

## Acceptor binding energies in GaN and AlN

Francisco Mireles and Sergio E. Ulloa

*Department of Physics and Astronomy, and Condensed Matter and Surface Sciences Program, Ohio University,  
Athens, Ohio 45701-2979*

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We employ effective-mass theory for degenerate hole bands to calculate the acceptor binding energies for Be, Mg, Zn, Ca, C, and Si substitutional acceptors in GaN and AlN. The calculations are performed through the  $6 \times 6$  Rashba-Sheka-Pikus and the Luttinger-Kohn matrix Hamiltonians for wurtzite (WZ) and zinc-blende (ZB) crystal phases, respectively. An analytic representation for the acceptor pseudopotential is used to introduce the specific nature of the impurity atoms. The energy shift due to polaron effects is also considered in this approach. The ionization energy estimates are in very good agreement with those reported experimentally in WZ GaN. The binding energies for ZB GaN acceptors are all predicted to be shallower than the corresponding impurities in the WZ phase. The binding-energy dependence upon the crystal-field splitting in WZ GaN is analyzed. Ionization levels in AlN are found to have similar "shallow" values to those in GaN, but with some important differences which depend on the band structure parametrizations, especially the value of the crystal-field splitting used. [S0163-1829(98)00931-X]

### I. INTRODUCTION

Wide-band gap III-V nitrides, particularly Ga, Al, and InN, and their semiconductor alloys, are materials currently under intense study. Some of their most promising applications in optoelectronics devices are, for instance, the fabrication of blue/green light-emitting diodes,<sup>1</sup> laser diodes,<sup>2</sup> and "solar-blind" UV photodetectors.<sup>3</sup> The performance improvements of these and related optoelectronic devices depend strongly on the features of the intrinsic and extrinsic impurity defects in the nitride compounds. For example, defects and impurities provide free carriers under suitable conditions. Therefore, knowing the accurate position of the donor and acceptor levels of these systems is an issue of great importance in the understanding of optical properties and practical applications of these nitrides.

At present, Mg and Zn are the impurity materials most widely employed in the  $p$  doping of GaN. The experimental thermal ionization energy (acceptor binding energy) associated with Mg is estimated at 250 meV.<sup>4</sup> The highest doping achieved reaches hole concentrations of approximately  $3 \times 10^{18} \text{ cm}^{-3}$  at room temperature.<sup>5</sup> It is also known that in order to activate the dopants and improve the  $p$ -type conductivity, the samples must be treated with low-energy electron-beam irradiation, furnace annealing, or rapid thermal annealing after growth.<sup>6</sup> On the other hand, Zn doping seems to be inefficient because of its relatively deep ionization energy (340 meV).<sup>4</sup> Other dopants have been considered, but experimental problems like instability and/or hole compensation due to the formation of acceptor-H neutral complexes is still at issue. Estimates for the binding energies of several substitutional acceptors in GaN have been obtained in the past, mostly through photoluminescence spectra.<sup>4</sup> However residual impurities and defects in this material complicates the identification of these levels. In contrast, little is known about the doping and spectrum of impurity levels in AlN. In fact, no conclusive results for the doping of AlN with sufficiently high conductivity have yet been reported.

Apart from the question of successful  $p$  doping in GaN and AlN using various impurities, there are still at least two other important issues that are under scrutiny. The first one is related to the determination of the origin of the chemical shift observed in the acceptor spectrum levels in GaN, apparently induced by the differences in the cores of the various impurity atoms, and some possible lattice relaxation around the impurity atom.<sup>4</sup> The second question is whether acceptors with smaller binding energies ( $< 230$  meV) exist for wurtzite and zinc-blende GaN. The occurrence of relatively large ionization energies for acceptors in GaN has been attributed in part to the fact that the III-V nitrides are more ionic than other III-V compounds (such as GaAs, GaP, and InP), for which the acceptor binding energies are an order of magnitude smaller than those found in GaN. It has also been suggested that the enhanced binding energies found for some acceptors like Zn and Cd are associated to the relaxation of the  $d$ -electron core.<sup>7</sup> On the other hand, impurities without  $d$ -electron states, such as Mg, C, and Si, appear to induce rather shallow acceptor levels. Indeed, very recently, Park and Chadi<sup>8</sup> examined the stability of acceptor centers in GaN, AlN and BN using first-principles calculations. They concluded that the small bond lengths in III-V nitrides inhibit large lattice strain relaxations around impurities (mainly Be, Mg, and C), giving rise to relatively shallow states for these species. This would suggest that a similar lack of relaxation accompanies other substitutional impurities in these hosts, producing relatively shallow levels, as long as there are no  $d$  cores close to the valence-band energies.

Very recently, the formation energies and impurity levels for a few donor and acceptor species have been studied theoretically by several groups,<sup>9-13</sup> employing quantum molecular-dynamics schemes and total-energy calculations in the local-density approximation of density-functional theory. In general, consistency is found among those groups, as well as with experimental reports for some impurity levels, such as  $\text{Mg}_{Ga}$  acceptors ( $X_Y$  indicates the ion  $X$  substi-

tuting in the  $Y$  site). However, this is not the case for other acceptors like  $C_N$ , where discrepancies of factors of 3 exist among theoretical values. Although the calculated energy levels for these approaches appear reliable for most cases, the impurity levels reported for some acceptors are close to the systematic error bars introduced in the calculations. The delicate and complex nature of these calculations, which require intensive computations, suggests that alternative methods should be explored in the study of impurity levels in these systems. There is also, no doubt, the need for careful experiments in the better-characterized materials now available, to clarify these discrepancies. The features of the acceptor states in the different crystal phases, wurtzite (WZ) and zinc blende (ZB), have not been discussed either. In order to address these questions, here we present a contribution toward the theoretical treatment of the impurity levels in GaN and AlN based on the effective-mass approach for degenerate bands.

