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Failure of the transitivity rule for $(GaAs)_3/(Ge)_6$ (110) and $(AlAs)_3/(Ge)_6$ (110) superlattice valence-band offsets

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For $(GaAs)_3/(Ge)_6$ (110) and $(AlAs)_3/(Ge)_6$ (110) we use the relativistic norm-conserving pseudopotential, Gaussian-orbital expansion method to calculate valence-band offsets of 0.558 and 1.073 eV, respectively. Previously, for $(AlAs)_3/(GaAs)_3$ we obtained 0.447 eV. Thus the transitivity rule $\Delta E_V(\text{AlAs/GaAs})=\Delta E_V(\text{AlAs/Ge})-\Delta E_V(\text{GaAs/Ge})$ fails by 68 meV. This failure is attributed to the large diamond–zinc-blende interfacial mismatch which is reflected in the large values calculated for the formation enthalpies, 390 and 664 meV, respectively, for $(GaAs)_3/Ge_6$ and $(AlAs)_3/Ge_6$, compared with 27.8 meV for $(GaAs)_3/(AlAs)_3$ (110).

I. INTRODUCTION

The thermodynamic theory[1–4] of valence- (and conduction-) band offsets as well as effective–midgap-point theories, whether based on charge-neutrality levels,[5,6] dielectric theory,[7] or transition-metal impurity levels,[8,9] all have two consequences. We write

$$\Delta E_{ab}(A/B)=E_a(A)-E_b(B) \tag{1}$$

where $E_a(A)$ and $E_b(B)$ are energy levels in semiconductors A and B measured relative to some common level and where a and b are usually both valence-band or both conduction-band edges but need not be. Then the first consequence is that $\Delta E_{ab}(A/B)$ is independent of the interfacial orientation of the heterojunction or superlattice. The second is that the transitivity rule

$$\Delta E_{ab}(A/B)=\Delta E_{ad}(A/D)-\Delta E_{bd}(B/D) \tag{2}$$

is valid. The identity of $\Delta E_{vv}(\text{GaAs/AlAs})$ for (001), (110), and (111) interfaces has been verified to within 20 meV by van de Walle and Martin[10] and by us[11–14] to within 5 meV. (We gloss over the fact that ΔE_{vv} is not really a difference of one-electron eigenvalues.) It was[13] and is our belief that this is a consequence of the fact that the superlattice can be considered to be an ionic perturbation of a virtual-crystal potential with wave-vector components $\mathbf{G}+\mathbf{q}$ (where $\mathbf{G}$ is any reciprocal-lattice vector) and that within linear response theory for $\mathbf{q}\rightarrow\mathbf{0}$, the self-consistent screening potential is independent of the direction from which $\mathbf{q}\rightarrow\mathbf{0}$. Thus we think it likely that larger interfacial orientation dependences will be found when pairs of semiconductors are studied whose potentials differ sufficiently that linear response theory is not valid.

van de Walle and Martin[15] have tested the transitivity rule in three cases and Christensen[16] in five and in all cases (except one involving HgTe which seems to have convergence problems) the rule was violated by no more than 60 meV. (Note, however, that the two groups disagree by 100 meV in the transitivity error for ZnSe/GaAs/Ge when the sign is taken into account.) Similarly, the transitivity rule should hold only when the ionic pseudopotential differences among A, B, and D are small so that the self-consistent response to these differences is linear. One case where it does not hold is $A=$GaAs, $B=$AlAs, and $D=$vacuum. Then if a and b are taken to be conduction-band edges and d the vacuum zero, the right-hand side of (2) is the difference between the GaAs and AlAs electron affinities and the left-hand side is ΔE_{cc}. Using the experimental affinities[17] and $\Delta E_{vv}=\Delta E_{\text{gap}}-\Delta E_{cc}$ yields $\Delta E_{vv}(\text{GaAs/AlAs})=0.075$ eV, compared with directly measured values which range between[18] 0.43 and 0.56 eV.

