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# A correlated *ab initio* treatment of the zinc-blende wurtzite polytypism of SiC and III–V nitrides

Beate Paulus<sup>†</sup>, Fa-Jian Shi<sup>†</sup> and Hermann Stoll<sup>‡</sup>

<sup>†</sup> Max-Planck-Institut für Physik komplexer Systeme, Bayreuther Straße 40, 01187 Dresden, Germany

<sup>‡</sup> Institut für Theoretische Chemie, Universität Stuttgart, 70550 Stuttgart, Germany

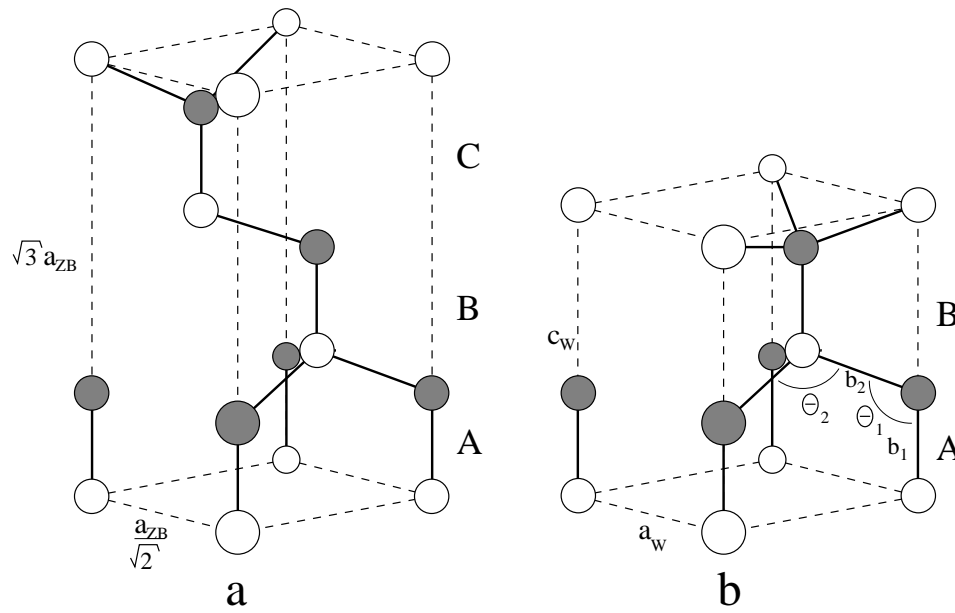
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**Abstract.** Ground-state properties of SiC, AlN, GaN and InN in the zinc-blende and wurtzite structures are determined using an *ab initio* scheme. For the self-consistent-field part of the calculations, the Hartree–Fock program CRYSTAL has been used. Correlation contributions are evaluated using the coupled-cluster approach with single and double excitations. This is done by means of increments derived for localized bond orbitals and for pairs and triples of such bonds. At the Hartree–Fock level, it turns out that for SiC the zinc-blende structure is more stable although the very small energy difference from the wurtzite structure is an indication of the experimentally observed polytypism. For the III–V nitrides the wurtzite structure is found to be significantly more stable than the zinc-blende structure. Electron correlations do not change the Hartree–Fock ground-state structures, but energy differences are enlarged by up to 40%. While the Hartree–Fock lattice parameters agree well with experiment, the Hartree–Fock cohesive energies reach only 45% to 70% of the experimental values. Including electron correlations, we recover for all compounds about 92% of the experimental cohesive energies.

## 1. Introduction

SiC and the III–V nitrides (especially GaN) are the most promising wide-band-gap semiconductors for short-wavelength optoelectronics and for high-power, high-temperature microelectronic devices [1]. But it is difficult to grow high-quality single crystals of these materials. This is due to the polytypism occurring between zinc-blende (an ABCABC... sequence along the 111 direction; see figure 1(a)) and wurtzite structure (an ABABAB... sequence along the 100 direction; see figure 1(b)). SiC shows many more complicated stacking sequences built up as a mixture between the fully cubic structure (zinc-blende) and the fully hexagonal structure (wurtzite) with different percentages of hexagonality. Therefore it is important to understand the bulk properties of these materials, from a theoretical point of view, at least for the two simplest structures (zinc-blende and wurtzite).

