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Electronic Structure of Cubic GaN with Self-Energy Corrections.

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Abstract. – We present the results of a calculation for the bulk electronic structure of gallium nitride in the zincblende phase. We determine the equilibrium lattice constant, the cohesive energy and the bulk modulus in the Density Functional approach within the Local Density Approximation (DFT-LDA). The one-particle eigenvalues of the DFT Kohn-Sham equation do in principle not agree with the experimental band structure. Therefore, we calculate the quasi-particle energies by including self-energy corrections to the DFT-LDA exchange correlation potential, with the GW approximation for the electron self-energy. We use norm-conserving pseudopotentials and a large plane-wave basis set (100 Ry cut-off) for a converged calculation in the DFT-LDA. The LDA band gap turns out to be very sensitive to the crystal volume. We find that GW corrections to the LDA band gap are significant. A detailed comparison with other DFT-LDA results and approximate GW calculations and with existing experimental data is given.

The group-III nitrides (BN, AlN, GaN, InN) are large-band-gap semiconductors of great interest in microelectronics. In particular, GaN is promising for applications in lasers and blue-light-emitting diodes. It exists in the wurtzite structure, and has recently been grown in the zincblende structure on a cubic substrate. The nearest-neighbour positions in the wurtzite and in the zincblende phase are similar, but the zincblende nitrides might show improved electronic properties due to the reduced phonon scattering [1], hence the importance of its electronic structure. Mostly optical measurements have yielded experimental band gaps that range from 3.18 to 3.87 eV [2-5]. The great variance in the experimental results constitutes a challenge for theoretical work aimed at giving a reliable description of the band structure of zincblende GaN. Using the empirical pseudopotential approach, Bloom *et al.* [6] have found a direct gap at the Γ -point for the wurtzite phase of 3.6 eV, and of 3.5 eV for zincblende. Passing to *ab initio* calculations, gaps of 1.48–2.8 eV [7, 8] have been obtained by the pseudopotential method, and LMTO calculations

have given results of 2.03–2.29 eV [9–11]. The *ab initio* calculations show the typical underestimate of the band gap with respect to the experimental one, due to the use of the Density Functional-Local Density (DFT-LDA) formalism. To describe correctly the excited states, the electron self-energy must replace the DFT-LDA exchange correlation potential. Such band structure calculations have been carried out successfully for a wide class of materials [12, 13] using Hedin's GW approximation for the self-energy [14]. An attempt to correct the DFT band structure of cubic GaN has already been made in ref. [9] in which a simplified version of the GW approximation according to [15] has been used and a gap of 3.6 eV has been obtained (0.6 eV less than for the wurtzitic phase). The authors have noted, however, that this approximation leads to too large gaps in some wide-gap materials. The same method of ref. [15] has been applied to GaN by Wenchang *et al.* [16], who obtained a gap of 3.9 eV for the zincblende (3.65 eV wurtzite). These calculations can hence give a first hint to the role of self-energy effects, but they are not necessarily reliable. Therefore, there is still a need for a full first-principles calculation of the electronic structure of cubic GaN, including self-energy effects.

Such a calculation, preliminary details of which were given in ref. [17], is presented in this paper⁽¹⁾. We start from a DFT-LDA calculation using the pseudopotential method, and include self-energy effects perturbatively according to the GW approach [12, 13], using the plasmon pole approximation for the energy dependence of the dielectric matrix [20]. We compute the band structure near the gap and show that the resulting direct gap for zincblende is 3.2 eV. Moreover, we discuss the limits of precision which are due to the uncertainty in the choice of the geometrical parameters (equilibrium lattice spacing) at the basis of the band structure calculation; in the case of materials like GaN, this uncertainty turns out to be considerable.

We start with a DFT-LDA calculation using the Ceperley-Alder form for the exchange correlation contribution [21], and *ab initio* norm-conserving non-local pseudopotentials [22]. In order to correct for the relatively extended Ga *d* electron states, we apply a non-linear core correction scheme [23].

