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Quasiparticle energies in GaAs and AlAs

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We calculate the quasiparticle band structures of GaAs and AlAs and compare them with previous experimental assignments. Generally good agreement is obtained, except for the L conduction-band minimum in AlAs, which is found to be 0.8 ± 0.2 eV above the X minimum rather than the 0.3 eV as found in the literature. A new interpretation of the experimental data is therefore proposed.

The electronic properties of GaAs, AlAs, and their alloys $Al_xGa_{1-x}As$ have been studied widely.[1,2] In particular, the minimum band gap (which is $\Gamma_v - \Gamma_c$ in GaAs and $\Gamma_v - X_c$ in AlAs) and other direct and indirect band gaps have been measured as a function of the concentration x. There have also been theoretical calculations of the band structures,[3-5] but all *ab initio* calculations[5] have been performed using *density-functional theory* (DFT), which is formulated only to reproduce the exact ground-state electron density, and not quantities related to electronic excitations such as quasiparticle energies. In addition, the DFT calculations use the local-density approximation (LDA) for exchange and correlation. For the electronic gaps these calculations give the well-known errors[6] of about 0.5–1.0 eV.

To go beyond the LDA ground-state theory we have, as in Ref. 6, performed quasiparticle calculations using the (GW) approximation[7] for the self-energy operator which includes screened interactions but neglects higher-order vertex corrections. In GaAs, our calculation omits two partly canceling effects: core relaxation [which is believed to reduce the LDA direct gaps by 0.27, 0.02, and 0.12 eV at Γ, X, and L, respectively[5]] and a valence-core self-energy correction (which we estimate to increase the quasiparticle gaps by about 0.1 eV from the symmetry of the wave functions and the atomic Ge calculation in Ref. 8).

The quasiparticle energies, obtained by solving Dyson's equation with this self-energy operator, are listed in Tables I and II. As with our earlier results for Si, the GW quasiparticle energies generally reproduce experimental gaps, both direct and indirect, to within 0.1–0.2 eV. Similar agreement has been reported by Hybertson and Louie for Si, Ge, C, and LiCl.[8] There is, however, one glaring exception. The conduction band at L in AlAs is generally placed near 2.5 eV above the valence-band maximum. Our calculations yield 3.03 eV. The uncertainties in the calculation and the agreement obtained for the other gaps lead us to place an error bar of no more than 0.2 eV on this value, which could possibly lower it to about 2.8 eV—still 0.3 eV above the values reported in the literature.

The experimental value of about 2.5 eV is, however, *not* obtained from direct measurements. Although the direct gap at L is observed in ellipsometry[9] at 3.9 eV (the so-called E_1 threshold), the valence- and conduction-band energies relative to Γ_{15v} are not measured individually. Indirect evidence for the position of the L minimum in AlAs has been obtained primarily from the *extrapolation* of $Al_xGa_{1-x}As$ alloy data. First, transport studies by Lee, Juravel, Wooley, and Springthorpe[11] contain the L minimum implicitly through electron scattering. Alloy data in the range $0 < x < 0.6$ and a quadratic least-squares fit yield $E_L \approx 2.36$ eV. Second, core-level reflectivity data by Aspnes and Kelso,[12] which measure the shift of the indirect adsorption edge directly, are available only up to

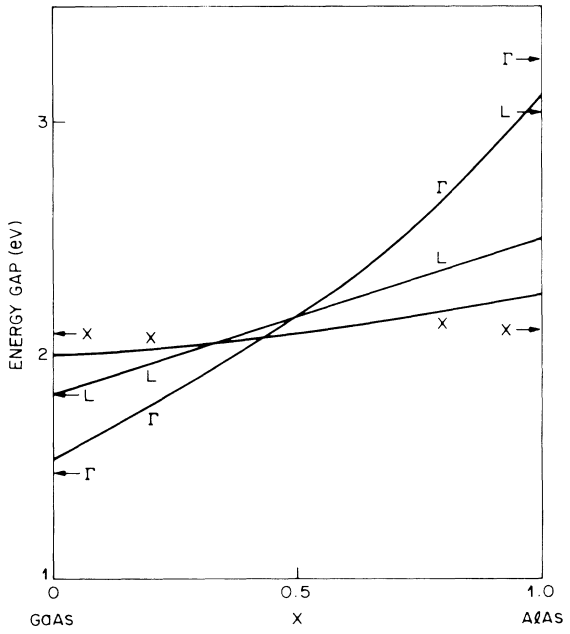

FIG. 1. Quasiparticle energies in GaAs and AlAs calculated in the GW approximation (arrows) superimposed on a plot of the experimental values for the alloy series $Al_xGa_{1-x}As$. Energies are shown relative to the valence-band maximum at Γ. Note the significant discrepancy at L in AlAs between the calculated value and the "experimental" value generally quoted.