In Refs. 11–14 we calculated formation enthalpies of $(GaAs)_n/(AlAs)_n$ which, depending on n and orientation, varied between 1.7 and 28 meV per pair of interfaces. This very small interfacial enthalpy is a consequence of the similarity of the GaAs and AlAs pseudopotentials and is completely consistent with the interfacial orientation independence of the band offsets. The Ge/GaAs and Ge/AlAs formation enthalpies have not previously been calculated but would be expected to be significantly larger than that of GaAs/AlAs, as the results presented in Sec. II confirm. Thus one might expect, and indeed we find in Sec. III, that there is a small but significant failure of the transitivity rule in the GaAs/AlAs/Ge system.

II. FORMULATION ENTHALPIES

As in II,[12] the first step in the calculation, after constructing a relativistic norm-conserving Ge pseudopotential,[19] is to obtain an optimal set of Gaussian basis functions by minimizing the total energy in a two–**k**-point calculation as a function of the Gaussian exponents. We obtained s and p exponents of 0.11, 0.3274, 0.9744, and 2.9 bohr^{-2} and a d exponent of 0.27 bohr^{-2} which may be compared with the Ga, Al, and As Gaussian exponents in Table I of II. Using these Gaussians in a ten–**k**-point Brillouin-zone (BZ) sample, we calculated the binding energy at three lattice constants and fit with a parabola to obtain the cohesive energy, equilibrium lattice constant, and bulk modulus of Ge, compared in Table I with experiment. This lattice constant is then

TABLE I. Calculated and experimental lattice constant, cohesive energy, and bulk modulus for Ge.

	Calculated	Experiment
a_0 (Å)	5.6694	5.658
E_{coh} (eV)	4.324	3.85
B (10^{10} N/m^2)	6.88	7.72

averaged with those obtained in the same way[20] in II (Ref. 12) for GaAs and AlAs to obtain the superlattice constants $a_0(\mathrm{Ge/AlAs}) = 10.7138$ bohrs and $a_0(\mathrm{Ge/GaAs}) = 10.6998$ bohrs. At the Ge equilibrium lattice constant of Table I we recalculated the Ge cohesive energy using the 24 bulk **k** points[21] corresponding to the (110) superlattice BZ points given in III and obtained 4.335 75 eV. This (110)-(001) BZ sampling difference is similar to that we found[22] for GaAs. Although small, in III (Ref. 13) it was crucial because the GaAs/AlAs formation enthalpies are so small. Here it will be seen to be less important.

In Table II we list the contributions to the total energy (calculated variationally as described[11] in I) for $(\mathrm{GaAs})_n/(\mathrm{Ge})_{2n}$ (110) and $(\mathrm{AlAs})_n/(\mathrm{Ge})_{2n}$ (110) for $n = 1$ and $n = 3$ both calculated in the $n = 3$ unit cell. Since the same atomic energies are subtracted from the superlattice and bulk semiconductor total energies to obtain their cohesive energies, they cancel from the formation enthalpies which are the cohesive energy differences. Although the Phillips[23] and Pauling[24] electronegativity scales disagree on the relative Ga and Al electronegativities, we found that charge was drawn from the Al to the Ga side for all three GaAs/AlAs interfaces[12–14] in agreement with Pauling's assessment of Ga being the more electronegative. Furthermore, in an unpublished contour plot of the difference between bulk GaAs and AlAs charge densities we found a larger charge around the cation and a smaller charge around the anion in GaAs. Hence GaAs is less ionic than AlAs and therefore its potential more nearly resembles that of Ge. Thus the fact that the $(\mathrm{AlAs})_n/(\mathrm{Ge})_{2n}$ have larger formation enthalpies than the $(\mathrm{GaAs})_n/(\mathrm{Ge})_{2n}$ was to have been expected. The enthalpy per unit cell (or pair of interfaces) decreases as n increases from 1 to 3, which is opposite to GaAs/AlAs. This perhaps can be understood in terms of the (001) superlattice. For GaAs/AlAs where the (001) interface is a plane of the common anion, we found[14] it to be the most stable interface. For AlAs/Ge or GaAs/Ge, where the (001) interface planes lie between a polar plane of cations or anions and a nonpolar plane of Ge atoms, the (001) superlattices are likely to be very unstable. Now, since the monolayer (110) superlattice is identical to the monolayer (001) superlattice (differing only by a 90° rotation of the unit cell), it seems reasonable that as n is increased from unity and the superlattice becomes uniquely (110), its enthalpy will decrease or increase depending on whether (110) is more or less stable than (001). We are unable to explain why this decrease is so much larger for GaAs/Ge than for AlAs/Ge unless it is that (as we shall see presently from the $\Delta\rho$ of Figs. 1 and 2 and to a lesser extent from the δ's in Table III) at $n = 3$ GaAs/Ge is more nearly converged in supercell size than is AlAs/Ge. Finally, we note that the formation enthalpies here are more than an order of magnitude larger than those of $(\mathrm{GaAs})_3/(\mathrm{AlAs})_3$ (110).