In this paper we report effective-mass theory calculations of the acceptor binding energies for various impurity atoms in GaN and AlN for both crystal structures WZ and ZB. Particular attention has been paid to chemical shifts introduced by the foreign atoms. An acceptor-pseudopotential model is used to take into account this effect. The approach used here is based on the effective-mass theory (EMT) for degenerate bands. Well-parametrized valence-band-structure calculations are used as input. The results obtained, with no adjustable parameters, are in very good agreement with experiments, as we will see below. Inevitably, the application of even a simple hydrogenlike model of acceptor states in group III-V semiconductors is more complicated than for idealized semiconductors with a single, isotropic and spin-degenerate valence band. The complications are due in part to the band warping and sixfold degeneracy or near degeneracy of the valence-band structure close to the  $\Gamma$  point ( $\mathbf{k} = 0$ ). Since the perturbing potential introduced by the foreign atoms can be seen to zeroth order as purely Coulomb-like, the problem can be seen as a generalized hydrogenic problem, where the kinetic structure of a hole, in the rather complicated valence-band structure of the III-V materials, is properly described by a  $6 \times 6$  matrix Hamiltonian which describes well the dispersion features of the various hole bands. The EMT calculations of the binding energies of Be, Mg, Zn, Ca, and C acceptor impurities are shown to be in very good agreement with the available experiments, and consistent in general with other theoretical calculations employing other methods (with the exceptions discussed above for C, for example). The applicability of EMT for the calculation of impurity levels with 0.2–0.4 eV binding energies is then verified *post facto*, likely due to the large band gap in these materials, which yields negligible mixing of conduction-band states.

Additionally, we find that the binding energies for acceptors in the ZB structures are predicted to be shallower than their counterparts in the WZ structures, suggesting that doping of ZB material would be of significant practical advantage. We notice that the difference on parameters, mainly the existence of a crystal-field splitting for the WZ nitrides, strongly affects the band mixing and correspondingly the binding energies in the two polytypes. It is also likely that differences in the hole masses contribute to the different cal-

culated binding energies. Although substitutional impurities do not represent a strict test of the different band parametrizations, the subtle interplay of the different valence bands on the resulting binding energies provides an interesting overall consistency check of the parametrized band structure.

The paper is organized as follows. In Sec. II, we present the characteristics of the generalized acceptor problem. The explicit matrix form of the ZB and WZ valence-band Hamiltonians are also given there. The trial form of the envelope wave functions is presented in Sec. III. The impurity pseudopotential model is discussed in detail in Sec. IV. The correction due to polaron effects is briefly described in Sec. V. The results and discussion are given in Sec. VI, and the conclusions in Sec. VII.

## II. GENERALIZED SHALLOW ACCEPTOR PROBLEM

Substitutional impurities with one fewer valence electron than the host atom of the pure crystal introduce well-localized acceptor states lying just above the top of the valence band structure. The theory of shallow donor and acceptor states in semiconductors has been reviewed in detail by Pantelides.<sup>14</sup> We assume, as usual, that all acceptor levels in the semiconductor are described within the effective-mass theory for degenerate band structures by the matrix equation

$$H(\mathbf{r})\mathbf{F}(\mathbf{r}) = [\mathcal{H}(\mathbf{r}) + U(\mathbf{r})\mathbf{1}]\mathbf{F}(\mathbf{r}) = E\mathbf{F}(\mathbf{r}), \quad (1)$$

where  $H(\mathbf{r})$  is the full acceptor Hamiltonian with eigenvalues  $E$  for the acceptor states. Here  $\mathcal{H}(\mathbf{r})$  is Hamiltonian properly constructed from crystal symmetry considerations, which entirely describes the spectrum and eigenvalues of a hole near the valence-band extremum at the  $\Gamma$  point. Symmetry-invariance group theory<sup>15,16</sup> and  $\mathbf{k} \cdot \mathbf{p}$  perturbation theory for degenerate bands<sup>17,18</sup> have been used to derive the proper effective-mass Hamiltonian for strained semiconductors depending upon the crystal structure.

The potential  $U(\mathbf{r})$  is the perturbation produced by the acceptor ion on the otherwise pure and periodic host crystal. In a simple idealized case,  $U(\mathbf{r})$  is taken to be the Coulomb potential  $U(\mathbf{r}) = e^2/\epsilon_o|\mathbf{r}|$ , where  $\epsilon_o$  is the static dielectric constant of the crystal,  $\epsilon(q=0, \omega=0)$ , representing a point charge in a dielectric medium. Notice that the screening of the simple hydrogenic potential by a dielectric function  $\epsilon(\mathbf{q})$  has been considered in the past as an approach to consider the contribution to the acceptor spectrum of the short-range potential from the real impurity.<sup>19</sup> Although this model gives an insight into the specific character of the different atomic acceptor levels, the model results in a generic value for all the impurity defects. This, clearly, neglects the chemical signature of the foreign atoms in the host material (the so-called central-cell contribution).<sup>14</sup> Given these limitations, instead we employ an *ab initio* pseudopotential  $U_{ps}(r)$  corresponding to the difference between the bare model potential of the impurity and the host atoms. Since the chemical correction induced by different species is expected to be small, and because the pseudopotential used is fairly smooth and without discontinuities, the effective-mass approach is expected to yield an appropriate description of the system. More details on the impurity potentials used are given in Sec. IV.

