})$ below its well center by 0.15 eV (even below the alloy Γ_{1c} state by 0.04 eV), while raising the $\overline{\Gamma}_{1c}(X_{3c})$ energy relative to its well center (by 0.18 eV). It is precisely this repulsion which causes the wave function of the lower state $\overline{\Gamma}_{1c}(\Gamma_{1c})$ (mostly *s* like) to show a preferential wave function localization on the GaAs sublattice, whereas the higher energy state $\overline{\Gamma}_{1c}(X_{3c})$ (also *s* like) is localized on AlAs sublattice (see Table IV). This illustrates the mechanism for obtaining spatial localization even in the limit of monolayer superlattices through level repulsion.

As the repeat period n in $(GaAs)_n (AlAs)_n$ increases from n = 1 to n = 2, we find that the energy of $\overline{\Gamma}_{1c}(\Gamma_{1c})$ moves up (Fig. 3), increasing its weight on the AlAs sublattice (Table IV). Besides the reduced level repulsion when nincreases, this increase in energy of $\overline{\Gamma}_{1c}(\Gamma_{1c})$ is also caused by the fact that the repelling state $\overline{\Gamma}_{1c}(X_{1c})$ in n = 2 is below $\overline{\Gamma}_{1c}(\Gamma_{1c})$ (Tables III and IV). The state folded in from X_{3c} now has $\overline{\Gamma}_{4c}$ symmetry. This $\overline{\Gamma}_{4c}(X_{3c})$ state is repelled downwards by a folding $\overline{\Gamma}_{4c}(\Delta_c)$ state (not shown). For $n \ge 2$, the lowest state at $\overline{\Gamma}$ is expected to localize on the GaAs sublattice; its energy is lowered monotonically with n, approaching for $n \to \infty$ the value of the GaAs well minimum.

Hence, our calculation provides four predictions regarding the states $\overline{\Gamma}_{1c}$. First, the energy level of $\overline{\Gamma}_{1c}(\Gamma_{1c})$ will show a nonmonotonical change with n for small n. This nonmonotonicity in the energy of $\overline{\Gamma}_{1c}(\Gamma_{1c})$ will also be reflected in the E_0 transition $\overline{\Gamma}_v \to \overline{\Gamma}_{1c}$. Second, in contrast with previous results, ^{10,12} the superlattice $\overline{\Gamma}_{1c}(\Gamma_{1c})$ energy for n = 1 is predicted to be *below* the corresponding alloy Γ_{1c} level (unless the superlattice is structurally intermixed, hence partially an alloy). Third, a new pseudodirect state $\overline{\Gamma}_{1c}(X_{3c})$ for n = 1 will appear at $E_v + 2.83$ eV, above the corresponding alloy state X_{3c} at $\sim E_v + 2.65$ eV. Despite the fact that its energy is outside the corresponding X_{3c} well [Fig. 1(d)], this state is predicted to be localized (on the AlAs sublattice). For n = 2, a pseudodirect state $\overline{\Gamma}_{1c}(X_{1c})$ is calculated at $E_v + 2.02 \text{ eV}$, and is predicted to be the conduction-band minimum (see below). Fourth, the $\overline{\Gamma}_{1c}(\Gamma_{1c})$ level is predicted to be above the alloy X_{1c} level (its CBM) for small n values, but to cross it and become the overall CBM for larger *n* values (denoted "X- Γ crossing" in Fig. 3).

Experimentally the direct $\overline{\Gamma}_{1c}(\Gamma_{1c})$ superlattice state was found to be at²⁸ $E_v + 2.12$ eV (low temperature) in photoluminescence excitation spectra for $n \simeq 3$. The temperature dependence was characteristic of a direct gap; at room temperature, where $\overline{\Gamma}_{1c}(\Gamma_{1c})$ was populated, its emission nearly coincided with its photoreflectance, hence exhibiting a very small Stokes shift. Ellipsometry measurements²³ of the $\overline{\Gamma}_{v} \to \overline{\Gamma}_{1c}(\Gamma_{1c})$ (denoted as "E₀" transition) give for $n = 1 E_v + 2.08$ eV at room temperature (hence, expect about 2.18 eV at low temperatures³⁹). Our calculated value [Fig. 1(c) and Table IV] gives 2.18 eV. In agreement with our predictions, the energy of this E_0 transition was found²³ to increase in going from n = 1 to 2 (by ~0.06 eV, compared with our calculated value of 0.05 eV; Table IV), whereas for larger n's it decreases monotonically towards the GaAs value. Raman experiments at low temperatures²⁴ show a strong resonance at ~ 2.15 eV for n = 1, which we assign to $\overline{\Gamma}_{1c}(\Gamma_{1c})$. All of these values for the $\overline{\Gamma}_v \to \overline{\Gamma}_{1c}(\Gamma_{1c})$ transition energies agree well with our calculated value and further confirm the prediction that the superlattice $\overline{\Gamma}_c$ is lower than the alloy Γ_{1c} state (measured at 2.095 eV at room temperature; hence, 2.22 ± 0.02 eV at low temperature³¹⁻³³). No experimental results exist as yet for the predicted pseudodirect (hence, weak) $\overline{\Gamma}_{\mu} \rightarrow \overline{\Gamma}_{1c}(X_{3c})$ transition which we calculated at ~ 2.83 eV.

