Valence-band splittings in cubic and hexagonal AlN, GaN, and InN

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Modern parameter-free band-structure calculations are applied to the uppermost valence bands near the Γ point. They are based on a nonlocal exchange-correlation starting point for the iteration of the quasiparticle equation and include spin-orbit interaction. The Ga 3*d* and In 4*d* electrons remarkably influence the valence-band splittings. Quasiparticle effects shrink the crystal-field splitting Δ_{cf} for GaN and increase the inverted $\Gamma_1-\Gamma_5$ distance for AlN. Beyond the quasicubic approximation, we find a small anisotropy of the spin-orbit splittings. While for AlN Δ_{so} does only weakly depend on the crystal structure, variations are found between zinc blende and wurtzite for GaN or InN. © *2010 American Institute of Physics*. [doi:10.1063/1.3524234]

The group-III mononitrides AlN, GaN, InN, and their alloys are among the most intensively investigated semiconductors for light emitting devices, laser applications, and photovoltaics. However, the electronic band structures, especially of InN, continue to be a subject of debate. In particular, the details of the valence bands are controversially discussed. Also, the influence of the polytype, i.e., zinc blende (zb) or wurtzite (wz), and of the spin-orbit coupling Δ_{so} (SOC) is not understood. While the smallness of the crystal-field (cf) splitting Δ_{cf} of the uppermost Γ_5- and Γ_1-type (without SOC) valence bands in wz-GaN and wz-InN as well as the larger size and the opposite sign of Δ_{cf} in AlN are accepted,[1,2] the details of the spin-orbit interaction are controversially debated. However, the exact knowledge of these splittings is most important for the understanding of the spin relaxation of holes and the polarization dependence of emitted light.

In the past 15 years, a huge number of (mainly optical) measurements (see Refs. 1–4) aiming at the determination of Δ_{cf} and Δ_{so} have been published. For AlN and GaN, their results are of the same order of magnitude. However, there are strong variations of the splittings $\Delta_{cf}=9,\ldots,38$ meV and $\Delta_{so}=11,\ldots,20$ meV (see data collection in Ref. 4). In addition, for wz-GaN, only one experiment[5] has tried to determine the splitting of the SOC constants into $\Delta_{so_\parallel}$ and $\Delta_{so_\perp}$ due to the hexagonal crystal field. Because of the sample quality, the situation is worse for InN. For instance, a wide range of crystal-field parameters $\Delta_{cf}=17,\ldots,301$ meV has been published for wz-InN (see Ref. 4).

Modern *ab initio* band-structure calculations do not have to deal with sample-related problems due to strain, doping, noncrystallinity, etc. However, they suffer from different possible approximations for exchange and correlation (XC) of the electron-electron interaction, the "true" equilibrium atomic geometry, and, sometimes, the proper inclusion of the spin-orbit interaction. There is an enormous number of calculations of the crystal-field splitting based on the density functional theory (DFT) within the local density approximation (LDA) or including generalized gradient approximation (GGA). However, only in a few DFT-LDA or DFT-GGA treatments[5–8] has spin-orbit interaction been included. In addition, the DFT calculations exhibit the so-called band gap problem due to the neglect of the excitation aspect and the self-interaction in the Hartree term. To overcome these limitations, one has to take into account quasiparticle (QP) excitation effects within Hedin's *GW* approximation as well as the spin-orbit interaction. The high precision of such approaches has been recently demonstrated not only for III-V and II-VI zinc blende semiconductors without first-row anions[9] but also for group-II oxides with and without strain.[10,11] Unfortunately, the first application of such an advanced treatment[12] did not account for spin-orbit interaction.

In this letter, we apply a recently developed QP scheme[13] based on a starting electronic structure where XC are treated by the spatially nonlocal hybrid functional HSE03.[14] The remaining effect of the XC self-energy is treated iteratively. The Ga 3*d* and In 4*d* electrons are treated as valence electrons. The spin-orbit interaction is taken into account on the XC level of the hybrid functional.[15] We use a fine mesh of $8\times8\times8$ ($8\times8\times6$) Monkhorst–Pack **k** points to sample the Brillouin zone in the zb (wz) case. The resulting absolute QP gap energies are converged up to 10,…,20 meV with a much better accuracy for the splittings. The explicit calculations are carried out using the Vienna *ab initio* SIMULATION PACKAGE (VASP).[16]

The QP calculations need the atomic coordinates as input. We calculated the cubic (a_0) and hexagonal (a,c) lattice constants, as well as the internal cell parameter u of the wz structure, from a minimization of the total energy within DFT using the AM05 XC functional[17] that has been demonstrated to give reliable lattice parameters for semiconductors. The structural parameters resulting for the nitrides are listed in Table I. The results for AlN and GaN are in excellent

TABLE I. Computed lattice parameters for zb (a_0) and wz ($a,c,c/a,u$) polytypes. In parentheses are the experimental values (Refs. 18–20).