In Eq. (1),  $\mathbf{1}$  is the  $6 \times 6$  unit matrix and  $\mathbf{F}(\mathbf{r})$  is a column vector whose  $F_j(\mathbf{r})$  elements characterize the envelope func-

tion which modulates the Bloch functions  $\phi_j(\mathbf{r})$  of the unperturbed crystal at the top ( $\mathbf{k} \approx 0$ ) of the valence structure. Correspondingly, the wave functions for the shallow states are given by

$$\psi(\mathbf{r}) = \sum_{j=1}^6 F_j(\mathbf{r}) \phi_j(\mathbf{r}). \quad (2)$$

The trial form chosen for the envelope functions  $F_j(\mathbf{r})$  is discussed in detail in Sec. III. In the following subsections we briefly describe the explicit form of the hole Hamiltonian  $\mathcal{H}(\mathbf{r})$  for the two crystal polytypes (WZ and ZB), in which the bulk GaN and AlN semiconductors grow.

### A. Wurtzite valence-band Hamiltonian

In order to consider the motion of a carrier at the top of the valence band in a wurtzite semiconductor we must take into account its sixfold rotational symmetry, which induces a crystal-field splitting. Moreover, in the case of spin-orbit interaction, the  $\Gamma_{15}$  level splits into the  $\Gamma_9$  state, upper  $\Gamma_7$  level, and lower  $\Gamma_7$  level, corresponding to the heavy-hole, light-hole, and split-off hole bands.<sup>15</sup> The appropriate effective-mass Hamiltonian that reflects those features of the WZ GaN bulk crystal should thus be described by the Rashba-Sheka-Pikus (RSP) Hamiltonian,<sup>15,16</sup> as discussed recently by Sirenko *et al.*<sup>20</sup> In the vicinity of the valence-band maximum, and to second order in  $k$ , the six states (including the spin index) of the RSP Hamiltonian for unstrained WZ structures can be written explicitly in a matrix representation as follows:

$$\mathcal{H}_{\text{WZ}}(\mathbf{k}) = \begin{pmatrix} F & 0 & -H^* & 0 & K^* & 0 \\ 0 & G & \Delta & -H^* & 0 & K^* \\ -H & \Delta & \lambda & 0 & I^* & 0 \\ 0 & -H & 0 & \lambda & \Delta & I^* \\ K & 0 & I & \Delta & G & 0 \\ 0 & K & 0 & I & 0 & F \end{pmatrix}, \quad (3)$$

where

$$\begin{aligned} F &= \lambda + \theta + \Delta_1 + \Delta_2, \\ G &= \lambda + \theta + \Delta_1 - \Delta_2, \\ \lambda &= A_1 k_z^2 + A_2 k_{\perp}^2, \\ \theta &= A_3 k_z^2 + A_4 k_{\perp}^2, \\ H &= i(A_6 k_z k_+ + A_7 k_+), \\ I &= i(A_6 k_z k_+ - A_7 k_+), \\ K &= A_5 k_+^2, \\ \Delta &= \sqrt{2} \Delta_3, \end{aligned} \quad (4)$$

with  $k_{\perp}^2 = k_x^2 + k_y^2$  and  $k_{\pm} = k_x \pm i k_y$ . Here  $\Delta_1$  corresponds to the energy splitting produced by the anisotropy of the hexagonal symmetry,  $\Delta_2 = \Delta_{so}^{(z)}/3$  and  $\Delta_3 = \Delta_{so}^{(\perp)}/3$  are the energy

splittings for the  $z$  and perpendicular directions produced by the spin-orbit (SO) interaction.<sup>20</sup> The  $A$  constants are related to the inverse of the hole masses, in units of  $\hbar^2/2m_o$ , where  $m_o$  is the bare electron mass. Notice that when the linear terms in Eq. (3) are negligible ( $A_7=0$ ; which is in fact nearly the case in GaN and AlN), the RSP Hamiltonian has complete inversion symmetry. This symmetry allows for helpful simplifications in dealing with the acceptor problem in the envelope-function framework, as we discuss below.

### B. Zinc-blende valence-band Hamiltonian

In the case of semiconductors with a ZB structure, the hole wave functions characterizing the sixfold degenerate  $\Gamma_{15}$  state split, due to the effects of spin-orbit interaction, into fourfold-degenerate  $\Gamma_8$  states corresponding to heavy- and light-hole bands and spin-split-off hole states  $\Gamma_7$ .<sup>15</sup> A Hamiltonian which takes all these features of the cubic symmetry for ZB semiconductors into account is the well-known Luttinger-Kohn (LK) Hamiltonian,<sup>17</sup> which, at the valence-band extremum, and to second order in  $k$ , is expressed in terms of only four empirical parameters—the so-called Luttinger-Kohn parameters  $\gamma_1, \gamma_2$  and  $\gamma_3$ , and the spin-orbit splitting  $\Delta_o$ . Thus the LK Hamiltonian  $\mathcal{H}_{\text{ZB}}$  is written in matrix form as follows:

$$\mathcal{H}_{\text{ZB}}(\mathbf{k}) = \begin{pmatrix} P & L & M & 0 & N & S \\ L^* & Y & 0 & M & R & \sqrt{3}N \\ M^* & 0 & Y & -L & \sqrt{3}N^* & R \\ 0 & M^* & -L^* & P & -S^* & N^* \\ N^* & R^* & \sqrt{3}N & -S & W & 0 \\ S^* & \sqrt{3}N^* & R^* & N & 0 & W \end{pmatrix}, \quad (5)$$

where

$$\begin{aligned} L &= -2\sqrt{3}i\gamma_2 k_z k_-, \\ M &= \sqrt{3}\gamma_3(k_x^2 - k_y^2) - 2\sqrt{3}i\gamma_3 k_x k_y, \\ N &= \frac{i}{\sqrt{2}}L, \\ P &= \gamma_1 k^2 - \gamma_2(2k_z^2 - k_{\perp}^2), \\ Q &= \gamma_1 k^2 + \gamma_2(2k_z^2 - k_{\perp}^2), \\ R &= -\frac{\sqrt{2}}{3}i(P - Q), \\ S &= -i\sqrt{2}M, \\ W &= \frac{1}{3}(2P + Q) + \Delta_o, \\ Y &= \frac{1}{3}(P + 2Q). \end{aligned} \quad (6)$$

Here  $L, M, P$  and  $Q$  are in units of  $\hbar^2/2m_o$ . Notice that the higher symmetry of the ZB structure produces a much simpler  $\mathcal{H}(r)$  and fewer parameters than for the RSP case. In both cases, the operator  $\mathcal{H}(\mathbf{r})$  is obtained via the usual transformation  $k_\alpha \rightarrow i(\partial/\partial x_\alpha)$  in  $\mathcal{H}(\mathbf{k})$ .