TABLE I. LDA eigenvalues, GW quasiparticle energies, and experimental energies in GaAs, in eV.

	LDA[a,b]	GW[a,b]	Experiment[b]
Γ_{15v}	0.0 (−0.34)	0.0 (−0.34)	0.0 (−0.34)[c]
Γ_{1c}	0.56	1.47	1.52[c]
Γ_{15c}	3.70	4.52	· · ·
X_{5v}	−2.66 (−2.73)	−2.73 (−2.80)	−2.78 (−2.85)[c]
X_{1c}	1.38	2.08	1.98[d] 2.01[e]
X_{3c}	1.55	2.30	· · ·
L_{3v}	−1.07 (−1.28)	−1.11 (−1.32)	−1.19 (−1.40)[c]
L_{1c}	1.04	1.82	1.82[d] 1.84[e]
L_{3c}	4.57	5.41	· · ·
Γ direct gap	0.56	1.47	1.52
X direct gap	4.04	4.81	4.76
L direct gap	2.11	2.93	3.01

[a]Experimental spin-orbit splittings added (Ref. 1).
[b]Valence-band maxima aligned. The lower energy of a spin-orbit pair is shown in parentheses.
[c]Reference 1.
[d]Reference 9.
[e]Reference 10.

TABLE II. LDA eigenvalues, GW quasiparticle energies, and experimental energies in AlAs, in eV.

	LDA[a,b]	GW[a,b]	Experiment[b]
Γ_{15v}	0.0 (−0.28)	0.0 (−0.28)	0.0 (−0.28)[c]
Γ_{1c}	2.29	3.26	3.11[d]
Γ_{15c}	4.23	5.05	· · ·
X_{5v}	−2.21 (−2.36)	−2.34 (−2.49)	−2.30 (−2.45)[e]
X_{1c}	1.28	2.09	2.24[c]
X_{3c}	2.14	2.99	· · ·
L_{3v}	−0.80 (−1.00)	−0.88 (−1.08)	−1.31 (−1.51)[c]
L_{1c}	2.13	3.03	2.49[d] 2.54[e]
L_{3c}	4.58	5.48	· · ·
Γ direct gap	2.29	3.26	3.11[d]
X direct gap	3.47	4.41	4.54[c]
L direct gap	2.93	3.91	3.90[e]

[a]Experimental spin-orbit splittings added (Ref. 1).
[b]Valence-band maxima aligned. The lower energy of a spin-orbit pair is shown in parentheses.
[c]Reference 1.
[d]Reference 10.
[e]Reference 9.

$x=0.5$, and the quadratic extrapolation usually employed yields $E_L \approx 2.5$ eV for AlAs. Third, a combination of the ellipsometry measurements[9] of the direct gap at L with the assumption of a rigid valence band (thus assuming it to be As-like) across the range of alloy compositions would predict the L minimum to lie at about 2.8 eV.

The third estimate is the closest to our value of 3.03 eV. The remaining 0.2-eV discrepancy is exactly accounted for by the fact that the valence band is *not* completely rigid: We calculate that the valence band at L is 0.2 eV higher in AlAs than in GaAs (see Tables I and II).

We believe that the first two experimental estimates are incorrect because the quadratic extrapolation from $x \approx 0.5$ to $x=1$ is inadequate. There is other experimental evidence that this may be the case. Optical data on the Γ minimum by Monemar[13] across the entire composition range bend upwards sharply near $x \approx 0.6$ and can only be fitted with a sizable cubic term. Similarly, the ellipsometry data[9] on E_1 also show a strong upwards bend near $x \approx 0.5$, and a cubic fit is again needed.

Finally, we note that the ability of the LDA calculations to predict the correct dispersion of the individual bands in AlAs is much better than a comparison of the LDA results with the previously accepted experimental data would suggest. Displacing the LDA conduction bands rigidly upwards by 0.9 eV yields a band structure within 0.1 eV of the GW calculations in the bands closest to the gap. The same accuracy is obtained in GaAs with a displacement of 0.8 eV.

In conclusion, we have reported quasiparticle energies for electrons and holes in GaAs and AlAs, calculated using the GW method, which are generally in good agreement with experiment. An exception is the L conduction-band minimum in AlAs, which we propose to place at least 0.3 to 0.5 eV higher in energy than previously believed.

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