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Effective-mass single and double acceptor spectra in GaAs

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Effective-mass acceptor spectra are calculated for GaAs using the Baldereschi-Lipari Hamiltonian inclusive of cubic terms and the split-off band. For single acceptors, calculated odd-parity states agree well with observed spectra; empirical central-cell corrections are included to treat even-parity states. A reevaluation is given of the ground-state binding energies of the various species. The ionized state of the "78-203" double acceptor is also considered: the calculated excited states reproduce well recent experiments.

I. INTRODUCTION

Infrared and Raman spectroscopies are important tools for studying impurities in semiconductors. Theoretical support to these techniques has also contributed important information to the identification of such centers. A milestone in the theoretical treatment of shallow impurities is the work by Lipari and Baldereschi,[1,2] who established the Hamiltonian of an acceptor in a cubic semiconductor within effective-mass theory (EMT). Both single[1,2] and double[3] acceptors in a number of semiconductors have been dealt with by this approach; spectral line intensities have also been studied.[4] Here I deal with the excitation spectra and binding energies of single acceptors in GaAs; in addition, the so called "78-203" double acceptor is considered.[13] For single acceptors in GaAs, the present work improves upon previous investigations,[2] which did not include cubic terms[1] in the acceptor Hamiltonian, nor dispersive impurity screening.[1] Both of these ingredients are taken into account here. The results are in remarkably good agreement with experimental observations.

Technical matters

The full effective-mass acceptor Hamiltonian,[1] including cubic and linear (see below) terms, split-off band coupling and dispersive screening, is used. The Luttinger parameters and dielectric constant used are[5] $\gamma_1 = 6.95$, $\gamma_2 = 2.24$, $\gamma_3 = 2.86$, and $\varepsilon_0 = 12.40$; other technical details of the solution procedure are analogous to those described in Refs. 1 and 3. The screened point-charge potential is used as impurity potential, which is a good approximation for the shallow states dealt with here. Dispersive (q-dependent) screening of the impurity potential is described by a wave-vector-dependent dielectric function parametrized by a "Thomas-Fermi wave vector" α. The latter is used as a free parameter to fit the function to the numerical results of Ref. 6, and its best value for GaAs is found to be $\alpha = 1.5$ a.u. The use of diagonal screening (i.e., the q-dependent $\mathbf{G}=\mathbf{G}'=\mathbf{0}$ part of the dielectric matrix) is a good approximation in a low-ionicity system such as GaAs, expecially for shallow states.

GaAs is a zinc blende compound, and its symmetry group (T_d) does not contain inversion. Therefore the valence band top states, whence the acceptor wave functions are predominantly built, have Γ_8 symmetry rather than Γ_8^+, the representation of the O_h cubic group appropriate for the diamond structure. Thus, there is no rigorous distinction between odd-parity (p-like) and even-parity (s-like) impurity states, and a term linear in the wave vector appears in the acceptor Hamiltonian, as shown in Ref. 2. While the formalism used here allows inclusion of this term, its leading coefficient is unknown for GaAs. However, it is known experimentally[7] that the valence band offset caused by this "fine structure" term is very small (of order 0.1 meV extrapolating at 2 K). Also, although the cubic selection rules could, in principle, be violated by, e.g., some IR transitions ending up in "even" final states, IR and Raman spectroscopy data[8] indicate a quite clear-cut distinction between odd- and even-parity final states in the spectra of acceptors in GaAs. It seems, therefore, safe to assume a vanishing leading coefficient for the linear term; indeed, tests show that the spectra are quite insensitive to small deviations of that parameter from zero.[9] A rigorous distinction is thus reestablished between odd (Γ_i^-) and even (Γ_i^+) states, and the O_h labeling convention will be used henceforth.

Using a perturbative approach beyond EMT, Altarelli, Hsu, and Baldereschi[10] have investigated (among others) the effects of high-wave-vector "*umklapp*" components in the impurity potential on the acceptor, and have estimated the ensuing site corrections to the ground-state binding energies of acceptors in semiconductors. While these effects are, in principle, beyond the limits of EMT, the resulting corrections are quite small for most cases (including GaAs), which indicates that the basic EMT approximations are admissible in simple semiconductors. The values of the site-dependent corrections are imported here from Ref. 10.