TABLE IV. Mapping of the states of the zinc-blende structure ("ZB label") into superlattice states (denoted with a bar; see Table III for notation) for $(GaAs)_n(AlAs)_n; n = 1, 2$. LDA corrected energy levels are given in eV, relative to the $\overline{\Gamma}_{sv}$ valence-band maximum; the uncertainty is ± 0.05 eV or less. For n = 1, we give the energies calculated for the relaxed structure ($R_{Ga-As} = 2.4590$ Å, $R_{Al-As} = 2.4502$ Å; a = 5.6569 Å, and c = 5.6922 Å) and for the unrelaxed structure (a = c = 5.6569 Å, $R_{Ga-As} = R_{Al-As} = 2.4495$ Å). For n = 2, we use the unrelaxed structure with a = 5.6569 Å. For each state, we also give the percentage of s, p, and d character (first row, second row, and third row, respectively) within the atomic spheres for each type of atom. The equivalent number of atoms for each type of atom in the (n,n) unit cell is given in the parenthesis. The notations As', As^{Ga}, and As^{Al} for n = 2 refer to interfacial As atom, interior As atoms bonded to Ga, and interior As atom bonded to Al, respectively. We use sphere radii of 2.265 a.u. for all atoms. The charge not included in these spheres is defined as interstitial charge.

	n = 1; Relaxed			n = 1; Unrelaxed			n = 2; Unrelaxed						
ZB label	State label	E	E	As(2)	Ga	Ai	State label	ε	As ⁱ (2)	As ^{Ga}	As ^{Ai}	Ga(2)	Al(2)
$\overline{L_{1c}}$	\overline{R}_{1c}	1.88	1.92	14.5 4.8 3.2	25.3 1.1 0.5	0 3.6 1.2	\overline{X}_{1c}	2.35	0 2.4 2.3	9.1 2.4 0.7	5.3 0 0.4	16.4 3.1 0.7	9.1 1.4 1.0
	\overline{R}_{4c}	2.93	2.95	15.1 2.1 4.0	0 2.5 1.0	26.0 1.9 0.6	\overline{X}_{4c}	2.37	14.5 2.1 1.2	0 2.2 1.1	0 0.3 1.2	15.4 2.6 0.8	9.9 2.1 0.7
X _{1c}	<i>M</i> .	2.09	2.10	6.4 0	0 5.8	0 6.4	\overline{M}_{1c}	2.10	0 0 3.4	3.4 0 0.5	3.0 0 0.6	0 5.8 1.6	0 6.3 2.3
	50			4.5	1.6	2.3	\overline{M}_{2c}	2.06	6.3 0.2 1.1	0 0 1.3	0 0 2.0	0 6.1 1.2	0 6.0 2.8
	$\overline{\Gamma}_{4c}$	2.20	2.17	6.4 2.4 4.3	0 4.1 2.5	0 8.0 1.2	$\overline{\Gamma}_{1c}$	2.02	6.2 0.1 2.1	0.6 0 0.8	0.4 0 1.4	0.2 4.5 1.5	0.9 7.2 2.2
X _{3c}	\overline{M}_{ic}	2.07	2.13	0 11.1 5.8	18.0 0 0.7	0 0 3.6	\overline{M}_{5c}	2.60	0 4.7 3.1	0 4.1	0 1.0	10.3 0	8.5 0 2 3
	\overline{M}_{2c}	3.14	3.14	0 7.3 7.0	0 0 2.5	19.9 0 1.4				2.0	A. /	1.0	dan v
	$\overline{\Gamma}_{1c}$	2.84	2.83	6.8 6.3 5.4	1.5 0 1.2	19.1 0 2.1	$\overline{\Gamma}_{4c}$	2.56	0.1 3.3 2.9	0 6.9 2.5	0 0.4 0.5	13.8 0.3 2.1	4.0 0.6 1.6
Γ _{tc}	$\overline{\Gamma}_{1c}$	2.14	2.18	29.6 3.3 0.9	24.3 0 0.3	6.2 0 0.5	$\overline{\Gamma}_{1c}$	2.23	14.0 2.3 0.3	8.7 0 0	9.3 0 0.1	22.0 0 0.1	9.0 0.5 0.4
Γ ₁₅₀	$\overline{\Gamma}_{s_{\vartheta}}$	0	0	0 51.8 0.6	0 4.0 2.1	0 3.2 3.1	$\overline{\Gamma}_{5\nu}$	0	0 25.8 0.3	0 15.6 0.2	0 10.2 0.1	0 4.6 2.3	0 3.0 2.7
	$\overline{\Gamma}_{4v}$	- 0.09	- 0.05	0.1 49.6 0.8	0 5.6 1.5	0 1.8 3.8	$\overline{\Gamma}_{4\nu}$	- 0.02	0 26.2 0.3	0 12.8 0.2	0 12.1 0.1	0.1 4.9 2.0	0.1 2.5 3.1