Our results have been obtained with a kinetic-energy cut-off $E_{\text{cut}} = 100$ Ry, in order to guarantee good convergence for the electronic structure; at this cut-off the DFT-LDA gap is almost twice as big as that obtained at a cut-off of 32 Ry (hence the discrepancy with earlier pseudopotential works [7]). We sampled the irreducible part of the BZ with 2 *k*-points for the zincblende structure, which yields a precision on the gaps of some hundredths of an eV. The lattice constant is small; *in situ* high-energy electron diffraction gives a value of ≈ 8.5 a.u. In our calculation we obtain 8.368 a.u., hence the typical underestimate of 1.5% due to the use of the LDA. (Neglect of the NLCC leads to a lattice constant of only 8.16 a.u.) Other ground-state properties are also in satisfactory agreement with experiment: we obtain 10.64 eV for the cohesive energy (difference between the polarized ground-state free pseudoatom energies and the total energy per molecule), and a bulk modulus $B_0 = 223$ GPa. The experimental cohesive energy for the wurtzite structure is 9.28 eV, and the bulk modulus for the cubic structure, evaluated on the basis of the elastic constants of the wurtzite phase, is 186 GPa [24]. Figure 1 (continuous line) shows the DFT band structure calculated including the NLCC, and using the theoretical lattice constant of 8.368 a.u. The direct gap at

⁽¹⁾ In the meantime, we have become aware of a work by another group [18] on the quasi-particle band structure of GaN using the GW approximation with a model dielectric function, with the LDA band structure calculated at the LDA equilibrium volume taken from ref. [19]. In spite of the more approximate dielectric function, these authors obtain a gap correction relatively close to ours.

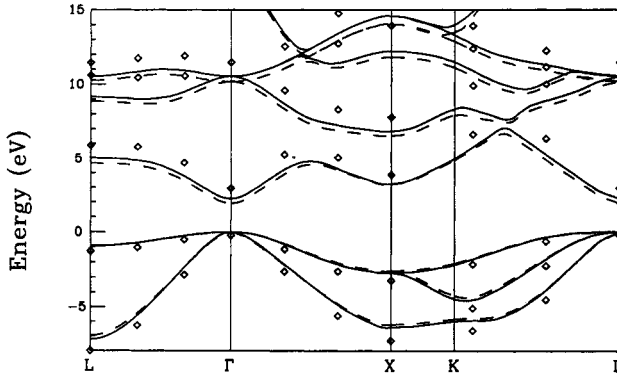


Fig. 1. – LDA band structure of cubic GaN obtained at the calculated equilibrium lattice constant $a_0 = 8.368$ a.u. (full lines) and the *experimental* value $a_0 = 8.5$ a.u. (dashed lines). Diamond are the GW-corrected values at the theoretical lattice constant.

Γ is 2.21 eV⁽²⁾, as can also be seen from the set of transition energies given in table I. For comparison, we have also listed the transition energies calculated at the *experimental* lattice constant $a = 8.5$ a.u. (dashed lines in fig. 1). The difference is striking: an increase in the lattice constant of 1.5% decreases the DFT gap by as much as 0.3 eV. We have carried out the calculation of the gap at Γ as a function of the lattice constant for several values of a . In the range of $a = 8.0$ to 8.6 a.u., the behaviour is well fitted by $E = E_0 + a_1(\Delta a/a)$, with $a_1 = -20.85$ eV, whereas a fit to the gap-*vs.*-pressure curve yields $E = E_0 + b_1 p + b_2 p^2$, with $b_1 = 3.42$ eV/Mbar and $b_2 = -3.1$ eV/Mbar². The importance of the lattice constant in band structure calculations has already been pointed out by Fiorentini [25]. The strong effect found here in GaN is not too surprising and similar to other gallium compounds.

