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Determination of the hole effective masses in GaAs from acceptor spectra

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State-of-the-art calculations of acceptor energy levels in GaAs show that the currently used hole effective masses are at variance with spectroscopic data on shallow acceptors. These data, as well as most available data from quantum-well spectroscopy and cyclotron resonance, are explained by the set of parameters $\gamma_1 = 7.10 \pm 0.15$, $\gamma_2 = 2.02 \pm 0.15$, and $\gamma_3 = 2.91 \pm 0.10$, which corresponds to a larger valence-band anisotropy than reported in interband magneto-optical studies. Values of the acceptors ionization energies are also derived: 26.3, 27.8, 28.2, 30.1, 34.2, and 34.3 meV, for C, Be, Mg, Zn, Si, and Cd, respectively.

The interpretation of the electronic properties of bulk semiconductors requires an accurate knowledge of the dispersion of the energy-band extrema. The top of the valence band of cubic semiconductors is described by the Luttinger inverse hole masses γ_1, γ_2, and γ_3, whose values are known with an accuracy better than 1% only for the elemental semiconductors Ge and Si.[1] For GaAs, the most studied among III-V compounds because of its technological importance for modern high-speed electronic devices, the hole effective masses are not yet known with the desired accuracy. An accurate determination of these masses is important not only for the interpretation of the optical and transport measurements in bulk GaAs, but also for the prediction of the electronic properties of GaAs quantum-well structures.

The valence-band dispersion of GaAs has been investigated by several techniques including cyclotron resonance,[2] interband magneto-optics,[3,4] and recently two-photon magnetoabsorption measurements.[5] The resulting band masses are generally given with large experimental uncertainties and do not provide a satisfactory interpretation of recent spectroscopic data on GaAs/AlAs quantum-well structures.[6] This has led some authors to propose a set of γ values for GaAs to selectively explain the GaAs/AlAs data.[6,7]

Limiting ourselves to the most commonly employed values[2-4] (see Table IV in Ref. 5) and those recently determined from high-resolution spectroscopic measurements,[5-7] we notice large variations and inconsistencies. The range of reported values is especially wide for γ_2 (40%) and γ_3 (15%), while smaller variations exist for γ_1 (5%). We note that the γ_2 values obtained from quantum-well spectroscopy[6,7] and magnetoreflectance[3] are inconsistent with that obtained from two-photon magnetoabsorption experiments.[5] A further inconsistency exists between the values of γ_1 determined by magnetoreflectance[3] and two-photon magnetoabsorption measurements.[5] These inconsistencies cannot be explained by polaron effects. It is true that different band-mass renormalizations apply to free holes, holes in a magnetic field, and bound holes of excitonic systems, but polaron effects are small in GaAs, and should not account for more than a few percentages of variation in the measured hole masses.[2]

The energy spectrum of shallow acceptors is very sensitive to the hole effective masses, and therefore available data for acceptors in GaAs can be used to improve our knowledge of the γ values of this material. Here we exploit this and derive two conditions that the γ values must satisfy to be compatible with available acceptor data. We also discuss the quality of existing γ values, and propose a reference set, which is consistent with most available experimental data.

In the acceptor problem, the valence-band dispersion is conveniently described by means of the three parameters:[8] γ_1, $\mu = (6\gamma_3 + 4\gamma_2)/5\gamma_1$, and $\delta = (\gamma_3 - \gamma_2)/\gamma_1$. The average hole inverse mass γ_1 has mainly a scaling effect on the acceptor spectrum, while both the spherical parameter μ and the warping parameter δ are responsible for specific splittings of the acceptor levels. Comparison between experiment and theory is most easily made on the odd-parity acceptor states which are not affected by chemical effects, and whose binding energies are well described in the effective-mass approximation.

The most accurate data on odd-parity states are the infrared transition energies from the ground state to the $2P_{3/2}$, $2P_{5/2}[\Gamma_8]$, and $2P_{5/2}[\Gamma_7]$ states.[9] Data for the higher excited states are less accurate, and have been measured for GaAs:C only. Such data will not be used in this work. We will use the energy splitting Δ between the $2P_{5/2}[\Gamma_8]$ and the $2P_{5/2}[\Gamma_7]$ states, the binding energy E_1 of the $2P_{3/2}$ state and the energy E_2 of the center of gravity: $\{2E(2P_{5/2}[\Gamma_8]) + E(2P_{5/2}[\Gamma_7])\}/3$ of the $2P_{5/2}$ states. While Δ is due to the cubic term in the Hamiltonian, and is very sensitive to δ, the energies E_1 and E_2 contain information on μ, since they are mostly controlled by the spherical heavy-hole mass $m_e/(1-\mu)\gamma_1$, where m_e is the free-electron mass.