B. $\overline{\Gamma}_{4c}(X_c)$ and $\overline{\Gamma}_{4v}(\Gamma_{15v})$

The second pair of states showing level repulsion are of $\overline{\Gamma}_4$ symmetry. The alloy Γ_{15v} state splits in the superlattice into $\overline{\Gamma}_{5v} + \overline{\Gamma}_{4v}$. [Inclusion of spin-orbit interaction gives three levels: the upper two ($\overline{\Gamma}_{7v}$ and $\overline{\Gamma}_{6v}$) split by 0.03 eV into light- and heavy-hole states, respectively, whereas the lower, split-off band $\overline{\Gamma}_{7v}$ is at $E_v - 0.33$ eV]. The alloy X_{1c} state in n = 1 folds in the superlattice into the $\overline{\Gamma}_{4c}(X_{1c})$ state. The two states $\overline{\Gamma}_{4v}(\Gamma_{15v})$ and $\overline{\Gamma}_{4c}(X_{1c})$, having the same Γ_4 symmetry, repel each other, displacing $\overline{\Gamma}_{4c}(X_{1c})$ up

and $\overline{\Gamma}_{4v}(\Gamma_{15v})$ down by 0.05–0.07 eV [Fig. 1(c)]. We predict that the $\overline{\Gamma}_{4c}(X_{1c})$ conduction band (with a wave function primarily delocalized on the tetrahedral interstitial,¹⁸ see Table IV) will have its energy at $E_v + 2.17$ eV, i.e., above its well center and above the corresponding alloy state X_{1c} . For n = 2, the repelling state $\overline{\Gamma}_{4c}(X_{3c})$ is higher in energy, hence the $\overline{\Gamma}_{4v}(\Gamma_{15v})$ state is lowered by only 0.02 eV. As the repeat period increases $(n \ge 2)$, the splitting between $\overline{\Gamma}_{5v}(\Gamma_{15v})$ and $\overline{\Gamma}_{4v}(\Gamma_{15v})$ is expected to show a monotonic decrease. The weak Raman resonance observed²⁴ at low temperatures for n = 1 at 1.93 eV was interpreted²⁴ as a tran-

S. -H. Wei and A. Zunger 5799

sition to $\overline{\Gamma}_{4c}$, based on the closeness to their calculated value. Our calculation does not support this assignment, but provides an alternative one (see below).

Our foregoing discussion shows that whereas for small n, the superlattice states at $\overline{\Gamma}_c$ would be classified by conventional models as "mass-delocalized" states, they are more properly thought of as "level-repulsion localized states."

VI. SEGREGATING SUPERLATTICE STATES

Not all of the alloy states at X fold in the (001)-oriented superlattice into $\overline{\Gamma}$; the sixfold degenerate X_c conduction band splits in the tetragonal cell of the superlattice into two degenerate longitudinal states (which fold into $\overline{\Gamma}$), and four transverse states (oriented parallel to the interface), which do not fold into $\overline{\Gamma}$, remaining at the X point⁴⁵ (\overline{M} in the tetragonal notation). We find these nonfolding states to be at a lower energy than the folding states for n = 1, whereas this order is reversed for n = 2 due to the repulsion effect discussed above (changing the substrate lattice constant can also alter this level ordering⁴⁵). Despite the small transverse electron mass of the X_{3c} alloy state, from which one would expect that the state folded from X_{3c} will be mass delocalized (hence located near the well centers), we find that the alloy X_{3c} state creates in the n = 1 superlattice the $\overline{M}_{1c}(X_{3c})$ state at $E_v = 2.13$ eV and the $\overline{M}_{2c}(X_{3c})$ state at $E_v = 3.14$ eV, both outside the X_{3c} potential well [Fig. 2(b)]. The former is predominantly localized on the GaAs sublattice with zero s wave function on the Al site (most of the amplitude of this state is in the tetrahedral interstitial space between adjacent As sites), whereas the latter is predominantly localized on the AlAs sublattice with zero s wave function on the Ga site. Since the s potential on the Ga site is more attractive than that on the Al site,¹⁸ there is a large splitting ($\sim 1 \text{ eV}$) between $\overline{M}_{1c}(X_{3c})$ and $\overline{M}_{2c}(X_{3c})$.

The second pair of segregating states results from folding the alloy L_{1c} states onto themselves. This gives rise to the pair of states $\overline{R}_{1c}(L_{1c})$ at $E_v + 1.92$ eV and $\overline{R}_{4c}(L_{1c})$ at E_v + 2.95 eV [Fig. 2(b)]. $\overline{R}_{1c}(L_{1c})$ is localized almost exclusively on the GaAs sublattice and has zero s wave function on the Al site; its energy is indeed close to the GaAs L_{1c} energy $E_v + 1.81$ eV. $\overline{R}_{4c}(L_{1c})$ is localized on the AlAs sublattice with zero s wave function on Ga site; its energy is close to the AlAs L_{1c} level at $\sim E_v + 3$ eV. The large splitting between \overline{R}_{ic} and \overline{R}_{4c} (~1.1 eV) reflects a symmetry-imposed constraint: the former state samples the $V_1 = V_{\text{Gas}}$ piece of the potential, whereas the latter state samples the $V_4 = V_{Al,s}$ piece. Again, despite their being nominally "mass-delocalized state," their energies are near the respective well bottom (\overline{R}_{1c}) and well top (\overline{R}_{4c}) , rather than at the well center. The $\overline{R}_{1c} - \overline{R}_{4c}$ splitting is so large, that the lowest member $\overline{R}_{1c}(L_{1c})$ becomes the conduction-band minimum of $(GaAs)_1(AlAs)_1$ [whereas for the equivalent alloy, X_{1c} is the minimum; Fig. 1(b)].