As pointed out above, in order to compare with experiment, the self-energy corrections should be added to the band structure. Within Hedin's GW approximation [14], the self-energy reads

$$\Sigma(\mathbf{r}, \mathbf{r}'; \omega) = \frac{i}{4\pi} \int_{-\infty}^{+\infty} \exp[i\omega'\delta] W(\mathbf{r}, \mathbf{r}'; \omega') G(\mathbf{r}, \mathbf{r}'; \omega + \omega') d\omega';$$

$W(\mathbf{r}, \mathbf{r}'; \omega)$ is the dynamical screened Coulomb interaction, and $G(\mathbf{r}, \mathbf{r}'; \omega)$ is the one-particle Green's function. Hence, one has first to calculate the full inverse dynamical dielectric matrix, and from that and the Green's function construct the self-energy. In view of the about 2500 plane waves used in the expansion of the wave function in the DFT calculation on GaN, this might seem an impossible task⁽³⁾. However: *a*) generally it has been shown that it is sufficient to evaluate the self-energy correction in first-order perturbation theory with respect to the DFT calculation [13]. Hence, even if the matrix elements of the self-energy are

⁽²⁾ In a previously determined band structure of GaN, we obtained $a_0 = 8.41$ a.u. and a gap of 2.65 eV [17]. In that calculation the d -component of the pseudopotential was included in the local part, as is often done in expensive calculations. The inclusion of NLCC in that choice would have carried to the overestimation of the lattice parameter (8.70 a.u.) and a consequent underestimation of the gap (1.64 eV).

⁽³⁾ We have included core contributions in V_{xc} only. The net correction left out by our calculation is estimated to be of the order of -0.1 eV.

TABLE I. – Self-energy corrections for valence and conduction bands at high symmetry points of the Brillouin zone for cubic GaN, calculated at the LDA equilibrium lattice parameter and at the experimental lattice constant. LDA and GW values for the main gaps are also given (units are eV).

	$a = 8.368$		$a = 8.5$	
	E_{nk}^{LDA}	ΔE_{nk}	E_{nk}^{LDA}	ΔE_{nk}
Γ				
Γ_{15}^v	0.00	-0.22	0.00	-0.17
Γ_1^c	2.21	0.75	1.89	0.71
Γ_{15}^c	10.56	0.94	10.21	0.90
X				
X_3^v	-6.38	-0.92	-6.20	-0.72
X_5^v	-2.71	-0.51	-2.58	-0.46
X_1^c	3.25	0.62	3.22	0.60
X_3^c	6.86	0.95	6.56	0.95
L				
L_1^v	-7.23	-0.76	-6.96	-0.72
L_3^v	-0.93	-0.33	-0.90	-0.29
L_1^c	5.03	0.85	4.67	0.82
L_1^c	9.15	1.46	8.87	1.39
L_3^c	10.55	0.90	10.26	0.88
	LDA	GW	LDA	GW
$\Gamma_{15}^v - \Gamma_1^c$	2.21	3.18	1.88	2.76
$\Gamma_{15}^v - \Gamma_{15}^c$	10.56	11.71	10.21	11.28
$\Gamma_{15}^v - X_1^c$	3.25	4.10	3.22	3.98
$\Gamma_{15}^v - L_1^c$	5.03	6.10	4.67	5.66
$X_5^v - X_1^c$	5.96	7.09	5.80	6.86
$L_3^v - L_1^c$	5.96	7.14	5.56	6.66

not fully converged with respect to the number of plane waves, the matrix elements of the difference Σ minus V_{xc} may be converged. b) The convergence is determined not only by the behaviour of the coefficients of the wave functions, but it is accelerated by the decrease as $|\mathbf{G}|^{-2}$ of the Coulomb interaction which multiplies the Green's function. c) The total number of electrons in the system is reproduced already within 0.5% when one retains only about one seventh of the plane waves in the wave functions, so that the system «seen» by the extra particle at reduced cut-off is relatively close to the original one. In fact, we have performed tests that show that for the three mentioned reasons, good convergence in the GW calculation (better than 0.15 eV in absolute and relative quasi-particle energies) is achieved when 331 plane waves are used to calculate the matrix element of $\Sigma_x - \Sigma_{xc}$, Σ_x being the bare exchange contribution, and 169 plane waves are used to describe the screened Coulomb interaction and the subsequent calculation of the correlation contribution to the self-energy correction. In order to obtain such precision, 6 special points in the calculation of the dielectric matrix, and 10 special points in the final evaluation of $\langle \Sigma \rangle$ have been sufficient. The corrections ΔE_{nk} to the LDA eigenvalues are calculated in first-order perturbation theory in $\Sigma - V_{xc}$.