### III. TRIAL FORM FOR THE ENVELOPE FUNCTIONS

To solve the effective-mass equation for degenerate bands [Eq. (1)], we use the fact that the effective-mass Hamiltonian is invariant under inversion with respect to the origin, so that the envelope functions  $F_j(\mathbf{r})$  can be chosen to have definite parity. Since the features of the acceptor problem are rather like those of a hydrogeniclike problem, it has proved convenient to choose the envelope functions basically as an expansion in spherical harmonics and a linear combination of hydrogeniclike radial functions. In particular, we have chosen the explicit form

$$F_j(\mathbf{r}) = \sum_{l,m} f_l^j(r) Y_{lm}(\theta, \phi), \quad (7)$$

summing over all  $l$  even (or odd), and with radial functions for a given hole band  $j$  and angular momentum quantum number  $l$  of the form

$$f_l^j(r) = \sum_{i=1}^N A_i^j r^l e^{-\alpha_i r}. \quad (8)$$

In this work, however, we are mostly interested in the ground state (the highest binding acceptor state), and in such a state only even  $l$  will contribute to the expansion—as one would expect for a ground state with even parity. This convenient simplification can be relaxed straightforwardly if desired, with little effect on the results. For numerical convenience, we find it useful to minimize or evaluate the acceptor binding energy, choosing  $\alpha_i$ 's in the progression  $\alpha_k = \alpha_1 e^{\beta(k-1)}$ , such that  $\beta = (N-1)^{-1} \ln(\alpha_N/\alpha_1)$ , and the end point conditions are chosen as  $\alpha_1 = 1.2 \times 10^{-2} a_o^*{}^{-1}$ , and  $\alpha_N = 3.5 \times 10^2 a_o^*{}^{-1}$ . Here  $a_o^* = \tilde{\gamma}_1 \epsilon_o a_o$  is the effective Bohr radius, and  $\tilde{\gamma}_1$  is defined by

$$\tilde{\gamma}_1 = \begin{cases} -(2m_o/\hbar^2)(A_2 + A_4) & \text{for WZ} \\ \gamma_1 & \text{for ZB,} \end{cases} \quad (9)$$

such that the effective Rydberg energy is defined as  $E_o^* = m_o e^4 / 2\hbar^2 \tilde{\gamma}_1 \epsilon_o^2 = e^2 / 2a_o \tilde{\gamma}_1 \epsilon_o$ . The range of  $\alpha_i$  values was designed to cover a wide spectrum of length scales. In the limit case of  $\tilde{\gamma}_1 = \epsilon_o = 1$  (with  $N=25$  and for  $l=0$  and 2, one obtains the hydrogen spectrum, so that for the first five states we obtain (in Ry)  $E_1 = 1.0000$ ,  $E_2 = 0.2500$ ,  $E_3 = 0.1111$ ,  $E_4 = 0.0625$  and  $E_5 = 0.0399$ , as expected.

### IV. IMPURITY ATOM PSEUDOPOTENTIAL

As mentioned above, a simple hydrogenic (scaled Coulomb) potential would not yield the observed variations in the binding energy of acceptor states for different impurity atom species. Photoluminescence measurements show indeed important differences in the acceptor binding energies in WZ GaN for different impurities.<sup>4</sup> To study those ‘‘chemi-

cal’’ shifts one needs to use impurity potentials properly constructed to insure that their physical properties reflect the expected shifts. The impurity potential here is obtained from an analytical representation of the pseudopotential for the bare impurity and host atoms. The analytic form follows Lam, Cohen and Zunger,<sup>21</sup> who fit the first-principles pseudopotentials developed earlier by Zunger and Cohen<sup>22</sup> in a density-functional formalism. Notice then that the acceptor potential is truly an impurity pseudopotential, having its origin in *ab initio* calculations. The pseudopotential for a bare atom can be written as<sup>21</sup>

$$U_{ps}(r) = \sum_l V_{ps}^l(r) \hat{P}_l - \frac{Z_v}{r}, \quad (10)$$

with

$$V_{ps}^l(r) = \frac{C_1^l}{r^2} e^{-C_2^l r} - \frac{Z_c}{r} e^{-C_3 r}, \quad (11)$$

where  $V_{ps}^l(r)$  represents the atomic core pseudopotential.  $\hat{P}_l$  is the projection operator which picks out the component of the wave function with angular momentum number  $l$ . The constants  $C_1^l$ ,  $C_2^l$  and  $C_3$  are the fitted parameters, with  $Z_c$ , and  $Z_v$  representing the core and valence electron charges, respectively, as defined in Ref. 21. The first term in Eq. (11) represents a potential barrier which replaces the kinetic energy of the true valence states, while the second term arises from electrostatic screening of the nucleus by the core electrons and exchange-correlation forces. Using these pseudopotentials, the impurity model potential is constructed as follows.

When the substitutional impurity atom replaces the host atom in the crystal, the impurity potential is defined as the difference between the impurity and host ion pseudopotentials. If  $l=0$ , for instance,

$$U(r) = \frac{e^2}{\epsilon_o} \Delta V_{ps}^o(r) - \frac{\Delta Z_v e^2}{\epsilon_o r}, \quad (12)$$

with

$$\Delta V_{ps}^o(r) = \pm [V_{ps,host}^o(r) - V_{ps,imp}^o(r)] \quad (13)$$

for  $Z_{host} \cong Z_{imp}$ .