Parameter	AlN	GaN	InN
a_0 (Å)	4.37 (4.37)	4.50 (4.49)	5.01 (4.98)
a (Å)	3.11 (3.11)	3.18 (3.18)	3.55 (3.54)
c (Å)	4.98 (4.98)	5.18 (5.17)	5.74 (5.72)
c/a	1.60 (1.60)	1.63 (1.62)	1.62 (1.61)
u	0.380 (0.382)	0.376 (0.375)	0.378 (0.375)

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agreement with experimental values,[18–20] independent of the polytype. For InN, the computed lattice constants for zb and wz seem to be 0.8% smaller than the respective experimental values.[21] However, because of the agreement for the AlN and GaN polytypes and the reduced sample quality in the InN case, we apply the computed lattice parameters.

We focus the discussion on the three uppermost valence bands at the Γ point of the Brillouin zone. For zb crystals, we compute the spin-orbit splitting constants Δ_{so}^0 that are defined as the splitting between the Γ_8 and Γ_6 levels. In the hexagonal wz crystals, these bands are influenced by the crystal-field and the spin-orbit interaction. In a $\mathbf{k}\cdot\mathbf{p}$ approach, the three levels with Γ_9, Γ_{7+}, and Γ_{7-} symmetry (wz) obtained within the described QP approach can be characterized by[22] (using the nomenclature $\Delta_{cf}=\Delta_1$, $\Delta_{so_\parallel}=3\Delta_2$, and $\Delta_{so_\perp}=3\Delta_3$)

$$\varepsilon(\Gamma_9) = \Delta_{cf} + \tfrac{1}{3}\Delta_{so_\parallel},$$

$$\varepsilon(\Gamma_{7+/-}) = \tfrac{1}{2}\left(\Delta_{cf} - \tfrac{1}{3}\Delta_{so_\parallel}\right) \pm \tfrac{1}{2}\sqrt{\left(\Delta_{cf} - \tfrac{1}{3}\Delta_{so_\parallel}\right)^2 + \tfrac{8}{9}\Delta_{so_\perp}^2}. \quad (1)$$

Here, Δ_{cf} denotes the hexagonal crystal-field splitting. The hexagonal crystal structure gives rise to an anisotropy of the spin-orbit splittings, which is related to the orientation of the valence states either parallel ($\Delta_{so_\parallel}$) or perpendicular ($\Delta_{so_\perp}$) to the *c*-axis. The QP energies of the uppermost valence states are plotted in Fig. 1. The level energies and the corresponding splittings are listed in Table II.

For the zb polymorphs, we find a decrease of Δ_{so}^0 along the row AlN, GaN, and InN. The calculated values are in good agreement with the computations of Cardona and Christensen,[6] Δ_{so}=20.0 meV(AlN), 18.5 meV (GaN), and 12.6 meV (InN). We find slightly larger values due to the stronger localization of the HSE03 wave functions compared to the ones obtained using the LDA for XC in the Kohn–Sham equation. The larger deviations for InN may be due to larger errors of the LDA that affect the band-structure parameters of the III-nitrides. Carrier and Wei[23] who, however, used a semiempirical potential, attributed these errors, in part, to the overestimated coupling between the conduction band and the valence light hole. Also, the values calculated within the quasicubic approximation for wz-AlN and wz-GaN of 20.4/18.9/19 meV (AlN) and 15.5/18.9/16 meV (GaN) (Refs 7, 8, and 23) are in reasonable agreement with our results for the zb polymorphs. The agreement indicates the most important contribution from the atomic regions to the SOC and the use of similar all electronlike wave functions.

For the wz crystals, the crystal-field splitting parameters $\Delta_{cf}^0=\varepsilon(\Gamma_5)-\varepsilon(\Gamma_1)$ (in the absence of the spin-orbit interaction) as well as the differences between the QP energies $\varepsilon(\Gamma_{7+})$, $\varepsilon(\Gamma_9)$, and $\varepsilon(\Gamma_{7-})$ (taking the SOC into account) are given in Table II. Even though we found the influence of the QP effects on the relative shift of the uppermost valence bands to be small, it is not negligible. The QP correction for the Γ_5 level is larger than the one for the Γ_1 level, leading to a shrinkage of Δ_{cf}^0 in the case of wz-GaN and wz-InN. On the contrary, for wz-AlN, the QP corrections increase the difference, resulting in Δ_{cf}^0=−275 meV, which is still in the range of measured values around −230 meV.[1,3] Our results are in reasonable agreement with values from DFT-LDA calculations.[7,8,23] Nevertheless, the actual value indeed depends on the applied atomic coordinates and the QP shifts. A biaxial strain of about 1% may change Δ_{cf}^0 up to several tens of meV.[24] Our findings for Δ_{cf}^0 are better than the −295 meV (AlN) and 34 meV (GaN) reported in another QP calculation.[12] However, the value for InN, Δ_{cf}^0=66 meV of