The limit of vanishing wave vector of the dielectric matrix has been converged separately, using 10 special \mathbf{k} -points and taking into account the commutator of the operator \mathbf{r} and the

non-local pseudopotential $[r, V_{NL}(r, r')]$ which is evaluated as in ref. [26]; it lowers the dielectric constant by about 15%, whereas local-field effects amount to about 9%. We adopt the single plasmon pole approximation [20] to the dielectric matrix, fitting the two parameters of the model (for each element of $\epsilon_{G,G'}^{-1}(\mathbf{q})$) to our full calculation on the imaginary energy axis. After performing this calculation at the *theoretical* lattice constant, we obtain an RPA dielectric constant of $\epsilon_0 = 6.01$. This result can only be compared with the available experimental values obtained for the wurtzitic phase of GaN ($\epsilon_\infty = 5.35$ [27] when the field is along the *c*-axis, 5.8 [28] when the field is in the basal plane). The resulting self-energy correction at $a_0 = 8.368$ are at the Γ -point the following: -0.22 eV for the valence band and $+0.75$ eV for the lowest conduction band, giving a total correction to the gap of 0.97 eV. The resulting band gap is 3.18 eV. Choosing instead the *experimental* lattice constant $a = 8.5$ a.u., ϵ_0 increases slightly to 6.14, due to the smaller LDA gap at that lattice constant.

Table I gives an overview of the band structure and transition energies with and without self-energy corrections. The correction to the gap, between the higher occupied and lowest unoccupied band, is important, of the order of 1.0 eV for the theoretical lattice constant, and almost constant throughout the BZ (within 0.22 eV). The corrections are larger for the transitions of wider energy. In fig. 1 the self-energy corrected band structure (diamonds) are compared to the LDA band structure (continuous line). Having evaluated the GW correction both at the experimental and the theoretical value, we can estimate the contribution of the self-energy correction to the linear coefficient in the expansion of the direct gap *vs.* the deformation: we obtain corrected values of $a_1 = -26.87$ eV and $b_1 = 4.41$ eV/Mbar, hence a slightly increased effect.

It is difficult to decide which results should be compared to experiment—the ones calculated at the theoretical, or at the experimental lattice constant. In the case of a DFT calculation, some arguments have been given in favour of the theoretical constant, for the sake of consistency [25]. However, it is not at all clear if the theoretical lattice constant which would follow from a total energy calculation based on the GW approximation were closer to one or another of the above two choices. We can hence only give a range of possible results, which do however clearly predict the gap to be situated in the low-energy range of the available experimental results, below 3.5 eV, hence in accordance, for instance, with the optical measurements of ref. [3]. The relatively small gap which we obtain for the cubic phase seems also reasonable if one compares with the wurtzite phase, where the direct gap of 3.5 eV is experimentally well established. From most theoretical calculations [6, 9, 19, 11] and from a comparable DFT calculation performed by us, it is found that the LDA gap of wurtzite is slightly larger than that of zincblende GaN (we obtain $E_g = 2.30$ eV at the theoretical lattice constant). Following the above arguments about the dielectric constant, and having in mind the overall similarity of the two phases, it is hence reasonable to expect that a GW correction in the wurtzite case were similar, at most slightly larger, as in the cubic phase. We would hence obtain a GW-corrected gap of about 3.3 eV for the wurtzite, in good agreement with experiment.

In conclusion, we have calculated ground-state properties and the band structure of cubic GaN. We first performed a DFT-LDA pseudopotential calculation, which gives a good description of such properties as the equilibrium lattice constant, and which serves as an input for the evaluation of the self-energy corrections to the DFT-LDA energy levels. We have used Hedin's perturbative GW formalism for the electron self-energy. Our results disagree with previous theoretical results obtained with greatly simplified GW calculations. Instead, they are consistent with measurements on the wurtzite phase, and give evidence in favour of the low-gap results obtained experimentally on the cubic phase. With this calculation it has been shown that a converged *full* GW calculation is possible, and worthwhile doing, even on materials requiring an extremely high plane-wave cut-off, like GaN.