Here,  $\Delta Z_v = Z_v^{host} - Z_v^{imp}$  ( $=1$  for single acceptors), and  $\epsilon_o$  is the dielectric constant of the host lattice. Clearly the first term in  $U(r)$  corresponds to the net potential produced by the difference between the bare core potentials of the impurity and the host; it is the short-range part. The last term is the long-range Coulombic potential due to the difference in the valence charge  $\Delta Z_v$ . The static dielectric constant  $\epsilon_o$  is introduced here to reflect the effect of the lattice polarizability (screening) of the host crystal. Notice that in this approach the net effect of the redistribution of charge near the impurity defect, and the accompanying screening of the foreign charge at ‘‘large’’ distances (several lattice units) are considered fully in the pseudopotential definition.

In a different approach, frequent in the literature,<sup>29</sup> the role of the pseudopotential is partly simulated using a  $q$ -dependent screening function  $\epsilon(q)$  ( $\rightarrow \epsilon_o$  for  $q \rightarrow 0$ ) in

TABLE I. Comparison between the experimental and EMT pseudopotential models of the acceptor binding energy for various impurities species in GaAs ( $\epsilon_o=12.4$ ). The energies are in meV. The experimental values and band parameters are taken from Ref. 40.

	C	Mg	Zn
Expt.	27.0	28.7	30.6
Theor.	27.4	27.7	28.3

the simple hydrogenic-style impurity potential. We avoid using  $\epsilon(q)$  thanks to the impurity-specific pseudopotential. We believe our approach to be better in this problem, as it requires no further adjustable parameters and yields the expected chemical shifts quite accurately.

To provide a simple and independent test of the model, we have calculated the binding energies for several acceptors in the well-characterized semiconductor GaAs. The results are shown in Table I. The theoretical binding energies are in excellent agreement with the experimental values, with no additional parameters.

## V. POLARON CORRECTION

We should also notice that since the nitride semiconductors (GaN and AlN) are polar materials, one would expect that the electron-LO-phonon coupling would introduce corrections to the bound states. In order to obtain an estimate of such a correction, we assume that the polaron contribution to the acceptor binding energy close to the  $\Gamma$  point is diagonal in the band index. Therefore the acceptor binding energies will be enhanced by  $[1 + \alpha_F(m_j^*)/6]E_{o,j}^*$  up to first order in the Fröhlich coupling constant  $\alpha_F$  for each hole band. This coupling constant is defined by<sup>23</sup>

$$\alpha_F(m_j^*) = \left( \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_o} \right) \left( \frac{E_o}{\hbar\omega} \frac{m_j^*}{m_o} \right)^{1/2}, \quad (14)$$

where  $E_o$  is one Ry,  $E_{o,j}^*$  is the ground-state energy of the impurity acceptor without the polaron correction,  $\hbar\omega$  is the LO-phonon energy, and  $m_j^*$  is the average  $j$ -hole effective mass. In this way, the contribution of each hole band to the polaron energy is taken into account explicitly in the multi-band calculation. Let us note that the resulting polaron correction is relatively small (not greater than 8%) in all cases, as shown in the tables below, despite the polar nature of these materials. This is presumably due to the fact that the coupling constant associated with each hole band is relatively small ( $\leq 1.5$ ) in all cases.<sup>24</sup>

## VI. RESULTS AND DISCUSSION

Since the reported values of effective-mass parameters obtained by different approaches for both the RSP and LK Hamiltonians may have significant discrepancies, we have used different sets of parametrizations in order to compare the resulting impurity states.<sup>25-30</sup> For the wurtzite system (Tables II and III), we use Kim *et al.*'s<sup>25</sup> RSP parametrizations obtained by full-potential linearized muffin-tin orbital band-structure calculations, in which the spin-orbit coupling

TABLE II. The Rashba-Sheka-Pikus valence-band parameters for wurtzite GaN. The hole parameters  $A_i$  are in units of  $\hbar^2/2m_o$ , while  $\tilde{\gamma}_1$  is dimensionless;  $\Delta_i$  values represent the energy splittings in meV;  $E_o^*$  is the effective Rydberg energy in meV. We use  $\epsilon_o=9.5$  as the dielectric constant in GaN. Signs of the  $A_5$  and  $A_6$  parameters of Ref. 25 have been changed to be consistent with those in the definition of the usual RSP Hamiltonian.

Ref.	WZ GaN			
	25	26	27	28
$A_1$	-6.4	-6.27	-6.4	-7.24
$A_2$	-0.5	-0.96	-0.8	-0.51
$A_3$	5.9	5.70	5.93	6.73
$A_4$	-2.55	-2.84	-1.96	-3.36
$A_5$	-2.56	-3.18	-2.32	3.35
$A_6$	-3.06	-4.96	-3.02	-4.72
$\Delta_1$	36	73	24	22
$\Delta_2$	5.0	5.4	5.4	11/3
$\Delta_3$	5.9	5.4	6.8	11/3
$\tilde{\gamma}_1$	2.91	3.80	2.76	3.87
$E_o^*$	51.8	39.7	54.6	39.0

effects were obtained via the atomic-sphere approximation. We have also used Ref. 26's RSP parameters obtained by full potential linearized augmented plane-wave calculations; a different set reported in Ref. 27 based on the norm-conserving pseudopotential plane-wave method, and a fourth set obtained in Ref. 28, whose authors employed an empirical pseudopotential method. Notice that differences in parameters between these two groups are typically small, but can be substantial in some cases (such as the value of the crystal-field splitting  $\Delta_1$ ), having important consequences on the binding energy calculations, as we see later.