III. VALENCE-BAND OFFSETS

Figures 1 and 2 display $\Delta\rho$, the planar average of the superlattice charge density minus that of its constituent semiconductors (calculated at the superlattice lattice constant) as well as $\Delta V(z)$, the potential due to $\Delta\rho$. The interfacial double layer potential Δ_{dip} given in Table III is the difference between $\Delta V(z)$ evaluated at each well center. It has been pointed out[25] that $\Delta\rho$ and hence Δ_{dip} are arbitrary because they depend on where the interfacial plane is chosen. However, if any position other than exactly midway between atomic (110) planes is chosen, the potentials of the bulk semiconductor slabs, which are subtracted from the superlattice potential to yield $\Delta V(z)$, will have a linear component and a constant electric field will have to be added to restore the superlattice periodicity to $\Delta V(z)$. In any event, arbitrary or not, Δ_{dip} is a useful concept when considering transitivity. Since $\Delta V(z)$ is the difference between the actual superlattice Coulomb potential and that of alternating slabs of bulk charge densities, we have

$$\Delta E_V(A/B) = \Gamma_8(A) - \Gamma_8(B) + \Delta_{\mathrm{dip}}(A-B)\ , \tag{3}$$

TABLE II. Four contributions to the total and cohesive energies and formation enthalpy of $3(\mathrm{GaAs})\mathrm{Ge}_2$, $(\mathrm{GaAs})_3\mathrm{Ge}_6$, $3(\mathrm{AlAs})\mathrm{Ge}_2$, and $(\mathrm{AlAs})_3\mathrm{Ge}_6$ at lattice constants $a_0(\mathrm{Ge/GaAs}) = 10.6998$ bohrs and $a_0(\mathrm{Ge/AlAs}) = 10.7138$ bohrs. The following cohesive energies are used: $E_{\mathrm{coh}}^{\mathrm{Ge}} = 4.335\,75$ eV, $E_{\mathrm{coh}}^{\mathrm{GaAs}} = 7.724\,88$ eV, and $E_{\mathrm{coh}}^{\mathrm{AlAs}} = 8.528\,87$ eV.