A crucial characteristic of the symmetry-enforced pairs of segregating states is that their energies oscillate with the repeat period n. This variation with n is simply a measure of the commensurability of the superlattice period with the period of the wave functions.⁴⁵ When the lattice is in *perfect* registry with the wave function (as is the case for n = 1), the superlattice states experience fully the differences between V_{Gas} and V_{Als} ; this results in a maximal splitting of ~ 1.1 eV. In contrast, for n = 2, both L_{1c} derived states are forced to equally experience the superlattice potential on the Ga and Al site. (The splitting caused by the potential difference between the interfacial As atom, bonded to two Ga and two Al atoms and the average of the two interior As atoms-one bonded to four Ga atoms and the other bonded to four Al atoms—is very small, see Table IV.) This results in a near degeneracy of the two L_{1c} -derived states for n = 2, as can be seen in Fig. 3; their energies are then near the well center and the states behave (much like in the alloy) as "averaging states." For n = 3, each wave function can have $\frac{2}{3}$ of its amplitude on one constituent and $\frac{1}{3}$ on the other, so the \overline{R}_{1c} $-\overline{R}_{4c}$ splitting is predicted to be about $\frac{1}{4}$ of the value for n = 1. In general, for n = even the splitting is nearly zero and for n = odd it is 1/n of the value for n = 1.

The pair of segregating states $\overline{M}_{1c}(X_{3c})$ and $\overline{M}_{2c}(X_{3c})$ exhibit similar energy oscillations to those apparent for $\overline{R}_{1c}(L_{1c}) - \overline{R}_{4c}(L_{4c})$ (Fig. 3). Again, for n = 2 these segregating states become "averaging states," collapsing into a single level (doubly degenerate) $\overline{M}_{5c}(X_{3c})$ state (Table III and Fig. 3) located at the well center. Since all segregating states (n = odd) become averaging states for n = even, the Kronig-Penney and other similarly simplified models are expected to be qualitatively valid only for even values of n of ultrathin superlattices.

The counterpart of the alloy X_{3c} and L_{1c} conduction states are the valence states X_{5v} and L_{3v} . These exhibit but a small valence-band discontinuity (Fig. 2). Consequently, the corresponding superlattice valence-band states have a very small segregation-induced splitting (since they have negligible cation s character) and their energies are near the respective well centers (Fig. 2): L_{3v} gives rise to $\overline{R}_{3v} + \overline{R}_{1v}$ $+ \overline{R}_{4v} + \overline{R}_{2v}$ at $\sim E_v - (1.1 \pm 0.1)$ eV, and X_{5v} produces in the superlattice $\overline{M}_{3v} + \overline{M}_{5v} + \overline{M}_{4v}$ at $\sim E_v$ $- (2.55 \pm 0.1)$ eV.

Our results for the segregating states suggest five predictions. First, since for n = 1 we find the conduction-band minimum to be at \overline{R}_{1c} , it could give rise to a ("forbidden") luminescence, lower in energy than the alloy X_{1c} emission. For n = 2, this luminescence would shift up in energy as \overline{R}_{1c} is displaced upwards, exposing the X_{1c} derived $\overline{\Gamma}_c(X_z)$ and \overline{M}_c (X_{x,v}) states, both at E_v + (2.04 ± 0.02) eV as the conduction-band minimum. Second, the oscillatory behavior of the \overline{R}_{1c} energy with *n*, coupled with the near *n* independence of the corresponding \overline{R}_v valence states, suggests that the \overline{R}_v $\rightarrow R_{1c}$ (denoted "E₁") transitions would also show oscillations with n, converging at large n to E_1 (GaAs). Third, the energy of the lower E_1 transition for n = 1 (denoted E_1^{Ga} and calculated at 3.0 \pm 0.2 eV, see Fig. 2) is predicted to be well below the average of the E_1 transitions in GaAs and AlAs (-3 and -4 eV, respectively). Fourth, a new E_1 like transition (denoted E_1^{Al}) is predicted at ~4.1 eV due to the \overline{R}_{o} $\rightarrow \overline{R}_{4c}$ excitation. Fifth, the $\overline{M}_{\nu} \rightarrow \overline{M}_{c}$ transitions (denoted E_2) in the superlattice are predicted to exhibit two branches. The first one connects \overline{M}_v with the averaging $\overline{M}_c(X_{ic})$ conduction bands folded from X_{1c} . The final state energies of this branch will vary smoothly and slowly with *n*, starting at $\sim E_v + 2.10 \text{ eV}$ for n = 1 and converging for $n = \infty$ to X_{1c} (AlAs) at $2.23 - \Delta E_v = 1.78 \text{ eV}$ above the GaAs VBM. The E_2 transition energies corresponding to this branch would be centered around 4.65 eV for small *n*, near the average of the E_2 energies for bulk GaAs and AlAs (4.7 and 4.5 eV, respectively). The second branch connects \overline{M}_v with the segregating $\overline{M}_c(X_{3c})$ conduction bands folded from X_{3c} . The final state energies of this branch will show strong damped oscillations with *n*, starting at $E_v + 2.13 \text{ eV}$ at n = 1 and converging to X_{3c} (GaAs) at $E_v + 2.30 \text{ eV}$. Notice that despite the large $X_{1c} - X_{3c}$ splitting in the bulk constituents, for n = 1, the energies of the two branches of the E_2 transitions in the superlattice are nearly overlapping.