Over the past decade, *ab initio* calculations based on density functional theory with a local-density approximation (LDA) have been performed for these materials. In some of them, the energy differences between the zinc-blende and the wurtzite structure have been evaluated [2–7]. There is no possibility of measuring these energy differences; thus a complement—and a comparison—with other *ab initio* methods is desirable. *Ab initio* Hartree–Fock self-consistent-field (HF) calculations for solids [8] are feasible nowadays, using the program package CRYSTAL [9]. They have the merit of treating the non-local exchange exactly although lacking electron correlations by definition. In LDA calculations



**Figure 1.** Diagram (a) shows the primitive hexagonal unit cell (dashed lines) of the zinc-blende structure, and diagram (b) that of the wurtzite structure. The solid lines mark the  $sp^3$  bonds. The stacking sequences ABC (zinc-blende) and AB (wurtzite) are indicated, too. Open and shaded circles refer to the two different atoms of the structures.

where both exchange and correlations are covered in an implicit way, a systematic improvement towards the exact results appears to be difficult. Treating the non-local exchange exactly yields a better (microscopic) understanding of the electron interaction in these materials and, at the same time, leads to a good starting point for a post-Hartree–Fock correlation treatment.

Electron correlations can be taken into account explicitly using many-body wavefunctions of the configuration-interaction or coupled-cluster type. These methods are well developed for finite systems like atoms and molecules. Infinite systems such as solids require a size-consistent approach which is achieved at the coupled-cluster level. Because of the local character of the correlation hole one can expand the correlation energy of the solid in terms of local increments [10]. The idea thereby is to determine the required matrix elements by studying local excitations in finite clusters which are accessible to a full post-HF quantum-chemical treatment. We apply this idea to the zinc-blende and the wurtzite structures of the title materials.

In the first part of this paper we want to report on Hartree–Fock calculations for SiC, AlN, GaN and InN using pseudopotentials and optimized gaussian basis sets for the zinc-blende and wurtzite structure (section 2). The method of increments, which is briefly described in section 3.1, is extended to the wurtzite structure; computational details are given in section 3.2. We discuss results for the energy differences, the lattice parameters, the cohesive energies and the bulk moduli in section 4. Conclusions follow in section 5.

## 2. Hartree–Fock calculation

The periodic Hartree–Fock method as implemented in the CRYSTAL92 program [9] is used in our calculations. The problem of accurately calculating the Coulomb and exchange contributions to the Fock operator is addressed by taking very tight tolerances in the evaluation of these series, which lead to convergence of the total energy to about  $10^{-4}$  Hartree. For the inert core electrons we use the scalar-relativistic energy-consistent pseudopotentials of Bergner *et al* [11]. Two exceptions are made: three-valence-electron pseudopotentials for the post-d elements gallium and indium have been found to underestimate the closed-shell repulsion of the underlying d shell on valence electrons of neighbouring atoms [12]; we therefore performed the SCF calculations for Ga and In compounds with 13-valence-electron pseudopotentials [13], explicitly treating the highest occupied d shell.