	$3(\mathrm{GaAs})\mathrm{Ge}_2$	$(\mathrm{GaAs})_3\mathrm{Ge}_6$	$3(\mathrm{AlAs})\mathrm{Ge}_2$	$(\mathrm{AlAs})_3\mathrm{Ge}_6$
$[\Sigma_{n\mathbf{k}}\varepsilon_{n\mathbf{k}} - \Sigma_{\mathbf{K}} V(\mathbf{K})\rho(\mathbf{K})]$ (Ry)	26.001 701	26.422 161	25.698 370	26.069 757
$(1/2)8\pi\Omega\Sigma_{\mathbf{K}}\rho^2(\mathbf{K})/K^2$ (Ry)	8.187 230	8.009 875	8.311 424	8.172 249
$\int[\varepsilon_{xc}(\rho_T)\rho_T - \Sigma\varepsilon_{xc}(\rho_c)\rho_c]$ (Ry)	−37.254 780	−37.253 410	−36.103 257	−36.121 999
E_{Ewald} (Ry)	−98.354 953	−98.669 853	−98.226 430	−98.540 918
E_{total} (Ry)	−101.420 802	−101.491 227	−100.319 893	−100.420 911
E_{atom} (Ry)	−97.904 337	−97.904 337	−96.676 974	−96.676 974
E_{coh} (eV)	47.8415	48.7996	49.5619	50.9363
$(3E_{\mathrm{coh}}^{M\mathrm{As}} + 6E_{\mathrm{coh}}^{\mathrm{Ge}})$ (eV)	49.1891	49.1891	51.6011	51.6011
Formation enthalpy (eV)	1.3476	0.3895	2.0392	0.6648
Enthalpy/unit cell (eV)	0.4492	0.3895	0.6797	0.6648

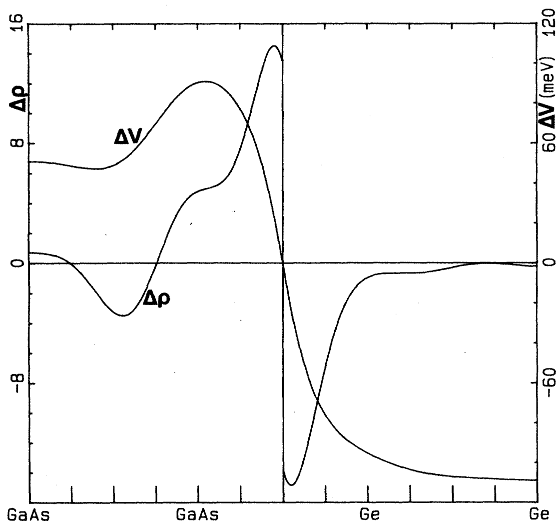

FIG. 1. $\Delta\rho$, the planar average of the $Ge_6(GaAs)_3$ superlattice charge density minus that of Ge and GaAs in units of 2.5×10^{-5} electrons per cubic bohr, and ΔV, the Coulomb potential due to $\Delta\rho$ which is arbitrarily zeroed at the interfacial plane. The plot extends from well center to interfacial plane to well center.

TABLE III. Interfacial double layer Δ_{dip} and valence-band offset ΔE_V. The valence-band offset calculated with respect to $\bar{V}$ is $\Delta E_V+\delta/2$ and with respect to $\hat{V}$ is $\Delta E_V-\delta/2$. (All in meV.) The sign convention is such that ΔE_V is the valence-band edge energy in the first semiconductor at the head of the column minus that in the second and Δ_{dip} is the Coulomb potential due to $\Delta\rho$ at the center of the first semiconductor minus that at the center of the second. The last column is taken from Ref. 13.

	$Ge_6(GaAs)_3$	$Ge_6(AlAs)_3$	$(GaAs)_3(AlAs)_3$
Δ_{dip}	-160.0	229.3	314.2
ΔE_V	558.1	1073.0	446.9
δ	-2.0	-6.2	5.0

where $\Delta E_V\equiv\Delta E_{vv}$ and $\Gamma_8(A)$ and $\Gamma_8(B)$ are the valence-band edges in A and B calculated relative to the average Coulomb potential in the A and B slabs of bulk charge. The zero of Coulomb potential is arbitrary in a bulk crystal but it is well defined as being the potential outside the slab as long as the slab is cut as we have cut it. For any other cut the linear part of the potential would cause it to be different on the two sides of the slab. If the same lattice constant were used for each semiconductor, the entire lack of transitivity would be contained in Δ_{dip}, i.e.,

$$[\Gamma_8(\text{Ge})-\Gamma_8(\text{AlAs})]-[\Gamma_8(\text{Ge})-\Gamma_8(\text{GaAs})] =[\Gamma_8(\text{GaAs})-\Gamma_8(\text{AlAs})]\ . \tag{4}$$