The experimental situation pertaining to the segregating states in GaAs-AlAs superlattices is as yet not conclusive. Cardona et al.²⁴ and Isu, Jiang, and Ploog³⁰ observed (for n = 1) a single line low-temperature photoluminescence (PL) with no resolved phonon side bands, at 1.931 eV, which we tentatively interpret to arise from states near \overline{R}_{1c} which we find at $E_v + 1.92 \text{ eV}$ (Table IV). Since the lowest conduction band between \overline{R}_{1c} and $\overline{\Gamma}_{1c}$ bows upwards (more than the corresponding valence band), contribution from emission from states at or away from \overline{R}_{1c} (towards $\overline{\Gamma}_{1c}$) will somewhat raise the energy of the PL peak away from our value calculated at \overline{R}_{1c} . An earlier work by Ishibashi et al.²⁹ on less structurally controlled superlattices showed for n = 1 a PL peak at ~ 2.05 eV at low temperature, attributed by the authors to an unspecified indirect transition based on the drop in the relative quantum efficiency. The discrepancy relative to the more recent value²⁴ of 1.931 eV may reflect structural imperfections in the superlattice reported by Ishibashi et al.: recall that the alloy shows a forbidden luminescence at³⁴ ~ 2.08 eV, close to the emission energy observed by Ishibashi et al. in their nominal n = 1 superlattice. Experimentally, the PL energy was found³⁰ to first increase with *n* (up to 2.033 eV for n = 3) and then to decrease. We interpret the increase in the PL energy in going from n = 1 to higher n to reflect a change in the identity of the emitting level. While for n = 1 the CBM is \overline{R}_{1c} at $E_v + 1.92$ eV, for n = 2 the CBM is either $\overline{\Gamma}(X_{1c})$ or $\overline{M}(X_{1c})$, both at $\sim E_{\nu}$ $+2.04\pm0.02$) eV. As *n* increases further, the $\overline{\Gamma}_{c}$, which is localized on GaAs, becomes the conduction-band minimum (Fig. 3) and its energy decreases as a function of n. Emission from this level is direct, hence strong. Therefore, we expect that the emission observed for small n values [either from \overline{R} or from $\overline{\Gamma}(X_{ic})$ or $\overline{M}(X_{ic})$ would exhibit nonexponential and slow decay, whereas for larger n values the emission should become exponential and fast. Further experimental studies appear necessary (decay rates, emission lifetime, etc.) to clarify the nature of the PL in this superlattice.

Garriga *et al.*²³ measured the E_1 spectra of $(GaAs)_n (AlAs)_n$ at room temperature, finding for n = 1 $E_1 = 3.2 \text{ eV}$ (our calculated value for E_1^{Ga} is $3.0 \pm 0.2 \text{ eV}$), well below the average E_1 energies of GaAs and AlAs at the same temperature. We interpret this large shift to reflect the lowering of \overline{R}_{1c} discussed above. The $\overline{R}_v \to \overline{R}_{4c}$ transition (E_1^{A1}) we predict for n = 1 at $\sim 4 \text{ eV}$ was not observed; according to Garriga *et al.*²³ this transition is pseudodirect,

hence it is too weak to observe. As n increases from n = 1, they find a weak, nearly *n*-independent E_1 transition at 2.92-2.98 eV, and a strong transition, first rising up in energy (to 3.3 eV for n = 2) relative to the n = 1 value (3.2 eV) and then, for large n's decreasing in energy. They interpret the weak transition as $\overline{R}_v \rightarrow \overline{R}_{1c}$ and the stronger transition as $\overline{\Lambda}_v$ $\rightarrow \overline{\Lambda}_{1c}$ (i.e., displaced from the R point towards $\overline{\Gamma}$ along the [111] direction) since their calculated value for $\overline{R}_v \to \overline{R}_{1c}$ in n = 1 (2.7 eV) is lower than the calculated value for $\overline{\Lambda}_{\nu}$ $\rightarrow \overline{\Lambda}_{1c}$ (3.0 eV) by the same amount (0.3 eV) that the weak transition for n = 2 (measured at $\sim 2.98 \text{ eV}$) is lower than the strong transition (measured at $\sim 3.3 \text{ eV}$). However, this interpretation is untenable since (i) a comparison²⁴ of calculations at n = 1 with measurements at n = 2 ignores the large oscillatory shifts of \overline{R}_{1c} (and $\overline{\Lambda}_{1c}$) with *n*, and (ii) the assignment of the lower energy transition to the allowed $\overline{R}_{1\nu}$ $\rightarrow R_{1c}$ excitation is inconsistent with it being weak. We suggest that the weak and essentially n-independent transition (measured at $\sim 2.9 \,\text{eV}$) is associated with a state folded from the alloy Σ point (see Table II), which exist only for $n \ge 2$.