**Table 1.** CRYSTAL-optimized basis sets for SiC, AlN, GaN and InN.

	s exponent	Coefficient	p exponent	Coefficient	d exponent	Coefficient
C	2.263 101	0.496 548	8.383 025	−0.038 544	0.55	1
	1.773 186	−0.422 391	1.993 132	−0.203 185		
	0.408 619	−0.599 356	0.559 543	−0.498 176		
	0.159 175	1	0.156 126	1		
Si	4.014 378	−0.039 508	1.102 481	0.084 583	0.40	1
	1.393 707	0.296 150	0.583 127	−0.185 748		
	0.251 658	−0.599 752	0.208 675	−0.554 852		
	0.135	1	0.15	1		
Al	2.786 337	−0.046 411	0.983 794	0.052 036	0.29	1
	1.143 635	0.274 472	0.358 245	−0.155 094		
	0.170 027	1	0.15	1		
Ga	32.955 00	0.000 215	2.562 424	0.017 921	76.205 27	0.007 822
	8.306 842	0.007 419	1.450 154	−0.100 112	25.528 35	0.068 978
	1.349 536	0.063 868	0.396 817	0.109 562	9.465 050	0.202 734
	1.145 804	−0.348 833	0.17	1	3.882 911	0.401 034
	0.294 700	0.212 388			1.504 741	0.410 996
	0.15	1			0.502 918	1
In	1.744 487	0.279 421	1.606 834	0.130 961	16.741 457	0.012 997
	1.055 194	−0.628 094	1.168 418	−0.247 565	4.550 192	0.187 048
	0.176 720	0.539 402	0.200 692	0.326 411	1.815 414	0.442 393
	0.12	1	0.12	1	0.725 833	0.427 724
				0.263 986	1	
N	32.656 839	−0.013 794	12.146 974	−0.041 296	0.82 <sup>a</sup>	1
	4.589 189	0.129 129	2.884 265	−0.214 009		
	0.706 251	−0.568 094	0.808 564	−0.502 783		
	0.216 399	1	0.222 163	1		

<sup>a</sup> 0.82 is the d exponent optimized for AlN; for GaN and InN it is 0.75.

For all of these pseudopotentials, corresponding atomic basis sets have been optimized [11, 13]. These are used in the Hartree–Fock calculations for the free atoms, which are performed with the program package MOLPRO94 [14]. For the solid we generated contracted [2s2p1d] gaussian valence basis sets (for Ga and In: [2s2p2d]) as follows: starting from the

energy-optimized atomic basis sets just mentioned, the inner functions of s and p symmetry are contracted using atomic ground-state orbital coefficients; the outermost s and p functions are left uncontracted. We re-optimized the exponents of these functions, together with an additional d polarization function, for the solid. Thus, we must pay attention to the fact that too diffuse exponents cause numerical problems in CRYSTAL. But the most diffuse exponents of the atom which are necessary for a correct description of the free atom have little effect in the solid, since due to the close packing, the basis functions of the neighbouring atoms take over their role. The CRYSTAL-optimized basis sets are listed in table 1.

In order to check the quality of the basis sets we calculated the ground-state energy of the zinc-blende structure with larger [3s3p1d] and [3s3p2d] basis sets for Si/C/Al/N and Ga/In, respectively. These basis sets are generated from the latter ones by de-contracting the outermost primitive gaussian of the inner s and p functions, thus leaving two outer gaussians uncontracted. The d functions are kept unchanged. There are very small changes in the cohesive energy due to this enlargement of the basis. The maximum deviation occurs for InN with 0.005 Hartree. An additional test of the basis set chosen is the comparison with the Hartree–Fock values given by Pandey *et al* [15] who calculated the ground state of GaN in the wurtzite structure with an all-electron basis of comparable quality: the deviation from our values is less than 0.4% for the lattice constant.

The geometry optimization is performed as follows. For the zinc-blende structure there is only one free parameter, the cubic lattice constant  $a_{zb}$ . This is varied in steps of 1% of the experimental value. Six points are calculated and a quadratic fit is applied to determine the position of the minimum and the curvature.

The wurtzite structure has three free geometry parameters. In the first place, the two lattice constants  $a_w$  (in the hexagonal plane) and  $c_w$  (perpendicular to the hexagonal plane), or one lattice constant and the ratio  $c/a$  which in the ideal case (bond lengths as in the zinc-blende structure) is  $\sqrt{8/3} = 1.6330$ , have to be optimized. The third parameter is the cell-internal dimensionless constant  $u$ , which denotes the position of the second atom along the  $c$ -axis. The ideal value would be  $\frac{3}{8}$ ; a deviation from it corresponds to a change in the bond angle away from the ideal tetrahedral one. We optimize all of these parameters in the following way. First we vary the volume of the unit cell in steps of 1% and determine  $V_{\min}$ , then, for fixed  $V_{\min}$ , we vary the ratio  $c/a$ , and, last, for fixed  $V_{\min}$  and  $(c/a)_{\min}$ , the cell-internal  $u$ . With the optimized  $u$ , we checked its influence on  $c/a$  and  $V$ , which in general is very small.