In the case of zinc-blende structures, the LK hole-parameters used are those reported in Refs. 25 and 26, as

TABLE III. The Rashba-Sheka-Pikus valence-band parameters for wurtzite AlN. We use  $\epsilon_o=8.5$  as the dielectric constant in AlN. Parameters have the same units as indicated in Table II. Notice the enormous discrepancy in the crystal-field splitting  $\Delta_1$  between Refs. 25, 27, and 26.

Ref.	WZ AlN		
	25	26	27
$A_1$	-3.86	-4.06	-3.82
$A_2$	-0.25	-0.26	-0.22
$A_3$	3.58	3.78	3.54
$A_4$	-1.32	-1.86	-1.16
$A_5$	-1.47	-2.02	-1.33
$A_6$	-1.64	-3.04	1.25
$\Delta_1$	-215	-58	-219
$\Delta_2$	6.8	6.8	6.6
$\Delta_3$	5.7	6.8	6.7
$\tilde{\gamma}_1$	1.57	2.12	1.38
$E_o^*$	119.9	88.8	136.5

TABLE IV. The Luttinger-Kohn valence-band parameters for zinc-blende GaN and AlN. Here the dimensionless  $\gamma_i$  are the hole band parameters;  $\Delta_o$  is the energy splitting due to spin-orbit interaction at the  $\Gamma$  point, and  $E_o^*$  are given in meV.

Ref.	ZB GaN			ZB AlN	
	25	26	29	25	26
$\gamma_1$	2.46	2.70	2.94	1.40	1.50
$\gamma_2$	0.65	0.76	0.89	0.35	0.39
$\gamma_3$	0.98	1.07	1.25	0.59	0.62
$\Delta_o$	19	20	17	19	20
$E_o^*$	51.3	55.8	49.3	134.5	125.5

mentioned above, and a third set in Ref. 29 based on pseudo-potential calculations. These parameters are summarized in Table IV.

We first examine our results for the acceptor levels in WZ nitrides. We should emphasize here that the experimental values of the acceptor levels in WZ GaN are not without controversy. Nevertheless, in order to show a trend of the binding energies for different dopants, we compare our theoretical calculations with the experimental values in the literature. For GaN, the results are listed in Table V (theoretical binding energy values are reported here to the nearest meV, but are calculated with much higher numerical accuracy for each set of parameters). We note that in general the binding energies for different impurities are in good agreement with those values observed in experiments. For instance, our calculations with the parameters of Ref. 26 give rise to a binding energy for  $\text{Be}_{\text{Ga}}$  and  $\text{Mg}_{\text{Ga}}$  (241 and 253 meV, respectively, with the polaron correction included) which would seem to be in better accord with the reported experimental value (250 meV). Indeed, Salvador *et al.*<sup>31</sup> recently reported room-temperature photoluminescence spectra of Be-doped GaN films. They found strong features in the 390–420-nm range which were attributed to the acceptor state formed by Be at about 250 meV above the valence-band edge. Even though residual impurities could also be responsible for this level, no experiments have been reported to confirm either claim. Very recently, Bernardini *et al.*,<sup>10</sup> using first-principles calculations, predicted that Be is a shallow acceptor in GaN with a binding energy (BE) of only 60 meV, in clear contrast with our calculations and with the experimental data. It is interesting to note, however, that our BE's for Mg ( $\sim 200$ – $250$  meV) are in satisfactory agreement with those theoretical values obtained from first principles calculations in Refs. 12 ( $\sim 230$  meV) and 11 ( $\sim 200$  meV).

In contrast, the binding energies with parameters from Ref. 26, for Zn and C impurities, are overestimated with respect to the experimental values (presumably due to the high value of the crystal field reported in Ref. 26). In principle we should expect the best fit precisely for these impurities, since they are isocoric with Ga and N, respectively, which would produce negligible local relaxations and core polarization effects. The best agreement occurs when we use the parameters from Ref. 25, suggesting that their parameter set is somewhat better. For example, for  $\text{Zn}_{\text{Ga}}$  in GaN, we obtain a BE of 331 meV using the parameters of Ref. 25, which is in good agreement with the experimental value of

TABLE V. Comparison between the calculated acceptor binding energies and experimental values for different substitutional impurities in wurtzite GaN.  $E_b^{**}$  and  $E_b^*$  denote the estimated binding energies with and without the polaron correction. All energies are in meV. The binding energies are obtained with band parameters from Refs. 25, 26, 27, and 28, respectively, arranged in descending order for each impurity.

Impurity <sub>site</sub>	WZ GaN		
	$E_b^*$	$E_b^{**}$	$E_b$ (Expt.)
$\text{Be}_{\text{Ga}}$	193	204	250 <sup>a</sup>
	233	241	
	195	208	
	185	193	
$\text{Mg}_{\text{Ga}}$	204	215	250 <sup>b</sup>
	245	253	
	208	221	
	197	204	
$\text{Zn}_{\text{Ga}}$	321	331	340 <sup>b</sup>
	411	419	
	394	406	
	352	360	
$\text{Ca}_{\text{Ga}}$	248	259	
	297	305	
	264	276	
	247	255	
$\text{C}_\text{N}$	220	230	230 <sup>c</sup>
	264	272	
	228	240	
	214	223	
$\text{Si}_\text{N}$	192	203	
	231	239	
	193	205	
	183	191	

<sup>a</sup>Reference 31.

<sup>b</sup>Reference 4.

<sup>c</sup>Reference 32.