Garriga et al.²³ have also measured the transitions in $(GaAs)_n (AlAs)_n$ in the ~5-eV range, finding at room temperature a nearly constant energy of 4.97–5.02 eV for all *n*'s. According to our calculation, this is the transition to the final $\overline{M}(X_{1c})$ state, whose energy is predicted to be nearly *n* independent. This is discussed next.

VII. AVERAGING SUPERLATTICE STATES

We have seen that in the absence of symmetry-enforced level repulsion and level segregation, a small potential well and a sufficiently light mass lead to delocalized states. Such is the case for the $\overline{M}_{5c}(X_{1c})$ conduction state. We find that for n = 1, it is at $E_v + 2.10 \text{ eV}$ (Fig. 2). Like its counterpart, the $\overline{\Gamma}_{4c}(X_{1c})$ state (which also evolves from the alloy X_{1c} state) $\overline{M}_{5c}(X_{1c})$ has much of its amplitude in the tetrahedral interstitial volume between Ga and Al. Unlike $\overline{\Gamma}_{4c}(X_{1c})$, however, which is somewhat repulsion localized, the $\overline{M}_{5c}(X_{1c})$ state is almost unperturbed relative to the alloy since no new state is fold in to the \overline{M} point. Its energy is very close to the superlattice X_{1c} well center ($E_v + 2.10 \text{ eV}$) or to the alloy X_{1c} state ($\sim E_v + 2.10 \text{ eV}$). As *n* increases to n = 2the X_1 derived states are weakly split into $\overline{M}_{1c}(X_{1c})$ $+ \widetilde{M}_{2c}(X_{1c})$ (for the same reason that the two L_{1c} derived states are split). For large n values the energy of the lowest \overline{M} state decreases monotonically to the X_1 (AlAs) well bottom at $E_v + 1.78$ eV. This state is well described by conventional Kronig-Penney models.

VIII. GENERAL TRENDS

Figure 3 summarizes the general trends in the superlattice levels with the repeat period n. We distinguish four regions:

A.*n*=1

Due to the strong segregation effects on the L point energies, the $\overline{R}_{1c}(L_{1c})$ level, a GaAs-like state, is the lowest conduction band at $E_v + 1.92$ eV. This level is expected to luminesce around this energy and is the final state of the E_1

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absorption near 3 eV. Both the valence and conduction-band extrema are localized on the GaAs sublattice, hence the system is a "type I, indirect Γ -L" superlattice. At higher energies, around $E_v + (2.12 \pm 0.02)$ eV, we find the $\overline{M}_{1c}(X_{3c})$ and $\overline{M}_{5c}(X_{1c})$ levels, close to the alloy X_{1c} state. The direct conduction-band state $\overline{\Gamma}_{1c}(\Gamma_{1c})$ is yet higher in energy at E_v + 2.18 eV but ~0.04 eV below the alloy Γ_{1c} state, giving rise to an E_0 transition near this energy. A new pseudodirect $\overline{\Gamma}_{1c}(X_{3c})$ state with no counterpart in the alloy is predicted to appear at $E_v + 2.83$ eV.

B. n=2 and n=3

The reduced level segregation effect displaces $\overline{X}_{1c}(L_{1c})$ $[\overline{R}_{1c}(L_{1c}) \text{ for } n = 3] \text{ and } \overline{M}_{c}(X_{3c}) \text{ to higher energies, ex-}$ posing n = 2 at the conduction-band minimum the $\Gamma_c(X_{1c})$ (also denoted as the " X_2 " state) at $E_v + 2.02 \text{ eV}$, with more weight on the AlAs site. This level could be the candidate luminescing state observed³⁰ for n = 2 at $\approx E_v + 1.97$ eV, whereas the observed PL for n = 3 at 2.03 eV could commence from $\overline{M}_{c}(X_{1c})$ (also denoted as " $X_{x,y}$ " states). [Recall that the ordering of $\overline{M}_{c}(X_{1c})$ and $\overline{\Gamma}_{c}(X_{1c})$ oscillates for n = even or n = odd in ultrathin superlattice]. The valenceband maximum, having a preferential localization on the GaAs sublattice even for n = 1, becomes further localized on this sublattice as n increases. Hence, the n = 2 superlattice is a "type II, pseudodirect Γ -X" superlattice and become a "type II, indirect Γ -X superlattice for n = 3. The $M(X_{x,y})$ states are very near in energy to the $\overline{\Gamma}(X_z)$ state. The direct state $\Gamma_{ic}(\Gamma_{ic})$ is yet higher in energy, at $E_v + 2.23$ eV for n = 2, above its value for n = 1 (or the alloy Γ_{1c} and X_{1c} states), giving rise to an *increase* in the E_0 transition energy relative to n = 1. The new pseudodirect $\Gamma_{c}(X_{3})$ state is lowered relative to n = 1 (due to opposite repulsion from folded in Δ states) and appears at $E_v + 2.56$ eV for n = 2.