### 3. Correlation calculations

#### 3.1. Methods of increments

Here we only want to sketch the basic ideas and some important formulae of the method of increments. A formal derivation and more details of the method for an infinite periodic system can be found in reference [16]. The method relies on localized bond orbitals generated in a SCF reference calculation. One-bond correlation-energy increments  $\epsilon_i$  are obtained by correlating each of the localized orbitals separately while keeping the other ones inactive. In the present work we are using the coupled-cluster approach with single and double substitutions (CCSD). This yields a first approximation to the correlation energy:

$$E_{\text{corr}}^{(1)} = \sum_i \epsilon_i \quad (1)$$

which corresponds to the correlation energy of independent bonds.

In the next step we include the correlations of pairs of bonds; only the non-additive part  $\Delta\epsilon_{ij}$  of the two-bond correlation energy  $\epsilon_{ij}$  is needed:

$$\Delta\epsilon_{ij} = \epsilon_{ij} - (\epsilon_i + \epsilon_j). \quad (2)$$

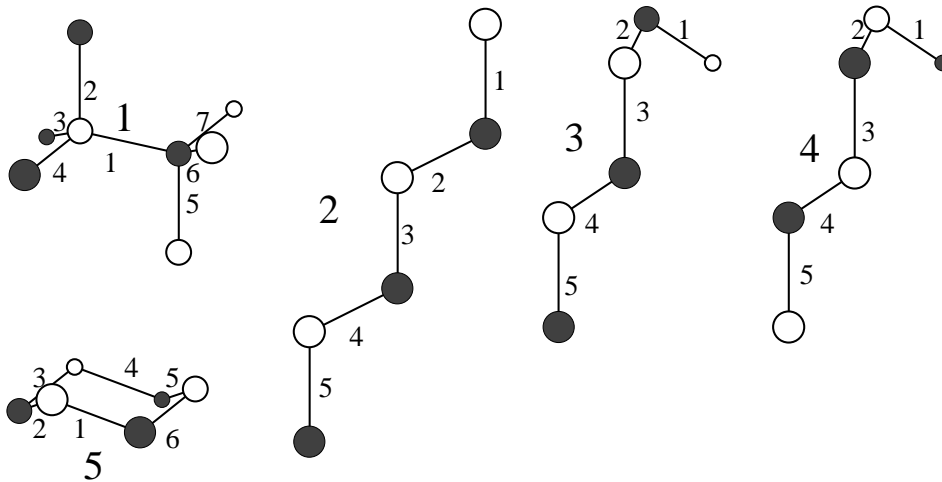
Higher-order increments are defined analogously. For the three-bond increment, for example, one has

$$\Delta\epsilon_{ijk} = \epsilon_{ijk} - (\epsilon_i + \epsilon_j + \epsilon_k) - (\Delta\epsilon_{ij} + \Delta\epsilon_{jk} + \Delta\epsilon_{ik}). \quad (3)$$

The correlation energy of the solid is finally obtained by adding up all of the increments with appropriate weight factors:

$$E_{\text{corr}}^{\text{solid}} = \sum_i \epsilon_i + \frac{1}{2} \sum_{\substack{ij \\ i \neq j}} \Delta\epsilon_{ij} + \frac{1}{6} \sum_{\substack{ijk \\ i \neq j \neq k}} \Delta\epsilon_{ijk} + \dots \quad (4)$$

It is obvious that on calculating higher and higher increments the exact correlation energy within CCSD is determined. However, the procedure described above is only useful if the incremental expansion converges well, i.e. if increments up to, say, three-bond increments are sufficient, and if increments rapidly decrease with increasing distance between localized orbitals. These conditions were shown to be met well in the case of elementary semiconductors [16] and cubic III–V semiconductors [17].