Before moving on to the results of the calculations, I give an example of the effects of the linear term in the Hamiltonian on acceptor energies for the case of InSb, for which the value of the leading coefficient is known.[2] In Ref. 2, where only a perturbative cubic correction was included, the single-acceptor EMT ionization energy was obtained to be 8.6 meV, without the linear term and 9.7 meV including it. The energies I obtain in the same cases are 9.7 meV and 10.8 meV, whereby the increase in binding energy must be attributed to the exact treatment of the cubic split-off band terms. The experimental value is 9.7 meV. However, in InSb (due to the small value of the gap, $E_g = 0.25$ eV), one should allow for coupling with conduction bands. On general grounds, such coupling will repel the acceptor level towards the valence band, decreasing the binding energy; indeed, I estimated that for InSb this effect cancels out the linear-term contribution, reestablishing the agreement with experiment.

II. RESULTS

A. Excited states and ionization energies of single acceptors

The calculated EMT ionization energy of the single acceptor is $E_{\mathrm{EMT}} = 32.9$ meV. Including site-dependent corrections,[10] one obtains $E_{\mathrm{Ga}} = 30.9$ meV and $E_{\mathrm{As}} = 38.9$ meV. If dispersive screening is neglected, one obtains $E_{\mathrm{EMT}} = 30.4$ meV. These values compare with previous results of about 26 meV.[2] It appears that both cubic term/split-off band contributions and dispersive screening are important (see also Ref. 3) in determining the ground-state energy.

Since an absolute ground-state binding energy cannot be experimentally determined with high precision, due to difficulties in identifying the ionization limit, the calculated and experimental line positions are aligned[3] to a common reference using as ionization energy a weighted average of the observed transition energies (usually the IR spectrum), increased by the corresponding calculated values. The calculated EMT binding energies of the odd-parity excited states are 12.55 meV (state Γ_7^-), 7.80 meV $(2\Gamma_7^-)$, 6.16 meV $(1\Gamma_6^-)$, and 5.72 meV $(3\Gamma_7^-)$. For a given impurity, one thus obtains the alignment of theoretical and experimental spectra, and an accurate experimental binding energy.

The experimental ground-state binding energies[5] are listed for several impurities in Table I. Theory compares favorably with these values. It is comforting that the experimental values closest to theory are those of the isocoric impurities Zn and Ge, for which one expects the smallest chemically-dependent "central-cell" corrections to the ground state. Also, it can be seen that these corrections can be of both signs.[3] The binding energy trends are indeed in qualitative agreement with the manner in which the difference of the *ab initio* ionic pseudopotentials[11] of the host and impurity atoms deviate from the Coulombic (point charge) behavior. For example, for C and Be, these differences (being essentially an unscreened impurity potential[12]) are appreciably repulsive in the core region.

TABLE I. New estimates of experimental ground-state binding energies (in meV) for acceptors in GaAs compared to EMT theoretical results. Isocoric impurities are closest to theory; chemical corrections can be of both signs.

Ga site		As site	
Be	28.6	C	27.6
Mg	29.4	Si	35.4
Zn	31.3	Ge	41.0
Theory	30.9		38.9

Next, I compare the calculated line positions with the experimental spectrum of Wagner *et al.*[8] in the lower panel of Fig. 1, for Zn on the Ga site and C on the As site. It is expected that the infrared transitions to odd-parity states be insensitive to the chemical nature of the impurity, since the final states have zero amplitude at the impurity site. The agreement of EMT results is indeed quite good with the main features of the infrared spectrum (lower panel of Fig. 1). On the other hand, the most prominent feature of the Raman spectrum of C and Zn in GaAs (upper panel of Fig. 1) is due to the $1\Gamma_8^+ - 2\Gamma_8^+$ transition from the ground state to the first even-parity state. The EMT binding energy of the state $2\Gamma_8^+$ is calculated to be 9.7 meV. Central-cell corrections due to the chemical nature of the impurity are generally