340 meV, and in excellent agreement with the theoretical value reported by Bernardini *et al.* (330 meV).<sup>13</sup> Concerning the  $\text{C}_\text{N}$  substitutional impurity in a N site, we find that, with the exception of the parameters of Ref. 26, all the hole band sets give BE's (223–240 meV) comparable to the experimental value of 230 meV from Fischer *et al.*<sup>32</sup> Note that using the parameters of Ref. 25 gives an acceptor level just even with the experimental value, in a nice but probably fortuitous agreement, considering the possible sources of systematic errors.<sup>33–36</sup> Boguslawski *et al.*<sup>9</sup> also predicted an ionization energy for  $\text{C}_\text{N}$  of  $\sim 200$  meV, while Fiorentini *et al.*<sup>12</sup> reported a deeper ( $\sim 600$  meV) value. The formation energy for this impurity is found to be substantially different (1.4 eV) between those authors. The relatively higher relaxation effects predicted by Ref. 9 seem to play a more crucial role here. Similar discrepancies are found between the

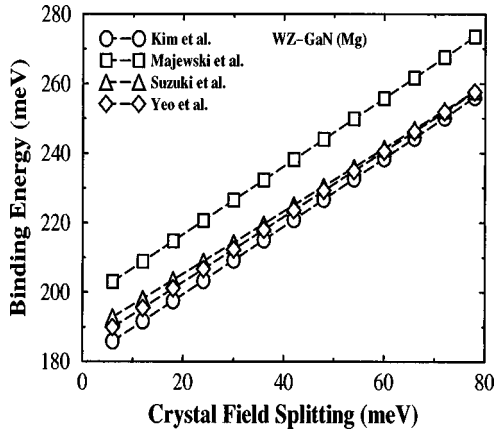


FIG. 1. Binding energies vs crystal-field splitting  $\Delta_1$ , in the  $\text{Mg}_{Ga}$  WZ GaN system for different parametrizations. Different symbols correspond to binding-energy values obtained from the effective-mass parameters,  $\circ$  for Ref. 25,  $\triangle$  for Ref. 26,  $\square$  for Ref. 27, and  $\diamond$  for Ref. 28, respectively.

present work and other calculations for  $\text{Ca}_{Ga}$  and  $\text{Si}_N$ .<sup>9</sup> We found that  $\text{Ca}_{Ga}$  has an acceptor level ( $\sim 260$  meV) close to that of the Mg. It is interesting to note that temperature-dependent Hall measurements of Ca-doped GaN have shown that the thermal ionization energy level of Ca ( $\sim 0.17$  eV) is similar to that found in Mg ( $\sim 0.16$  eV).<sup>37,38</sup> This could indicate that the acceptor binding energy for Ca is also close to that for Mg, as we have indeed predicted. Similarly,  $\text{Si}_N$  was found to have a rather shallow level in WZ GaN at about 0.2 eV. While the donor behavior of Si is well known, no reliable experimental proof of Si acceptor has been reported.

The collection of results discussed above indicates that the parametrization of Kim *et al.*<sup>25</sup> leads to acceptor binding energies in overall better agreement with the experiments and other theoretical estimates. Notice, however, that the differences in binding energies in GaN with other sets of parameters are not large in most cases, within a few percent from each other.

We would now like to comment on the effect of the crystal-field splitting on our calculations. Whereas recent experiments seem to indicate that the  $\Delta_1$  value is about 10 meV,<sup>33-35</sup> the theoretical estimates are still controversial, varying between 22 and 73 meV for GaN depending upon the approach used.<sup>25-28</sup> For example, Refs. 25 and 26 obtained  $\Delta_1 = 36$  and 73 meV, respectively. The former authors attributed the large theoretical discrepancy to the use of an ideal-cell internal structure parameter  $u$  in Ref. 26, instead of the relaxed one. In any case, to illustrate the effect of the binding energies upon the  $\Delta_1$  value, in Fig. 1 we show their dependence on this parameter for  $\text{Mg}_{Ga}$  in WZ GaN, over a wide range. A rather monotonic behavior is seen in the binding energies, as one would expect. Note that for all parameter sets (with exception of those in Ref. 27) the BE's are consistently close for each  $\Delta_1$  value. Note that using the experimental value of 10 meV for  $\Delta_1$  would produce smaller binding energies, giving values of about 0.19 eV, regardless of the set employed. The behavior for other dopants shows an analogous trend, where the energy shift on the binding energy is nearly the difference in  $\Delta_1$  values. This discussion indicates that additional experimental evidence for a smaller

TABLE VI. Calculated acceptor binding energies for different impurities in wurtzite AlN. Binding energies are set in descending order for parameters from Refs. 25, 26, and 27, respectively. The large discrepancy in the calculated values is mostly due to the important differences in the crystal-field splitting used.

Impurity <sub>site</sub>	WZ AlN	
	$E_b^*$	$E_b^{**}$
$\text{Be}_{Al}$	223	262
	446	472
	283	253
$\text{Mg}_{Al}$	465	514
	758	795
	721	789
$\text{Zn}_{Al}$	219	255
	438	464
	273	343
$\text{Ca}_{Al}$	204	240
	376	402
	203	273
$\text{Si}_N$	214	250
	415	441
	245	315

$\Delta_1$  value, and comparison with better optimized estimates, would be of interest.

The results for AlN in the wurtzite structure are given in Table VI. The first thing to notice here is that due perhaps to the large discrepancy in  $\Delta_1$  values,  $-215$ ,  $-219$ , and  $-58$  meV for Refs. 25, 27, and 26, respectively, the binding energies differ by almost a factor of 2 for different parameter sets. Notice further that values of  $A_5$  and  $A_6$  also differ substantially for different authors, strongly affecting the band mixing and corresponding binding energies. Given the better agreement of Ref. 25's parameters in WZ GaN, we are inclined to think that the corresponding results in WZ AlN will be perhaps closer to the experimental results. Unfortunately, as we mentioned earlier, the experimental spectrum for acceptors in AlN is unknown at present (due to the well-known difficulties in doping this material<sup>4</sup>). Further scrutiny of the parameters reported by these and future authors should be carried out to solve the disagreements. Notice that the BE of  $C_N$  in WZ AlN is found to exceed 0.65 eV in our calculations for all three sets of parameters (not shown in Table VI). This value, perhaps in the limit of validity of our EMT calculations, suggests, nevertheless that such an impurity will yield a somewhat deeper level than those reported in Table VI. Although substitutional impurity calculations do not represent a strict test of the band parametrizations, the subtle interplay of the different valence bands on the resulting binding energies (or even excited impurity states) provide an interesting overall consistency check.