**Figure 2.**  $X_n Y_n H_m$  clusters of the zinc-blende structure treated at the CCSD level for the correlation calculation; big numbers designate clusters, small numbers the bonds in each cluster; H atoms are not drawn.

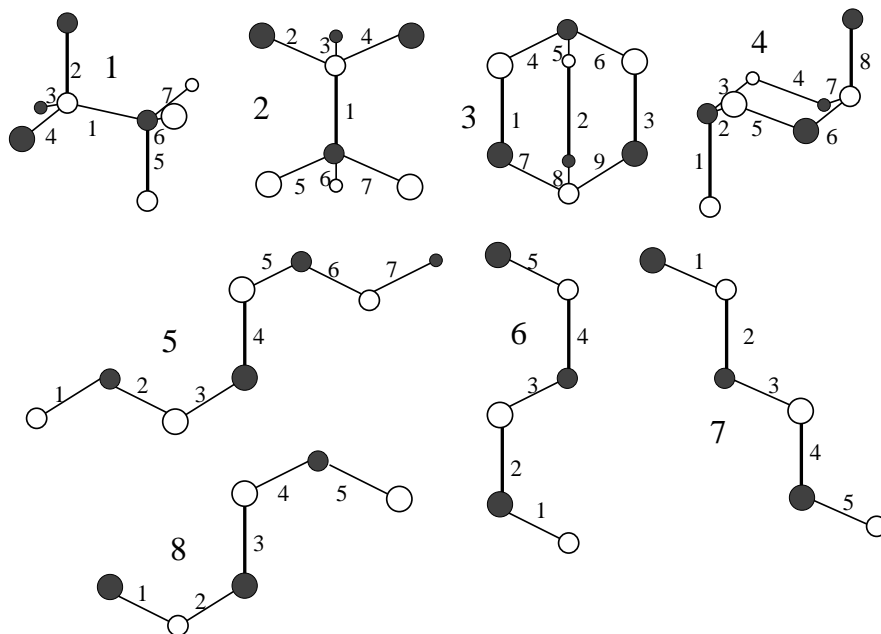
### 3.2. Computational details

We apply the procedure described above to calculate the correlation energies per unit cell (u.c.) for SiC and the III–V compounds AlN, GaN and InN, with the zinc-blende (2 atoms/u.c.) and wurtzite (4 atoms/u.c.) structures. We evaluate the symmetry-unique increments in equation (4) and multiply them by appropriate weight factors which are determined by the crystalline symmetry of the unit cell.

**Table 2.** Correlation-energy increments for SiC (in hartrees) for the zinc-blende and wurtzite structures, determined at the CCSD level using basis A. For the numbering of the clusters and bonds involved, see figures 2 and 3.