C. Intermediate n values

The states \overline{R} (L_{1c}) and \overline{M} (X_{3c}) are high in energy relative to the CBM. The candidates for the CBM in this region are the indirect \overline{M} and the pseudodirect $\overline{\Gamma}$ states, folded from X_{1c} or Δ line states and exhibiting a preferential AlAs character. The energies of these states are very close to each other and their order may oscillate for n even or odd. Since the VBM is still localized on GaAs, in this region the superlattice can be classified as a "type II, indirect or pseudodirect Γ -X" superlattice. The direct $\overline{\Gamma}_{1c}(\Gamma_{1c})$ state is higher in energy than the CBM or the alloy X_{1c} state. Samples in this region were studied extensively by Finkman et al.28 They found three classes of states for n = 3 and n = 7: (a) The lowest CB gave rise to a slow and nonexponential PL with three phonon side bands. For $n \simeq 3$, the emission was at 2.03 eV, while for $n \approx 7$ it was at 1.86 eV. (Cardona et al.²⁴ find the emission for n = 3 at 2.03 eV). They suggest²⁸ this is an $\overline{M}(X_{x,y})$ state. (b) The next highest state appears in photoluminescence excitation as a peak (not a shoulder) at 2.05 eV for $n \simeq 3$ and 1.85 eV for $n \simeq 7$. Its temperature dependence resembles that of the Γ point in GaAs; the intensity analysis reveals a small mixture with Γ character. They suggest²⁸ this is a $\overline{\Gamma}(X_z)$ state. Notice our calculation indicates that the ordering of the $\overline{\Gamma}(X_z)$ and $\overline{M}(X_{x,y})$ is thickness dependent. (c) The third highest level was the direct

 $\overline{\Gamma}_{1c}(\Gamma_{1c})$ which is the most prominent photoluminescence excitation line at 1.7 K, observed at 2.12 eV for n = 3 and 1.96 eV for n = 7. Its temperature dependence is akin to a direct transition. It is associated with two exciton lines at lower energy: a GaAs heavy-hole-electron exciton (Γ') and a GaAs light-hole-electron exciton (Γ_L). These excitons show short lifetimes, akin to direct transitions.

D. Large n values

For large *n* values, more and more states are folded in and couple to each other. States with the best registry to the potential well will have energy levels near the bottom (top) of the respective potential well. The lowest conduction band is at $\overline{\Gamma}_c$, approaching the GaAs bulk value $E_v + 1.52$ eV. The lowest conduction band at \overline{M} will approach the AlAs bulk value $E_v + 1.78$ eV, and lowest CB at $\overline{R}(\overline{X}, \text{ for } n = \text{e-ven})$ will converge to the GaAs bulk value $E_v + 1.81$ eV. The superlattice becomes "type I, direct."

IX. OTHER SUPERLATTICES

Very similar trends to those observed in $(GaAs)_1$ (AlAs)₁ are also found for⁴⁶ (HgTe)₁(CdTe)₁. Both CdTe and HgTe have a direct band gap at Γ . We find the n = 1superlattice to be also direct at Γ . We followed the same construction as shown in Figs. 1 and 2, using our calculated⁴² HgTe-CdTe valence-band offset of $\Delta E_v = 0.37$ eV. We find that:

(i) $\overline{\Gamma}_{1c}(\overline{\Gamma}_{1c})$ is repelled downwards from its well center only by 0.01 eV. This small repulsion is due to the fact that the folded state of the same symmetry, $\overline{\Gamma}_{1c}(X_{3c})$, is ~2.5 eV higher in energy than $\overline{\Gamma}_{1c}(\Gamma_{1c})$ [whereas in (GaAs)₁ (AlAs)₁ it is only ~0.35 eV higher.]

(ii) Whereas in GaAs, AlAs, and CdTe, the X_{3c} state is above the X_{1c} state, the strong relativistic effect in HgTe lowers its X_{3c} state (s like on Hg and p like on Te) below its X_{1c} state. Hence, the X_{3c} derived superlattice state $\overline{\Gamma}_{1c}(X_{3c})$ is below the X_{1c} derived $\overline{\Gamma}_{4c}(X_{1c})$ state. Hence, the three lowest superlattice states at $\overline{\Gamma}$ are (in increasing order of energy) $\overline{\Gamma}_{1c}(\Gamma_{1c})$, $\overline{\Gamma}_{1c}(X_{3c})$, and $\overline{\Gamma}_{4c}(X_{1c})$. Correcting for the LDA error, we find these states to be at 0.64, 3.44 \pm 0.2, and 3.64 \pm 0.2 eV, above the valence-band maximum, respectively (the energy of the latter two states has an uncertainty of \pm 0.2 eV since data which exist on the X point energies of CdTe and HgTe are insufficiently precise to obtain reliable LDA corrections).