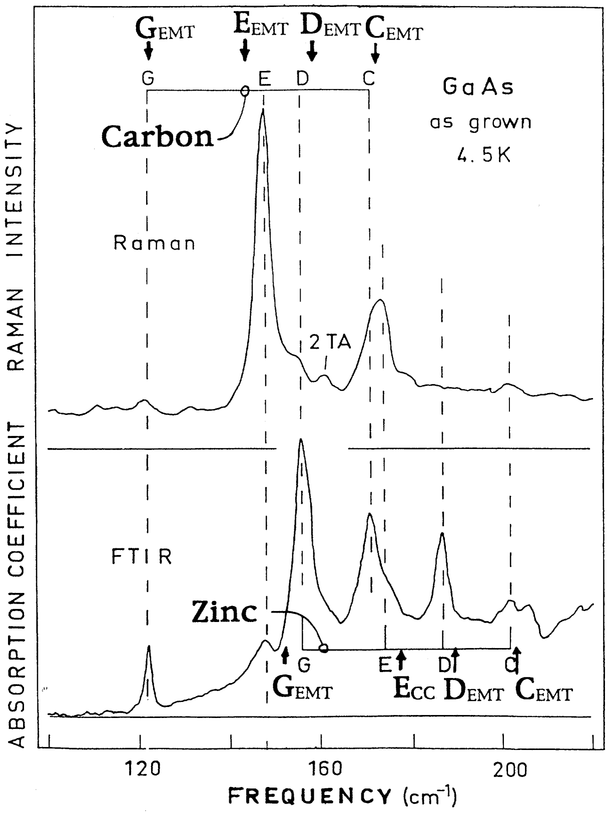

FIG. 1. Experimental spectra of the C and Zn acceptors in GaAs (after Wagner *et al.*, Ref. 8), compared with the present results. The theoretical and experimental line identification is displayed at the top and bottom of the figure for C and Zn, respectively. The theoretical line positions are indicated by arrows; the E_{CC} line for GaAs:Zn includes central-cell corrections. Upper panel: Raman spectrum; lower panel: IR spectrum.

relevant for these even-parity states, which have a sizable amplitude at the impurity site. I tentatively included such corrections for Zn using a short-range potential adjusted so as to fit the calculated ground-state energy to the experimental value. This potential is rather weak, and the position of the relevant line is quite insensitive to the correction. Indeed, as seen in Fig. 1, the corresponding EMT line positions are in good agreement with the observed ones for both C and Zn (which is isocoric to Ga). Some upward shift, which would improve agreement with experiment, is indeed expected for C:As, which has a sizable repulsive central-cell correction.

B. Ionized double acceptors

The full treatment of the ground state of double acceptors is very complicated.[3] However, ionized double acceptors can be dealt with in the same manner as single acceptors. The EMT binding energy for the singly-ionized double acceptor is somewhat sensitive to the screening treatment; with the present value of $\alpha = 1.5$, I calculate it to be 275 meV. An interesting case of double acceptor in GaAs is the well-known "78-203" center. Recently, Wagner *et al.* have recorded[13] quite detailed IR and Raman spectra of this impurity. I have investigated the excited states of the ionized configuration, including a short-range correction such as to adjust the calculated binding energy to the observed $E_B \simeq 203$ meV $[V_{sr}(r) = 3.0\,\mathrm{e}^{-2.0\,r}]$. The calculated excited states energies are compared to experiment[13] in Table II. The satisfactory agreement obtained for all states is quite encouraging, also considering that, while the odd-parity states are unaffected by the central-cell correction, the even-parity state is quite sensitive to it.

TABLE II. Experimental and calculated binding energies (in meV) of the excited states of the ionized "78-203" acceptor in GaAs.

	Expt.	Theory
Even	43.1	43.8
Odd	22.0	21.9
	31.0	30.9
	48.0	50.1

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[9] It should also be noted that "odd" and "even" essentially means "p type" or "s type" respectively, since as long as the impurity potential is spherical, the envelope function components affect only the inversion symmetry of the full impurity wave function, while deviations from cubic symmetry are due to the valence Bloch functions.

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