The experimental value $\Delta = 1.91 \pm 0.11$ meV is directly obtained from infrared data,[9] while to estimate E_1 and E_2, we first need accurate ground-state energies for different acceptors in GaAs. The most accurate ionization energies are, to our knowledge, those for GaAs:C and GaAs:Si.[10] Using such data, and the proportionality between the ionization energy and the $1S_{3/2}$-$2S_{3/2}$ energy difference, measured for most acceptors in GaAs from

bound-exciton two-hole transitions,[11] we can determine very accurate ground-state energies for the remaining acceptors. In Fig. 1, we show the experimental $1S_{3/2}$-$2P_{3/2}$ (G), $1S_{3/2}$-$2P_{5/2}[\Gamma_8]$ (D), $1S_{3/2}$-$2P_{5/2}[\Gamma_7]$ (C) transition energies and the ground-state ionization energy (E_0) versus the $1S_{3/2}$-$2S_{3/2}$ energy difference. The linear relations with identical slopes which appear in Fig. 1 can be justified by considering that for shallow acceptors the $1S_{3/2}$ and $2S_{3/2}$ chemical shifts have a constant ratio approximately given by $|\Psi_{1S_{3/2}}(0)/\Psi_{2S_{3/2}}(0)|^2$, where the wave functions are evaluated at the impurity site.[8]

From the slope in Fig. 1, we derive a ratio of 6.7 between the $1S_{3/2}$ and $2S_{3/2}$ chemical shifts. Using this value, with the accurate E_0 data for GaAs:C and GaAs:Si, and the $1S_{3/2}$ and $2S_{3/2}$ energy differences, we find the following values for the ground-state ionization energies E_0 of the different impurities: 26.3 meV for C, 27.8 meV for Be, 28.2 meV for Mg, 30.1 meV for Zn, 34.2 meV for Si, and 34.3 meV for Cd, with an accuracy of ± 0.1 meV. These values differ from the currently accepted ones by as much as 0.6 meV (GaAs:Zn). From these ionization energies and the infrared transition energies,[9] we deduce the values $E_1 = 11.10 \pm 0.15$ meV and $E_2 = 6.34 \pm 0.14$ meV, which together with $\Delta = 1.91 \pm 0.11$ meV will be compared with the theoretical results in order to determine the hole effective masses.

The acceptor energy levels are calculated within the effective-mass approximation, using the Hamiltonian for degenerate bands and variational techniques described in previous studies[8] of acceptors in Ge and Si. The Hamiltonian includes valence-band warping and coupling to the split-off valence band. For GaAs, we simulate the polar nature of the semiconductor with polaron-parameters γ_1, μ, and δ. A dispersive screening which takes into account the ionic polarization has also been included. However, its effect on the binding energy of the odd-parity states has been found to be negligible ($\Delta E < 1\%$).

In Fig. 2, we compare the odd-parity-state spectra calculated with the parameters obtained from cyclotron resonance[2] (spectrum a), interband magnetoreflectance[3] (spectrum b), two-photon magnetoabsorption[5] (spectrum c), quantum-well spectroscopy[6,7] (spectrum d), and the infrared spectrum of GaAs:C measured by Kirkmann, Stradling, and Lin-Chung[9] (spectrum e). In the latter spectrum, the absolute binding energies have been obtained using the ionization energy $E_0 = 26.3$ meV, given above. Spectra a, b, and c deviate significantly from the experimental data (spectrum e), all states appearing too strongly bound. Spectrum d is in far better agreement with experiment, but even in this case we observe small discrepancies between the calculated and experimental position of the G line, and the separation between the C-line components. We emphasize that for Ge, for which accurate γ values are available, one finds excellent agreement between the calculated spectrum and infrared data (typical discrepancies $< 1\%$).[8]