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REFERENCES

- [1] STRITE S. and MORKOC H., *J. Vac. Sci. Technol. B*, **10** (1992) 1237.
- [2] POWELL C., TOMASH G. A., KIM Y. W., THORNTON J. A. and GREENE J. E., *Mater. Res. Soc. Symp. Proc.*, **162** (1990) 525.
- [3] LEI T., MOUSTAKAS T. D., GRAHAM R. J., HE Y. and BERKOWITZ S. Y., *J. Appl. Phys.*, **71** (1992) 4993.
- [4] MARTIN G., STRITE S., THORNTON J. and MORKOC H., *Appl. Phys. Lett.*, **58** (1991) 21.
- [5] OKUMURA H., MISAWA S. and YOSHIDA S., *Appl. Phys. Lett.*, **59** (1991) 1058.
- [6] BLOOM S., HARBEKE G., MEIER E. and ORTENBURGER I. B., *Phys. Status Solidi B*, **66** (1974) 161.
- [7] VAN CAMP P. E., VAN DOREN V. E. and DEVREESE J. T., *Phys. Rev. B*, **38** (1988) 14.
- [8] MIN B. J., CHAN C. T. and HO K. M., *Phys. Rev. B*, **45** (1992) 3.
- [9] LAMBRECHT W. R. L. and SEGALL B., *Mater. Res. Soc. Proc.*, **242** (1992) 367.
- [10] FIORENTINI V., METHFESSEL M. and SCHEFFLER M., *Phys. Rev. B*, **47** (1993) 13353.
- [11] GORCZYCA I. and CHRISTENSEN N. E., *Solid State Commun.*, **80** (1991) 335; CHRISTENSEN N. E., private communication.
- [12] GODBY R. W., SCHLÜTER M. and SHAM L. J., *Phys. Rev. Lett.*, **56** (1986) 2415; *Phys. Rev. B*, **37** (1988) 10159.
- [13] HYBERTSEN M. S. and LOUIE S. G., *Phys. Rev. Lett.*, **55** (1985) 1418; *Phys. Rev. B*, **34** (1986) 5390.
- [14] HEDIN L., *Phys. Rev. A*, **139** (1965) 796.
- [15] BECHSTEDT F. and DEL SOLE R., *Phys. Rev. B*, **38** (1988) 7710.
- [16] WENCHANG L., KAIMING Z. and XIDE X., *J. Phys. Condens. Matter*, **5** (1993) 875.
- [17] PALUMMO M., REINING L., GODBY R. W. and BERTONI C. M., *The Physics of Semiconductors*, edited by P. JIANG and H.-Z. ZHENG (World Scientific) 1992, p. 89.
- [18] RUBIO A., CORKILL J., COHEN M. L., SHIRLEY E. L. and LOUIE S. G., *Phys. Rev. B*, **48** (1993) 11810.
- [19] VAN CAMP P. E., VAN DOREN V. E. and DEVREESE J. T., *Solid State Commun.*, **81** (1992) 23.
- [20] GODBY R. W. and NEEDS R. J., *Phys. Rev. Lett.*, **62** (1989) 1169.
- [21] CEPERLEY D. M. and ALDER B. I., *Phys. Rev. Lett.*, **45** (1980) 566; for the parametrization: PERDEW J. P. and ZUNGER A., *Phys. Rev. B*, **23** (1981) 5048.
- [22] STUMPF R., GONZE X. and SCHEFFLER M., *Research Report of the Fritz Haber Institute, April 1990*.
- [23] LOUIE S., FROYEN S. and COHEN M., *Phys. Rev. B*, **26** (1982) 1738.
- [24] SHERWIN M. E. and DRUMMOND T. J., *J. Appl. Phys.*, **69** (1991) 12.
- [25] FIORENTINI V., *Phys. Rev. B*, **46** (1992) 2086.
- [26] HYBERTSEN M. S. and LOUIE S. G., *Phys. Rev. B*, **35** (1987) 5587.
- [27] BARKER A. S. jr. and ILEGEMS M., *Phys. Rev. B*, **7** (1973) 2.
- [28] MANCHON D. D., BARKER A. S., DEAN J. P. and ZETTERSTROM R. B., *Solid State Commun.*, **8** (1970) 1227.