For the ZB phase, we notice that predicted binding energies are consistently smaller (by nearly a factor of 2) than in the WZ structure of GaN. Indeed, typical differences of

TABLE VII. Acceptor states for zinc-blende GaN and AlN. The three values shown for impurities in GaN correspond to those calculated with the parametrizations given by Refs. 25, 26, and 29, respectively. The two values for AlN correspond to Refs. 25 and 26.

Impurity	ZB GaN		ZB AlN	
	$E_b^*$	$E_b^{**}$	$E_b^*$	$E_b^{**}$
Be	124	133	265	292
	117	125	248	273
	126	133		
Mg	130	139	333	360
	123	130	305	330
	133	140		
Zn	170	178	261	288
	155	162	245	269
	177	184		
Ca	153	162	242	268
	143	151	227	252
	157	164		
C	138	147	353	380
	130	138	320	345
	141	148		
Si	123	132	255	281
	117	125	239	264
	125	132		

roughly 100 meV are found in the binding energies between the two phases (ZB and WZ) in this material. This would have important consequences in electronic uses once doping of ZB phases is stabilized. Concerning the resulting impurity binding energies for GaN, we observe that the LK parameters given by Refs. 25, 26, and 29 give rise to binding energies which are in close agreement with each other. We should also comment that a different set of band parameters in the ZB phase was given by Meney and O'Reilly, using a semiempirical perturbative approach.<sup>30</sup> However, using these parameters result in BE's much smaller than those presented here. This difference, even greater in the binding energies for ZB AlN, reflects the more approximate nature of the parameters in Ref. 30. Notice that the Luttinger  $\gamma$  parameters in Ref. 25 are slightly smaller than in Ref. 26 (or equivalently, slightly larger effective masses), which would be expected to yield slightly larger BE's for the former set of parameters, as is clearly seen in Table VII.

Recent PL spectra of cubic GaN by As *et al.*<sup>39</sup> claimed, as indeed we have predicted in our calculations, that acceptor BE's for cubic GaN may have energies shallower than these in wurtzite GaN. Acceptor energies of about 130 meV were estimated by these authors. This in very good agreement with our calculations; as we can see in Table VII, the BE's ranges from  $\sim 130$  meV for Si to  $\sim 180$  meV for Zn. This acceptor level has not been identified, and it is probably produced by residual impurities.

The smaller binding energies in ZB, with respect to im-

purities in the WZ structure, is an interesting result that should be understood in terms of the different band-structure parameters. Notice, however, that the difference in the effective Rydberg energy for WZ and ZB GaN is not large at all, as seen in Tables II and IV. Similarly, the effective Bohr radius for both structures is nearly the same, as illustrated in the fact that  $\tilde{\gamma}_1$  is of the same order in both cases, and that the dielectric constant for both polytypes has been taken as  $\epsilon_o=9.5$ . The polaron correction is certainly also relatively small, and is therefore not a possible source of the binding-energy difference in these polytypes. However, the parameter that apparently gives rise to these large shifts in the acceptor energies could be identified with the in-plane heavy-hole mass, which is indeed larger in wurtzite than in zinc blende for both GaN and AlN, and hence produces larger binding energies. In order to verify the effect of the different effective masses in the two polytypes, we have calculated the acceptor levels for WZ GaN using the quasicubic sets of parameters of Ref. 25, with the same crystal-field splitting as obtained for the nonquasicubic set. It turns out that the binding energies are correspondingly smaller, which confirms our assumption. One should also mention that, just as seen in Fig. 1, a vanishingly small  $\Delta_1$  (as is the case in ZB) would produce an even smaller binding energy for a given impurity. (This would also explain the agreement among the three sets of parameters, since  $\Delta_1$  differences are the most significant for different authors.) We then conclude that it is in fact a combination of the crystal-field splitting and slightly larger hole masses that produces larger binding energies in the WZ structure than in the ZB structure. An interesting and important effect of the different lattice and band structures.

## VII. CONCLUSION

We have carried out calculations for the shallow acceptor energies associated with different substitutional impurity atoms in GaN and AlN hosts. The calculations were performed within the effective-mass theory, taking into consideration the appropriate valence-band Hamiltonian symmetries for the WZ and ZB polytypes, and using the full  $6 \times 6$  acceptor Hamiltonian and including the actual spin-orbit energy splitting. In addition, the impurity pseudopotential and the electron-phonon (polaron) correction has been explicitly considered. These more realistic treatments allow us to compare directly with the observed data and verify that our calculation produces the appropriate "chemical shifts." Indeed, our calculations of the acceptor binding energies are in quite good agreement with photoluminescence experiments, as the introduction of the impurity pseudopotential seems to be an excellent model to describe the chemical shifts associated with each impurity atom. It is interesting that good fits were found without any adjustable parameters in the calculation, once the contribution due to the electron-phonon polar interaction was included. We find that small differences in the hole effective-mass parameters could lead to relatively large discrepancies in the binding energies. Our overall evaluation of parameters suggests that better BE values are obtained with the parameters in Ref. 25. Correspondingly, we refer the reader to the first line in each impurity case in Tables V, VI, and VII, for what we consider the best BE estimates,



within an error a few percent. Further refinement of experimental values would be desirable to set narrower constraints on the theoretical values. We also find that the binding energies for acceptors in ZB structures are much shallower than their counterparts in WZ structures, perhaps suggesting a much more efficient carrier doping in those systems (still to be observed experimentally).

Finally, we should mention that preliminary studies of the strain effects on the acceptor binding energies show an increase as the strain increases, although with a much stronger

dependence than in other III-V materials. A complete report of these studies will be presented elsewhere.

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