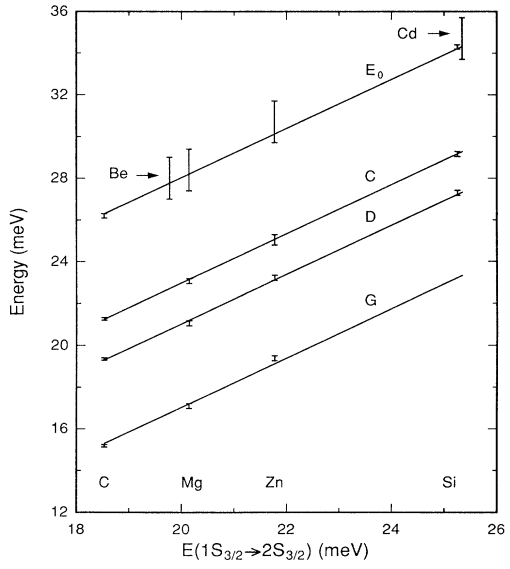

FIG. 1. Experimental absorption energies of C, Mg, Zn, and Si acceptors in GaAs corresponding the $1S_{3/2}$-$2P_{3/2}$ (G), $1S_{3/2}$-$2P_{5/2}[\Gamma_8]$ (D), $1S_{3/2}$-$2P_{5/2}[\Gamma_7]$ (C) transitions (Ref. 9), and ground-state ionization energies E_0 (Refs. 10 and 11) vs the $1S_{3/2}$-$2S_{3/2}$ energy difference (Ref. 11). Experimental ionization energies of GaAs:Be and GaAs:Cd are also indicated. Note the identical slope of all lines.

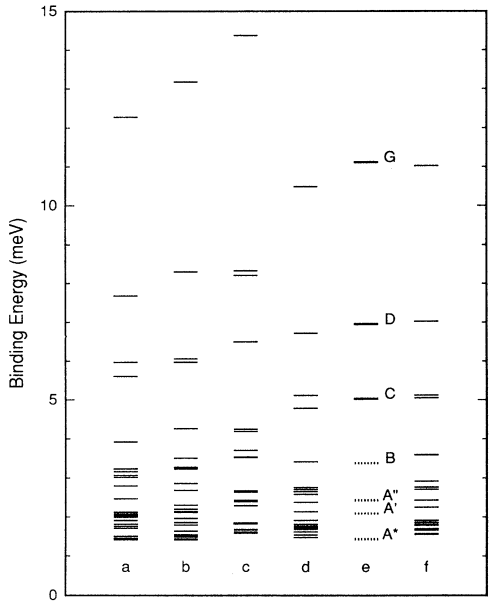

FIG. 2. Odd-parity acceptor spectra of GaAs calculated with the Luttinger parameters proposed by Skolnick *et al.* (Ref. 2) (spectrum a), Hess *et al.* (Ref. 3) (spectrum b), Neumann, Nöthe, and Lipari (Ref. 5) (spectrum c), Shanabrook *et al.* (Ref. 6), and Molekamp *et al.* (Ref. 7) (spectrum d). The spectrum e is the excitation spectrum of GaAs:C measured by Kirkmann, Stradling, and Lin-Chung (Ref. 9) where the absolute binding energies have been obtained using an ionization energy of 26.3 meV (see text). The spectrum f has been calculated with the parameters $\gamma_1 = 7.10$, $\mu = 0.719$, and $\delta = 0.124$, proposed in this work.

Varying γ_1 between 6.5 and 7.5, i.e., in a range sufficiently large to include all measured values of this parameter, calculations show that the E_1, E_2, and Δ values can be reproduced with $0.685 < \mu < 0.745$ and $0.105 < \delta < 0.145$. From accurate calculations of the acceptor levels in this range of parameter values, we derive the following analytical expressions for Δ, E_1, and E_2 in terms of γ_1, μ, and δ:

$$\Delta = \frac{\delta}{1-\mu}\left[0.2872+0.027\mu+\delta\frac{-1.021+1.58\mu}{1-\mu}\right] \mathrm{Ry}^* = (1.91 \pm 0.11)\ \mathrm{meV}, \tag{1}$$

$$E_1 = \frac{1}{1-\mu}\left[0.2965-0.099\mu+\delta^2\frac{-1.611+3.01\mu}{1-\mu}\right] \mathrm{Ry}^* = (11.10 \pm 0.15)\ \mathrm{meV}, \tag{2}$$

$$E_2 = \frac{1}{1-\mu}\left[0.2043-0.095\mu+\delta^2\frac{-0.59+1.13\mu}{1-\mu}\right] \mathrm{Ry}^* = (6.34 \pm 0.14)\ \mathrm{meV}, \tag{3}$$