	Zinc-blende structure			Wurtzite structure		
	Cluster/bond	Increment	Weight	Cluster/bond	Increment	Weight
$\Delta\epsilon_i$	1/1	-0.022 471	4	1/1	-0.022 428	3
				2/1	-0.022 511	1
$\Delta\epsilon_{ij}$	1/1, 2	-0.016 122	6	1/1, 4	-0.016 190	3
	1/1, 5	-0.003 929	6	1/1, 6	-0.003 901	3
				2/1, 2	-0.016 076	3
				2/1, 5	-0.003 932	3
$\Delta\epsilon_{ij}$	1/2, 5	-0.000 773	12	1/3, 6	-0.000 773	6
	1/2, 6	-0.000 682	24	1/3, 7	-0.000 681	6
				2/2, 6	-0.000 819	6
				2/2, 5	-0.000 640	3
				1/2, 5	-0.000 774	3
				1/2, 6	-0.000 680	6
				1/3, 5	-0.000 690	6
$\Delta\epsilon_{ij}$	2/1, 4	-0.000 247	6	3/1, 2	-0.000 265	3
	2/2, 5	-0.000 089	6	3/6, 7	-0.000 152	6
	5/1, 4	-0.000 249	12	4/3, 6	-0.000 271	3
	3/1, 4	-0.000 117	12	4/1, 6	-0.000 131	6
	3/2, 5	-0.000 195	24	4/2, 8	-0.000 205	6
	4/1, 4	-0.000 161	12	5/1, 4	-0.000 200	6
	4/2, 5	-0.000 076	24	5/4, 7	-0.000 078	6
				5/2, 5	-0.000 088	6
				5/3, 6	-0.000 167	6
				6/2, 5	-0.000 287	3
				6/1, 4	-0.000 098	3
				7/1, 4	-0.000 187	6
				7/2, 5	-0.000 070	6
				8/1, 4	-0.000 165	6
				8/2, 5	-0.000 076	6
				2 <sup>zb</sup> /1, 4	-0.000 248	3
			2 <sup>zb</sup> /2, 5	-0.000 088	3	
			3 <sup>zb</sup> /2, 5	-0.000 196	6	
			4 <sup>zb</sup> /2, 5	-0.000 076	6	
$\Delta\epsilon_{ijk}$	1/1, 2, 3	0.002 013	4	1/1, 3, 4	0.001 998	1
	1/1, 5, 6	0.000 138	4	1/1, 6, 7	0.000 130	1
	1/1, 2, 5	0.000 040	12	2/1, 2, 3	0.002 024	3
	1/1, 2, 6	0.000 134	24	2/1, 5, 6	0.000 139	3
				2/1, 2, 7	0.000 057	3
				2/1, 2, 5	0.000 181	6
				1/1, 2, 5	0.000 040	3
				1/1, 4, 6	0.000 133	6
				1/1, 4, 7	0.000 038	6
				1/1, 2, 6	0.000 132	6
				1/1, 3, 5	0.000 131	6

For the zinc-blende structure all four bonds of the unit cell are equivalent. In the wurtzite structure the two vertical bonds along the  $c$ -direction ( $b_1$  in figure 1(b)) differ from the six bonds of the buckling plane ( $b_2$  in figure 1(b)); these bonds will be called planar bonds in the following. For a direct comparison of the two structures we reduce the correlation energy per unit cell of the wurtzite structure by a factor of 2. The weight factors of all of the increments considered for both structures are listed in table 2.



**Figure 3.**  $X_n Y_n H_m$  clusters of the wurtzite structure treated at the CCSD level for the correlation calculation; the broader lines indicate the vertical bonds; big numbers designate clusters, small numbers the bonds in each cluster; H atoms are not drawn.

Since (dynamical) correlations are a local effect, the increments should be fairly local entities, at least for semiconductors and insulators. We use this property to calculate the correlation-energy increments in finite clusters. We select the clusters as fragments of the zinc-blende and wurtzite structures so that we can calculate all two-bond increments up to third-nearest neighbours and all nearest-neighbour three-bond increments. The clusters used for the zinc-blende structure are shown in figure 2, and those for the wurtzite structure in figure 3. In the zinc-blende structure all bond lengths and bond angles (tetrahedral,  $\Theta = 109.4712^\circ$ ) are the same. As mentioned before, in the wurtzite structure the vertical and planar bond lengths are different, and so are the planar-vertical ( $\Theta_1$  in figure 1(b)) and planar-planar ( $\Theta_2$  in figure 1(b)) bond angles, too. The numerical values for the bond lengths and bond angles are taken from the Hartree-Fock calculations for the periodic solid; for the zinc-blende structure these are  $b^{\text{SiC}} = 1.8963 \text{ \AA}$ ,  $b^{\text{AlN}} = 1.8941 \text{ \AA}$ ,  $b^{\text{GaN}} = 1.9579 \text{ \AA}$  and  $b^{\text{InN}} = 2.1594 \text{ \AA}$ , and for the wurtzite structure we have  $b_1^{\text{SiC}} = 1.9089 \text{ \AA}$ ,  $b_2^{\text{SiC}} = 1.8919 \text{ \AA}$ ,  $\Theta_1^{\text{SiC}} = 109.3706^\circ$ ,  $\Theta_2^{\text{SiC}} = 109.5717^\circ$ ;  $b_1^{\text{AlN}} = 1.8983 \text{ \AA}$ ,  $b_2^{\text{AlN}} = 1.8934 \text{ \AA}$ ,  $\Theta_1^{\text{AlN}} = 108.3516^\circ$ ,  $\Theta_2^{\text{AlN}} = 110.5684^\circ$ ;  $b_1^{\text{GaN}} = 1.9619 \text{ \AA}$ ,  $b_2^{\text{GaN}} = 1.9547 \text{ \AA}$ ,  $\Theta_1^{\text{GaN}} = 109.0063^\circ$ ,  $\Theta_2^{\text{GaN}} = 109.9321^\circ$ ;  $b_1^{\text{InN}} = 2.1677 \text{ \AA}$ ,  $b_2^{\text{InN}} = 2.1608 \text{ \AA}$ ,  $\Theta_1^{\text{InN}} = 108.8072^\circ$ ,  $\Theta_2^{\text{InN}} = 110.1270^\circ$ . The dangling bonds of the clusters are saturated by hydrogens. The internuclear