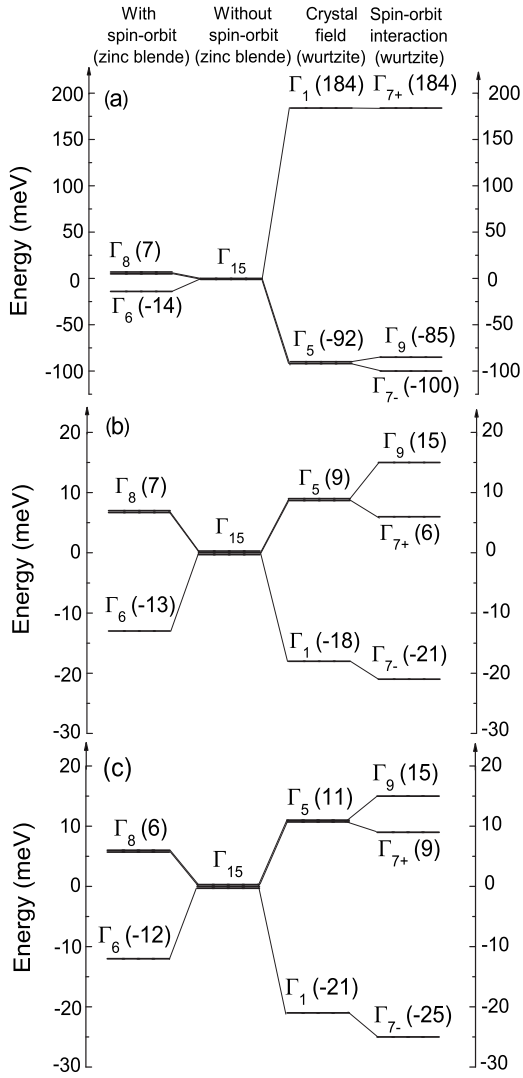

FIG. 1. Characteristic splittings and shifts due to the crystal-field splitting and the spin-orbit interaction for (a) AlN, (b) GaN, and (c) InN. The absolute energy values (in meV) are given in parentheses. The threefold degenerate Γ_{15} level of the zb polymorphs is used as energy zero.

TABLE II. Valence-band splittings (in meV) for zb and wz polytypes including QP effects. The index "0" indicates a valence-band splitting in absence of the other mechanism, i.e., Δ_{so}^0 for $\Delta_{cf}\equiv 0$ and Δ_{cf}^0 for $\Delta_{so}\equiv 0$. The values Δ_{so}^{qc} and Δ_{cf}^{qc} have been calculated using the quasicubic approximation ($\Delta_{so_\parallel}\equiv\Delta_{so_\perp}$). In addition, $\Delta_{so_\parallel}$ and $\Delta_{so_\perp}$ have been calculated assuming $\Delta_{cf}\equiv\Delta_{cf}^0$.

Splitting	AlN	GaN	InN
$\Delta_{so}^0=\varepsilon(\Gamma_8)-\varepsilon(\Gamma_6)$	21.8	20.2	17.4
$\Delta_{cf}^0=\varepsilon(\Gamma_5)-\varepsilon(\Gamma_1)$	−275.7	26.4	31.7
$\varepsilon(\Gamma_9)-\varepsilon(\Gamma_{7+})$	−268.9	8.4	6.3
$\varepsilon(\Gamma_9)-\varepsilon(\Gamma_{7-})$	14.9	36.0	39.9
Δ_{so}^{qc}	21.8	15.9	10.6
Δ_{cf}^{qc}	−275.8	28.5	35.6
$\Delta_{so_\parallel}$	21.7	18.0	14.5
$\Delta_{so_\perp}$	23.5	19.7	21.4

Ref. 12, is far away from our results and other values discussed in literature. The different signs of Δ_{cf}^{0} for wz-AlN and wz-GaN or wz-InN are mostly a consequence of the *pd* repulsion that occurs in GaN and InN.