(iii) The averaging state $\overline{M}_{5c}(X_{1c})$, like in other superlattices, is delocalized and very close (to within 0.03 eV) to its X_{1c} well center.

(iv) The segregating states have very large splitting due to large difference between Hg s potential and Cd s potentials. We find that $\overline{M}_{1c}(X_{3c})$ and $\overline{M}_{2c}(X_{3c})$ are split by 0.75 eV and $\overline{R}_{1c} - \overline{R}_{4c}$ are split by 0.74 eV. Both states have their energies outside their respective quantum wells. When *n* increases, we predict that the energies of these segregating states will show damped oscillation, exactly like (GaAs)_n (AlAs)_n.

For lattice-mismatched superlattices, like $(HgTe)_1(ZnTe)_1$ and $(CdTe)_1(ZnTe)_1$, the analysis become more complicated since deformation potential for each constitute has to be taken into account. We find for

 $(HgTe)(ZnTe)_1$ and $(CdTe)_1(ZnTe)_1$, at their relaxed geometry,⁴⁶ that the $\overline{\Gamma}_{1c}(\Gamma_{1c})$ states are about 0.11 eV below their well centers. The $\overline{M}_{1c} - \overline{M}_{2c}$ splittings are 1.54 and 0.68 eV for (HgTe)₁(ZnTe)₁ and (CdTe)₁(ZnTe)₁, respectively. The splittings of $\overline{R}_{1c} - \overline{R}_{4c}$ are 0.67 and 0.14 eV, respectively. Because of the large relaxation for the latticemismatched systems, the valence-band splittings are also large. They are about 0.6 eV at \overline{R}_v and 0.1 eV at \overline{M}_v .

X. SUMMARY

We have calculated the electronic structure of the (GaAs), (AlAs), superlattice by combining first principle results with corrections to the local density functional approach. We find for n = 1 that the system is indirect with a CBM at \overline{R} . For $n \ge 2$, the system is either pseudodirect or indirect with a CBM at \overline{M} for small n and becomes direct for large n's. For thin superlattices, besides the delocalized averaging states, we have identified two new types of localized states-repelling states and segregating states-whose energies and wave functions strongly depend on the layer thickness n. Based on our new theoretical results, we have reanalyzed recent experimental data and show a generally good agreement. Extension to II-VI superlattices show similar results.

Note added in proof

After the acceptance of our paper for publication, an experimental study appeared by Jiang et al.47 on the photoluminescence (PL) and its excitation (PLE) spectra in ultrathin AlAs-GaAs superlattices. They have interpreted their data in part in light of the non-self-consistent empirical pseudopotential calculation of Gell et al.¹⁶ Our fully selfconsistent all-electron calculation described in the main text produces qualitatively different results relative to those of Gell et al.,¹⁶ suggesting thereby a different interpretation, as follows:

(i) We find that the level repulsion effect produces an *increase* in the energy of the direct $\overline{\Gamma}(\Gamma_{1c})$ gap, from 2.18 eV in n = 1 to 2.23 eV in n = 2 (Fig. 3 and Table IV); the level then drops to ~ 2.15 eV for n = 3, and continues to drop monotonically with increasing n (due to reduced confinement). This closely agrees with the E_0 data²³ extrapolated to low temperatures, showing transitions at 2.18, 2.24, and 2.14 eV for n = 1, 2, and 3, respectively. In contrast, Gell et al.¹⁶ miss the level repulsion effect altogether, finding (their Fig. 7) the energy of $\overline{\Gamma}(\Gamma_{1c})$ to decrease from n = 1 (~2.49 eV) to n = 2 (~2.23 eV). Note that the PLE threshold energies of Jiang et al. [their Fig. 2(a)] do not follow the trends with n apparent in the E_0 spectra,²³ possibly due to contributions in PLE from states away from Γ .

(ii) Jiang et al. find PL maximum peaks at 1.94, 1.97, and 2.035 eV, for n = 1, 2, and 3, respectively, and a subsequent monotonic decrease as n increases. We interpret this as emission from our calculated $\overline{R}_1(L_1)$ (1.92 eV), $\overline{\Gamma}_1(X_Z)$ $(2.0 \pm 0.02 \text{ eV})$ and $\overline{M}(X_{x,y})$ $(2.08 \pm 0.04 \text{ eV})$ levels for n = 1, 2, and 3, respectively, showing the correct increase with n up to a maximum at n = 3, and a subsequent decrease with n (our Fig. 3). In contrast, Gell *et al.*¹⁶ do not show any L-derived level near the conduction band edge of n = 1. Furthermore, their calculated minimum gaps (Fig. 6 in Ref. 16)

shows a maximum at n = 2 in contrast with the PL data. Their predicted *increase* in the energy of $\overline{\Gamma}(X_z)$ from n = 1to n = 2 (Fig. 7 in Ref. 16) is also contradicted by our data showing a *decrease* with *n* (Table IV).

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5803 J. Appl. Phys., Vol. 63, No. 12, 15 June 1988

5803 S. -H. Wei and A. Zunger

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