X–H distances have been taken from the  $\text{XH}_4$  molecule for C and Si ( $b_{\text{CH}} = 1.102 \text{ \AA}$  and  $b_{\text{SiH}} = 1.480 \text{ \AA}$ ); for the other cases they have been optimized in CCSD calculations for the  $\text{XNH}_6$  cluster, yielding  $b_{\text{AlH}} = 1.614 \text{ \AA}$ ,  $b_{\text{GaH}} = 1.621 \text{ \AA}$ ,  $b_{\text{InH}} = 1.711 \text{ \AA}$ , and for  $\text{AlNH}_6$ , yielding  $b_{\text{NH}} = 1.016 \text{ \AA}$ . Using the finite clusters instead of the periodic solid, we can use the Foster–Boys criterion [18] to localize bond orbitals instead of constructing Wannier functions. Following the procedure described above we calculated the correlation-energy increments at the CCSD level, using the program package MOLPRO94 [14], successively correlating more and more of the localized X–Y bond orbitals while keeping the other cluster orbitals inactive.

**Table 3.** Energy differences and lattice parameters of the zinc-blende and wurtzite structure of SiC and the III–V nitrides.  $\Delta E_{\text{w-zb}}$  is the relaxed energy difference in hartrees per two atoms.  $a_{\text{zb}}$  (in  $\text{\AA}$ ) is the zinc-blende lattice constant;  $a_{\text{w}}$  and  $c_{\text{w}}$  are the lattice constants of the wurtzite structure and  $u$  is its cell-internal parameter. For comparison other theoretical values and the experimental values at room temperature are given.

		$\Delta E_{\text{w-zb}}$	$a_{\text{zb}}$	$a_{\text{w}}$	$c_{\text{w}}$	$c/a$	$u$
<b>SiC</b>	HF	+ 0.0004	4.3793	3.0914	5.0728	1.6409	0.3763
	HF + corr	+ 0.0007	4.3862				
	LDA [6]	+ 0.0007	4.3445	3.0692	5.0335	1.64	Ideal
	LDA [7]	+ 0.0007	4.2907	3.020	5.012	1.66	0.3758
	Experiment		4.3596	3.0763	5.0480	1.6409	
<b>AlN</b>	HF	−0.0030	4.3742	3.1002	4.9888	1.6092	0.3805
	HF + corr	−0.0036					
	LDA [2]	−0.0014	4.365	3.099	4.997	1.612	0.381
	LDA [4]		4.421	3.144	5.046	1.605	0.381
	LDA [5]		4.32	3.06	4.91	1.60(5)	0.383
	Experiment			3.110–3.1127	4.9798–4.982	1.5998–1.6019	
<b>GaN</b>	HF	−0.0010	4.5215	3.2011	5.1970	1.6235	0.3775
	HF + corr	−0.0013					
	HF [15]			3.199	5.176	1.618	0.38
	LDA [2]	−0.0007	4.364	3.095	5.000	1.633	0.378
	LDA [4]		4.446	3.146	5.115	1.626	0.377
	LDA [5]		4.46	3.17	5.13	1.62	0.379
	Experiment			3.160–3.190	5.125–5.190	1.6249–1.6279	
<b>InN</b>	HF	−0.0015	4.9870	3.5428	5.7287	1.6170	0.3784
	HF + corr	−0.0023					
	LDA [2]	−0.0008	4.983	3.536	5.709	1.615	0.380
	LDA [5]		4.92	3.53	5.54	1.57	0.388
	Experiment			3.5446	5.7034	1.6090	