When comparing the QP energies $\varepsilon(\Gamma_{7+})$, $\varepsilon(\Gamma_9)$, and $\varepsilon(\Gamma_{7-})$ to the results of optical measurements,[1–3,5] in principle, we have to take excitonic effects into account. However, the exciton binding energies for the A $(\Gamma_{9v}\rightarrow\Gamma_{7c})$, B $(\Gamma_{7+v}\rightarrow\Gamma_{7c})$, and C $(\Gamma_{7-v}\rightarrow\Gamma_{7c})$ excitons (the nomenclature follows the band ordering of wz-GaN and wz-InN) tend to be similar and, hence, do hardly affect the discussion when we compare differences of exciton binding energies E_B-E_A to $\varepsilon(\Gamma_9)-\varepsilon(\Gamma_{7+})$ or E_C-E_A to $\varepsilon(\Gamma_9)-\varepsilon(\Gamma_{7-})$. *Ab initio* calculations for GaN (Ref. 25) indicate an enlargement of the A/B exciton binding energies with respect to the one of the C exciton by about only 4 meV. In the case of wz-AlN, the differences $E_B-E_A=-218$ meV and $E_C-E_A=14$ meV (cf. Ref. 1) or $E_B-E_A=-267$ meV (cf. Ref. 3, biaxial strain of $\varepsilon_b=0.4\%$) agree well with our splittings given in Table II. The same is true for wz-GaN, in which case the results in Table II agree well with the splittings $E_B-E_A=5$ meV and $E_C-E_A=23$ meV (cf. Ref. 2) or $E_B-E_A=7$ meV and $E_C-E_A=28.7$ meV (cf. Ref. 5). Moreover, small variations of the crystal field due to c/a and u variations can also have a remarkable influence since residual strain in the samples cannot be excluded. From the spectroscopic data, Gil *et al.*[5] derived a deformation potential for biaxial strain ε_b of the order of 3.7 eV for wz-GaN. This leads to a variation of the crystal-field splitting of about 7 meV for $\varepsilon_b=0.2\%$.

When we compare the results to values derived within the $\mathbf{k}\cdot\mathbf{p}$ theory, we are facing the problem that the $\mathbf{k}\cdot\mathbf{p}$ theory does not give absolute level positions. Therefore, only differences of level energies can be compared to our parameter-free electronic-structure calculations. In theory, as well as in experiment, there are only two energy differences from which three band-structure parameters Δ_{cf}, $\Delta_{so_\parallel}$, and $\Delta_{so_\perp}$ have to be determined. We overcome the lack of information by additional assumptions. (i) The quasicubic approximation $\Delta_{so_\parallel}\equiv\Delta_{so_\perp}\equiv\Delta_{so}^{qc}$ directly yields the values Δ_{cf}^{qc} and Δ_{so}^{qc}. (ii) Another assumption could be $\Delta_{cf}\equiv\Delta_{cf}^{0}$, i.e., the spin-orbit interaction does not influence the crystal field. Due to the necessity of additional assumptions, we do not directly compare the splitting parameters with literature values. In the case of wz-AlN, the resulting values for Δ_{cf}^{qc} are in extremely good agreement with the crystal-field splitting Δ_{cf}^{0} computed for vanishing spin-orbit interaction, indicating that the quasicubic approximation is valid for this material. However, the difference between Δ_{cf}^{qc} and Δ_{cf}^{0} is slightly larger for GaN and InN. Therefore, we expect the quasicubic approximation to be less accurate in these cases. Furthermore, we find drastically reduced SOC constants Δ_{so}^{qc} for wz-GaN or wz-InN in comparison with their cubic values Δ_{so}^{0}. Moreover, Δ_{so}^{0}'s are almost identical even though one expects larger SOC values for GaN and InN in comparison to AlN because Ga and In are heavier than Al. These effects are again a consequence of the semicore *d* contribution to the SOC in GaN and InN. The negative Ga $3d$ or In $4d$ contribution largely cancels the effect due to the Ga $4p/\mathrm{N}\ 2p$ and In $5p/\mathrm{N}\ 2p$ electrons.[6,8] The effect of cancellation depends on the *pd* hybridization at the valence-band top.

Altogether, the most modern QP band-structure theory including spin-orbit interaction allows us to predict valence-band splittings in a consistent way for three nitrides crystallizing in two polytypes. Indeed, the many-body effects influence the energy differences. The calculated results are in overall agreement with the measured splittings. Deriving $\mathbf{k}\cdot\mathbf{p}$ parameters from the differences, however, asks for additional assumptions that influence the results, especially for GaN and InN. Their spin-orbit splittings are determined by the *pd* hybridization of the uppermost valence bands.

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