In Fig. 3 the planar average of the Coulomb potential of Ge and GaAs slabs is shown along with the average value of the potential and Γ_8 calculated relative to that potential. From Fig. 3 and Fig. 4 (which is the same as Fig. 3 but for Ge and AlAs calculated at the lattice constant of the Ge-AlAs superlattice) we can evaluate the left-hand side of Eq. (4): $(0.3788+0.4586)-(0.4043+0.3063) =(0.8374-0.7106)=0.1268$ eV. From Fig. 3 of III,[13] we can evaluate the right-hand side: $(-0.3065+0.4304)=0.1239$ eV. Thus the lack of transitivity due to bulk crystal lattice constant differences is only 2.9 meV, which is much smaller than the 25.5-meV difference between the two Γ_8(Ge) at different lattice constants in

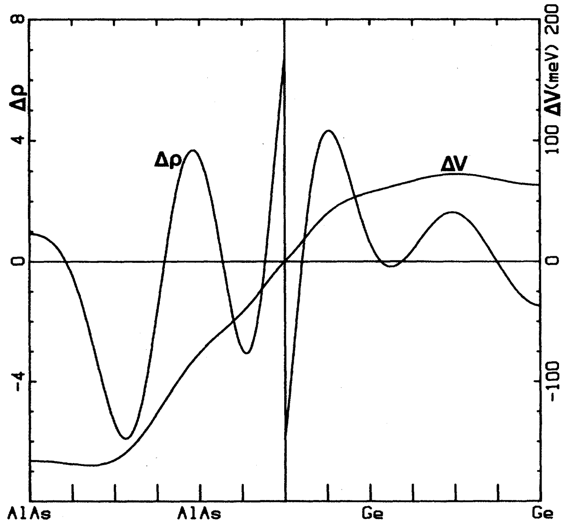

FIG. 2. Same as Fig. 1 but for $Ge_6(AlAs)_3$.

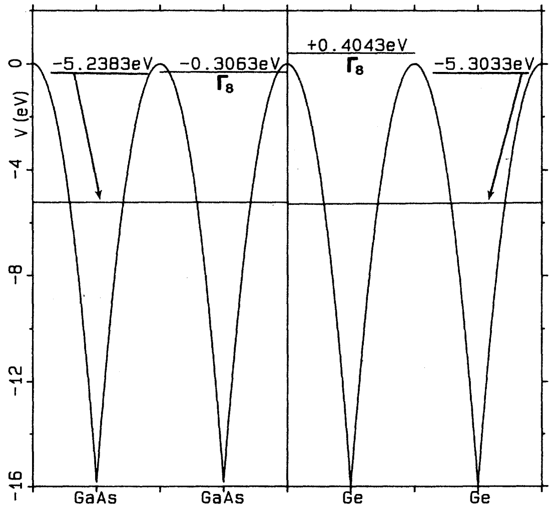

FIG. 3. Planar average of the Coulomb potential arising from (110) slabs of point ions and bulk pseudocharge densities of Ge and GaAs with lattice constant $a_0=10.6998$ bohrs. The long horizontal lines are the averages of these Coulomb potentials and the shorter lines are the tops of the valence bands (Γ_8 levels) calculated with respect to the average Coulomb potentials.

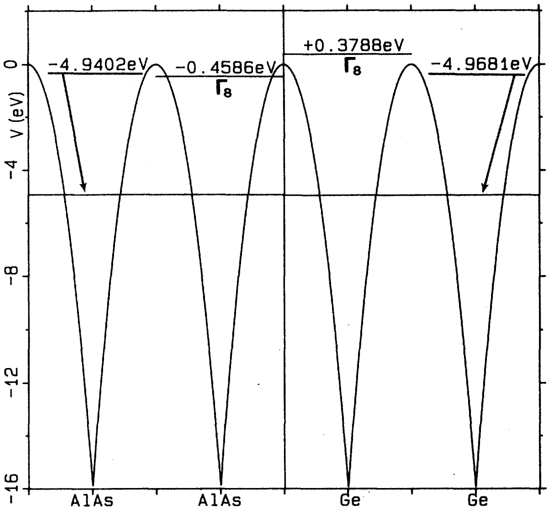

FIG. 4. Same as Fig. 3 but for Ge and AlAs with $a_0 = 10.7138$ bohrs.