where $\mathrm{Ry}^* = \mathrm{Ry}/\gamma_1\epsilon_0^2$ is the effective Rydberg, and $\epsilon_0 = 12.56 \pm 0.04$ the static dielectric constant[12] of GaAs. The second terms in Eqs. (1)–(3), with $6.5 \leq \gamma_1 \leq 7.5$, $0.685 < \mu < 0.745$, and $0.105 < \delta < 0.145$, reproduce our numerical results for Δ, E_1, and E_2 within 0.7%, 0.3%, and 0.2%, respectively.

For values of the parameters typical of GaAs, the quantities in brackets in the expressions for E_1 and E_2 are about constant, and E_1 and E_2 are approximatively proportional to $\mathrm{Ry}^*/(1-\mu)$, i.e., to the heavy-hole mass. The fact that the first excited states essentially depend on the heavy-hole mass makes an accurate determination of γ_1 very difficult, given the relatively wide range of experimental values available for E_1 and E_2. In fact, from our numerical results, we find that the experimental values restrict γ_1 only in the range $5 < \gamma_1 < 15$. For $6.5 \leq \gamma_1 \leq 7.5$, Eqs. (2) and (3) are not independent, only the lower limit on E_1 ($E_1 \geq 10.95$ meV) and the higher limit on E_2 ($E_2 \leq 6.48$ meV) restrict the acceptable sets (μ,δ) in the range of γ_1 considered. Taking into account these two limits, Eqs. (2) and (3) can be combined to give

$$\frac{1}{1-\mu}\left[0.2043-0.095\mu+\delta^2\frac{-0.59+1.13\mu}{1-\mu}\right] \mathrm{Ry}^* = [(6.835-0.06\gamma_1) \pm (0.06\gamma_1-0.355)]\ \mathrm{meV}, \tag{4}$$

which exactly reproduce the second condition and is slightly less restrictive (lower bound) than the first condition in the domain of band parameters allowed by Eq. (1) and $6.5 \leq \gamma_1 \leq 7.5$. The dependence of the right-hand side of Eq. (4) on γ_1 reflects the fact that the width of the (μ,δ) domain in parameter space decreases with γ_1 in the range of γ_1 values of interest.

The sensitivity of the first excited states to the light-hole mass or γ_1 is thus too weak to allow us to accurately determine all three band parameters. However, independent knowledge of the light-hole mass or of γ_1, together with the E_1, E_2, and Δ values, will allow us to determine very accurately the other two parameters. We already mentioned that among the three band parameters, γ_1 is by far the best known from earlier studies. The most accurate determination of γ_1 has been given by Neumann, Nöthe, and Lipari[5] as $\gamma_1 = 7.17 \pm 0.15$ from a fit of two-photon spectra of excitons in a magnetic field, while recent quantum-well spectroscopic data give[6,7] $\gamma_1 = 6.8 \pm 0.4$. We have decided to use a slightly different value of γ_1 which better corresponds to the compatibility range of the above two data, and which takes into account the fact that the cubic parameter δ proposed in Ref. 5 is much too small. We note that the authors themselves emphasized the difficulty of determining δ for GaAs from the two-photon spectra. In order to compensate for the unrealistically small value of δ, the fitting procedure[5] yielded a slightly increased value of γ_1, as can be seen from a comparison of the value of Ref. 5 with those of Refs. 2, 3, 6, and 7. Based on this consideration, we have decided to use $\gamma_1 = 7.10 \pm 0.15$, and from the relations (1) and (4) we find the following two band parameters:

$$\mu = 0.719 \pm 0.014, \quad \delta = 0.124 \pm 0.013, \tag{5}$$

or equivalently the Luttinger parameters $\gamma_2 = 2.02 \pm 0.15$, $\gamma_3 = 2.91 \pm 0.10$.

