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Exact-exchange calculations of the electronic structure of AlN, GaN and InN

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Abstract

The electronic structure of the zincblende (ZB) phase of AlN, GaN and InN has been investigated by using the exact-exchange (EXX) Kohn–Sham density functional theory, with the Ga $3d$ and In $4d$ electrons treated both as valence states and as part of the frozen core. Our EXX bandgaps for AlN and GaN (obtained with the semicore Ga $3d$ electrons included as core states) are found to be in good agreement with previous EXX calculations, GW results and available experimental data. When the semicore d electrons are treated as valence states, the EXX bandgap of ZB-GaN is found to be in excellent agreement with the GW results. However, both the EXX and GW bandgaps are about 0.4 eV smaller than experiment. For InN, where the application of the GW approach is problematic, due the negative LDA bandgap, the EXX approach allows for a fully consistent treatment. Contrary to common belief, the removal of the self-interaction, by the EXX approach, does not account for the large discrepancies between the LDA (or GGA) results and experiment for the position of the semicore d bands.
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1. Introduction

The group-III nitrides have attracted a lot of attention because of their technological applications [1]. In the present work we use the pseudopotential exact-exchange (EXX) Kohn–Sham density functional theory approach [2,3] to calculate the electronic structure of AlN, GaN and InN. The semicore d electrons of Ga and In are treated both as valence states and as part of the frozen core.

2. Computational details

The band structure calculations are performed using the SFHIngX code [4], which employs a plane

wave basis set and first-principles pseudopotentials (PPs) [5]. All three semiconductors considered are assumed to be in the zincblende (ZB) phase. Throughout this work the experimental lattice constants are used (4.37, 4.50 and 4.98 Å for AlN, GaN and InN, respectively). The norm-conserving scalar-relativistic EXX-PPs are generated as described in Ref. [6]. The transferability of these PPs and the corresponding LDA (local-density approximation for the exchange-correlation energy) ones is carefully checked. More details about the generation of these PPs will be given elsewhere [7].

The LDA calculations employ the Ceperley–Alder exchange-correlation data as parameterized by Perdew and Zunger [8]. In the EXX calculations, the above LDA correlation functional is utilized. Brillouin zone integration is performed on a regular $4 \times 4 \times 4$ Monkhorst–Pack mesh. A plane wave energy cutoff of 60, 65 and 70 Ryd is applied for AlN, InN, and GaN, respectively. To calculate the independent particle polarizability, χ_o (see Ref. [3]), plane waves up to an energy cutoff of 35, 45 and 55 Ryd are considered, respectively. Moreover, the Hamiltonian in the plane wave representation is fully diagonalized and all the obtained conduction states are included, in the calculation of χ_o. For GaN and InN, with the semicore d electrons treated as core states, the energy cutoffs used are exactly as those of AlN. The k-point sampling and the energy cutoffs are carefully tested [7], and found to give an excellent convergence.

3. Results and discussion

In Tables 1–3 we summarize the most important electronic structure parameters of the ZB phase of

Table 1
Selected EXX and LDA electronic structure properties of the ZB phase of AlN. The available experimental results (see Ref. [9]) are shown in parentheses. All tabulated quantities are in eV

Property	LDA	EXX
E_g^Γ	4.27	5.74
E_g^L	7.25	8.58
E_g^X (5.11)	3.27	5.06
Total VBW	14.81	14.95
Upper VBW	5.91	5.33

Table 2
As in Table 1, but for the ZB phase of GaN. The experimental results for GaN are taken from Refs. [17,18]

Property	LDA		EXX	
	no d	with d	no d	with d
E_g^Γ (3.3)	2.22	1.65	3.52	2.88
E_g^L	4.88	4.43	6.23	5.64
E_g^X (5.63)	3.43	3.30	4.99	4.66
E_d (17.7)	–	13.80	–	14.80
Total VBW (14.2)	15.40	16.00	15.63	16.00
Upper VBW	6.73	7.32	6.24	6.63

Table 3
As in Table 1, but for the ZB phase of InN

Property	LDA		EXX	
	no d	with d	no d	with d
E_g^Γ	0.27	−0.44	1.49	0.81
E_g^L	3.51	2.95	4.75	4.14
E_g^X	2.87	2.82	4.63	4.20
E_d	–	13.56	–	13.50
Total VBW	13.99	14.60	14.37	14.74
Upper VBW	5.53	6.10	5.09	5.49

AlN, GaN and InN, respectively, obtained using the LDA and EXX approaches. Consistent pseudopotentials are used in both LDA and EXX calculations. The listed properties are the direct bandgap at the Γ-point (E_g^Γ), indirect Γ to X bandgap (E_g^X), indirect Γ to L bandgap (E_g^L), position of the semicore d bands below the top of valence bands (E_d), total valence band width (VBW) and upper VBW. The available experimental results for AlN and GaN are also listed in Tables 1 and 2.