Eq. (4). From Table III we see that $\Delta_{\mathrm{dip}}(\mathrm{Ge/AlAs}) - \Delta_{\mathrm{dip}}(\mathrm{Ge/GaAs}) = 389.3$ meV, which is 75.1 meV larger than $\Delta_{\mathrm{dip}}(\mathrm{GaAs/AlAs})$.

We can also calculate the valence-band offsets from Eq. (3) and obtain $\Delta E_V(\mathrm{Ge/GaAs}) = 550.6$ meV and $\Delta E_V(\mathrm{Ge/AlAs}) = 1066.7$ meV. However, since the Coulomb and exchange-correlation potentials respond self-consistently to one another, we expect the potential difference between well centers to converge more rapidly in n if the total potential is considered rather than just the Coulomb (for large n the exchange-correlation difference between superlattice well center cells is identical to its difference between the bulk semiconductors and thus cancels out). In Figs. 5 and 6 are plotted the planar averages of the $(\mathrm{Ge})_6/(\mathrm{GaAs})_3$ and $(\mathrm{Ge})_6/(\mathrm{AlAs})_3$ total (except for the nonlocal parts of the pseudopotentials) potentials. The $\hat{V}$'s are the potentials at the well centers and the $\bar{V}$'s are the potentials averaged over central cells of the quantum wells. The valence band offset may be obtained by subtracting Γ_8's calculated in the bulk semiconductors where Coulomb zeroes have been chosen to make the bulk $\bar{V}$ or $\hat{V}$ agree with those in the quantum wells. In Table III we list the average of the ΔE_V obtained from $\bar{V}$ and $\hat{V}$ as well as their difference δ which must vanish as n gets large and thus represents an estimate of the error due to using $n = 3$. Our Ge/GaAs offset of 558 meV is in exact agreement with the experimental value[26] of 0.56 eV and our Ge/AlAs offset of 1.073 eV is in fair agreement with the experimental[26] 0.95 eV. However, considering the fact that recently measured GaAs/AlAs valence-band offsets span the 0.43–0.56 eV range and that not too many years ago 0.19 eV was the accepted value,[27] these single experimental values for Ge/GaAs and Ge/AlAs should not be taken as the final word.

The transitivity rule for ΔE_V in Table III fails by 68 meV, which compares reasonably well with the 0.04 and 0.05 eV found in Refs. 16 and 15. These authors thought that their transitivity errors were smaller than their com-

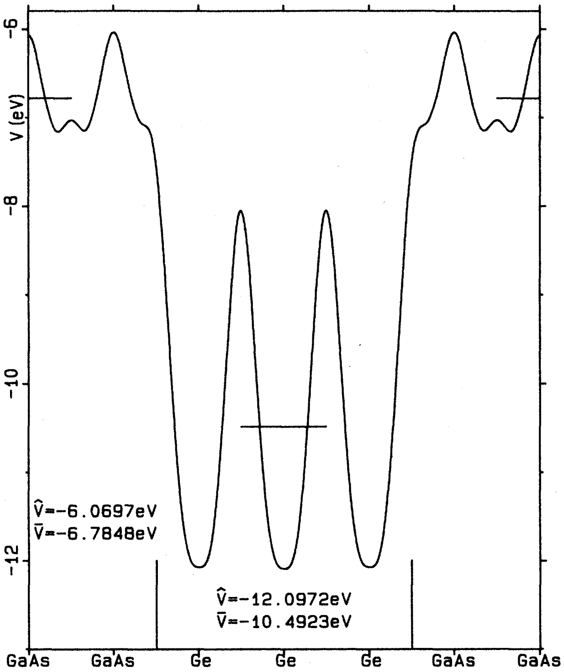

FIG. 5. Planar average of the total potential (excluding the nonlocal part of the pseudopotential) of $\mathrm{Ge}_6(\mathrm{GaAs})_3$. The vertical lines are interface planes and the horizontal lines are $\bar{V}$, the potential averaged over the central cells of the quantum wells. The $\hat{V}$ are $V(z)$ at the central planes of the wells.