The odd-parity-state spectrum obtained with these values is shown in Fig. 2 (spectrum *f*). We note that good agreement between the calculated and experimental splittings is also obtained for acceptor levels with lower binding energy which have not been considered until now. For example, the $3P_{3/2}$ and $2P_{5/2}[\Gamma_7]$ levels are predicted to be quasidegenerate, in Fig. 2 (spectrum *f*), and this is consistent with the experimental spectrum, where only one line (line *C*) is observed.[9] Conversely, spectra *a* and *d* of Fig. 2 correspond to a much larger splitting between such levels, so that two lines should appear in the high-resolution infrared spectrum, since both transitions have non-negligible oscillator strength (we calculate that $f(3P_{3/2})/f(2P_{3/2}) \approx 1$ and $f(2P_{5/2}[\Gamma_7])/f(2P_{3/2}) \approx 12$ for GaAs:C). The energy of the $3P_{5/2}[\Gamma_8]$ state in spectrum *f* is also in relatively good agreement with the position of the *B* line. The higher excited states experimentally appear slightly more bound (by $\sim$0.3 meV) than predicted by our parameters. Such excited states, however, have a relatively large radius and are therefore especially

TABLE I. Light- and heavy-hole cyclotron masses and band effective masses calculated using the valence-band parameters $\gamma_1 = 7.10 \pm 0.15$, $\mu = 0.719 \pm 0.014$, and $\delta = 0.124 \pm 0.013$ proposed in this work, together with the corresponding experimental masses determined from cyclotron resonance by Skolnick *et al.* (Ref. 2) and from quantum-well spectroscopy by Shanabrook *et al.* (Ref. 6) and Molekamp *et al.* (Ref. 7). The cyclotron masses have been evaluated with the expressions given by Hensel and Suzuki in Ref. 1, and the band effective masses are given by $m_{l(h)}^*[100] = [\gamma_1 \pm \gamma_1(\mu + 6\delta/5)]^{-1}$, $m_{l(h)}^*[111] = (\gamma_1 \pm \gamma_1(\mu + 4\delta/5)]^{-1}$.

	Cyclotron masses			Band masses	
	Present work	Cyclotron resonance		Present work	Quantum-well spectroscopy
$m_h^{cycl}[100]$	0.45 ± 0.03	0.465 ± 0.02	$m_h^*[100]$	0.33 ± 0.03	0.34 ± 0.02
$m_l^{cycl}[100]$	0.085 ± 0.003	0.082 ± 0.004	$m_l^*[100]$	0.090 ± 0.004	0.094 ± 0.005
$m_h^{cycl}[111]$	0.60 ± 0.06	0.585 ± 0.02	$m_h^*[111]$	0.77 ± 0.12	0.75 ± 0.05
$m_l^{cycl}[111]$	0.080 ± 0.003		$m_l^*[111]$	0.077 ± 0.003	0.082 ± 0.005

sensitive to extended perturbations. The hole effective masses proposed in this work not only reproduce the acceptor spectroscopic data, but are also consistent with the results of cyclotron resonance and quantum-well spectroscopy. This is shown in Table I, where we give the band and cyclotron masses obtained with the new values of the band parameters, together with the corresponding experimental results.

The value $\delta = 0.124 \pm 0.013$ of the warping parameter determined from the acceptor spectra (using the cubic splitting Δ) is much larger than the values derived from measurements less sensitive to the valence-band anisotropy.[4,5] Instead, the large warping is consistent with cyclotron resonance data[2] and spectroscopic studies of GaAs/AlAs structures grown on substrates with different orientations.[6,7] The values $\gamma_1 = 6.8$, $\gamma_2 = 1.9$, and $\gamma_3 = 2.73$ ($\mu = 0.705$, $\delta = 0.122$) obtained from quantum-well data[6,7] yield, as mentioned before, an acceptor spectrum in Fig. 2 (spectrum *d*), which is not very different from the experimental data (spectrum *e*). This set of values is just at the outer boundary of the parameter domain given by Eqs. (1) and (4), and gives heavy-hole masses almost identical to those proposed here. The sets of parameters obtained from magnetospectroscopy of excitons,[3,5] $\gamma_1 = 7.17$, $\gamma_2 = 2.88$, and $\gamma_3 = 2.91$ ($\mu = 0.808$, $\delta = 0.004$), and $\gamma_1 = 6.85$, $\gamma_2 = 2.1$, and $\gamma_3 = 2.90$ ($\mu = 0.753$, $\delta = 0.117$) are not in the range allowed by Eqs. (1) and (4). It should be mentioned that exciton levels in GaAs are dominated by the electron effective mass. They also depend on the average hole mass γ_1^{-1}, but their sensitivity to μ and δ is very weak, so that the latter parameters cannot, in general, be determined precisely from exciton data.

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