Let us start with the bandgaps of AlN and GaN, obtained with the semicore d electrons of Ga included as part of the core. The important features to note are as follows.

(i) Tables 1 and 2 show that both our LDA and EXX results are in excellent agreement with the corresponding results of Ref. [9], and the EXX results are in very good agreement with the GW calculations [9].

(ii) For GaN, the EXX value for E_g^Γ is in very good agreement with experiment, while that of E_g^X is about 0.6 eV smaller than experiment.

(iii) For AlN, experimental results are available only for E_g^Γ of wurtzite (W) phase (6.033 eV, Ref. [10]) and E_g^X of the ZB phase (5.11 eV, see Ref. [9]). Recent LDA calculations [11] have shown that for ZB and W structures of AlN the values of E_g^Γ are almost identical (by 0.01 eV). Table 1 shows that the EXX results are in good agreement with these experimental data.

(iv) The bandgaps are highly underestimated in LDA calculations, as expected.

Now we turn to our calculated LDA and EXX bandgaps of the ZB phase of GaN and InN, obtained with the Ga $3d$ and In $4d$ electrons treated as valence states. The remarkable features to note, in this case, are as follows.

(i) The EXX results for E_g^Γ are of 0.6 and 0.7 eV smaller than those obtained with the semicore d electrons treated as core states for GaN and InN, respectively.

(ii) Interestingly, these reductions are almost identical to those found in LDA calculations, using LDA-PPs. This shows that the nature of the p–d interaction [14] is the same within both approximations.

(iii) This makes the EXX value for the E_g^Γ of ZB-GaN of 2.88 eV, which is significantly smaller than experiment (see Table 2). Therefore, improved correlation (with respect to LDA) is required, when the semicore d electrons are explicitly included in the calculations. In fact, GW calculations based on EXX results [15] have yield improved bandgaps, over those of EXX, for GaN and some II–VI compounds.

We focus now on the bandgap of InN, which is still strongly debated [12]. Based on the EXX bandgap of ZB-InN (with the semicore d electrons included as valence states, see Table 3) and assuming the same error as that of the similarly calculated EXX bandgap of GaN, a bandgap for ZB-InN of 1.2 eV can be suggested. That of the W phase is about 0.2 eV higher [13]. This estimated bandgap for W-InN is higher than the recent experimental values (0.7–1.0 eV), and smaller than the previously widely accepted value, of 1.9 eV. However, one should note that the EXX-GW calculations do not always lead to

an increase in the EXX bandgap [9]. Thus, the present EXX estimate of the bandgap of W-InN can only be considered as tentative.

The EXX correction to the LDA bandgaps is found to be quite the same for the three considered compounds (about 1.3 eV), despite the large differences in their bandgaps. Moreover, the **k**-dependence of this correction is found to be very weak when the semicore d electrons are treated as valence states. When these electrons are included as part of the frozen core, the correction at the X-points is found to increase by 0.3–0.5 eV.

The EXX results for E_d are very close to those of the LDA, using LDA-PPs. This means that the removal of the spurious self-interaction, by the EXX approach, does not account for the discrepancy between LDA results and experiment. This is a remarkable finding, since it is in contradiction with common understanding [16] that such discrepancy is due to the self-interaction, present in the LDA calculations. These unexpected results are explained as follows [7]. In the case of pseudoatoms, the downward shifts in the eigenvalues the cation semicore d states by going from LDA to EXX calculations (i.e. by the removal of the self-interaction), are comparable to those of the N $2s$ and N $2p$ states, see Ref. [7] for more details.

4. Conclusions

The EXX approach is used to investigate the electronic structure of the zincblende phase of AlN, GaN and InN. Our main results and conclusions are as follows.

(i) The EXX bandgaps of AlN and GaN (with the Ga $3d$ electrons are treated as part of the core) are in very good agreement with previous EXX calculations, GW results and experiment (except for E_g^X of GaN).

(ii) Treating the semicore electrons as valence states reduces significantly the bandgaps of GaN and InN, making that of GaN appreciably smaller than experiment. This shows that improved correlation (over that of LDA) is necessary, in this case.

(iii) Contrary to common belief, the removal of the self-interaction, by the EXX method, does not ac-

count for discrepancy between LDA results and experiment for the position of the semicore *d* bands.

(iv) The EXX approach provides a fully consistent treatment for the bandgap of InN, where the application of GW is problematic due to the negative LDA bandgap. A tentative bandgap of 1.4 eV has been given for the wurtzite phase of InN.

Acknowledgements

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