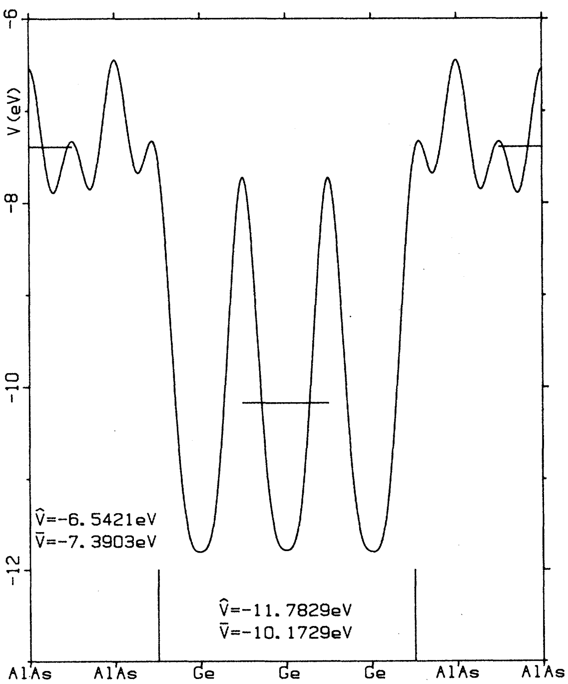

FIG. 6. Same as Fig. 5 but for $\mathrm{Ge}_6(\mathrm{AlAs})_3$.

putational uncertainties; however, we are confident that ours is not. The largest error in ΔE_V is probably the self-energy correction. But that, according to Louie,[28] is a bulk property and therefore transitive (except for a small contribution arising from lattice constant differences). The next largest error arises from lack of convergence in quantum well thickness. The δ of Table III indicate that this is about 10 meV. Also $(\mathrm{GaAs})_n/(\mathrm{AlAs})_n$ (111) is well converged[14] by $n=3$. If one accepts the interfacial orientation independence rule for this system, then the fact that the $n=3$ calculated (110) and (111) interface offsets differ by only 5 meV indicates that (110) is either nearly converged also for $n=3$ or that it is fortuitously correct for $n=3$. Another small error arises from the fact that the calculations were performed for superlattice lattice constants which are taken to be the average of the *calculated* bulk equilibrium lattice constants. These differ from each other by somewhat more than the experimental lattice constants. Therefore we overestimated this correction when we calculated ΔE_V(Ge/AlAs) at the (Ge/GaAs) lattice constant and found it increased by 6 meV, which also increases the transitivity failure by 6 meV.

Thus we have shown that a small but significant failure of the transitivity rule occurs for the (AlAs/Ge/GaAs) system. The physics behind this failure is identical to that for the much larger failure which is known to occur in the (AlAs/vacuum/GaAs) system.

Note added in proof. Christensen[29] has calculated transitivity-rule failures as large as 0.42 eV in systems containing CuBr as one of the constituents. This is consistent with our speculation that the larger the difference between the pseudopotentials of the constituents, the larger the transitivity-rule failure.

ACKNOWLEDGMENTS

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[20] There is an exact one-to-one correspondence between the ten-**k**-point bulk Brillouin zone sampling and the 12-**k**-point (100) monolayer superlattice BZ sampling used in II for GaAs and AlAs.

[21] These 24 points in the $\frac{1}{48}$ wedge of the BZ correspond to 864 points in the full BZ and are in an almost cubic $(\sqrt{2}/6\times\sqrt{2}/6\times\frac{1}{4})$ array. The ten-**k**-point sample is cubic and corresponds to 256 points in the full BZ.

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