The one-particle basis sets used in the cluster calculations can be characterized as follows. For hydrogen we chose Dunning’s double- $\zeta$  basis [19] without the p polarization function. For the other elements we use energy-consistent quasi-relativistic large-core pseudopotentials [11] with the corresponding valence basis sets optimized for the atoms. One basis set (basis A) has the same quality as that for the corresponding Hartree–Fock calculations of the solid: (4s4p)/[3s3p] supplemented with one d polarization function, which is optimized in a CCSD calculation for the  $\text{XYH}_6$  cluster [16, 17]. In addition, an extended basis set (basis B) has been generated by uncontracting the s and p functions of basis A and by replacing the single d function by a 2d1f polarization set [16, 17]. This basis

set is only used for the five largest increments, which are evaluated in  $X_2Y_2H_{10}$  clusters.

The convergence of the incremental expansion has been checked for all substances, but will be discussed here in detail only for SiC. In table 2 all of the required increments are listed for both structures. They rapidly decrease with increasing length of the bonds involved. The nearest-neighbour two-bond increments are about eight times larger than the weighted sum of all third-nearest ones. After the latter, we truncate the expansion of the correlation energy because with the fourth-nearest-neighbours' contribution we reach the van der Waals limit of the correlation energy (decay  $\sim r^{-6}$ ). The error due to the truncation can be estimated to be 0.5% of the correlation energy. The convergence with respect to the number of bonds simultaneously correlated in the incremental expansion is also satisfactory. For SiC, the one-bond increment contributes 38% of the correlation energy; the two-bond increments are very important (67%) but lead to an overestimation of the correlation energy, which is effectively reduced by the three-bond increments (5%). The most important four-bond increments contribute only 0.5% to the incremental expansion, and are neglected therefore. Thus, the overall error due to truncation of the incremental expansion is less than 1% of the correlation energy. The shortcomings of one- and many-particle basis sets in the determination of individual increments cause the largest part of the error of the correlation energy. The dependence on the one-particle basis is discussed in detail in reference [17] for the III–V compounds.

## 4. Results and discussion

### 4.1. The energy difference between the wurtzite and zinc-blende structures

As described in section 2, we separately optimized the geometries of the zinc-blende and wurtzite structures and determined the total Hartree–Fock energy for each structure at its equilibrium geometry. We compare the two total energies and calculate their difference,  $\Delta E_{w-zb}^{HF}$ , per two atoms in hartrees. In the second step, we calculated correlation energies, for the Hartree–Fock-optimized geometries, for both the zinc-blende and the wurtzite structure using the method of increments described above. The energy difference between the two structures  $\Delta E_{w-zb}^{corr}$  is calculated for the correlation part. The results are listed in the first column of table 3. In all cases, electron correlation yields the same energetic order of states as the Hartree–Fock method, but energy differences are enlarged by up to 40% for SiC, and are negligible for none of the substances.

For SiC we found that the zinc-blende structure is slightly more stable than the wurtzite one, but the energy difference is so small that it might be taken as an indication of the polytypism occurring. The LDA calculations lead to the same conclusion, but the absolute value of the relaxed LDA energy difference [7] is even smaller than ours, by about a factor of 10. Käckell *et al* found a strong influence of the relaxation on the energy difference (up to a factor of 10) which explains the large discrepancy between the two sets of LDA results listed in table 3. The large deviation between our result and the relaxed LDA result can be understood from a comparison of the corresponding volumes of the unit cell. Whereas in the work of Käckell *et al* the zinc-blende volume was found to be smaller by about  $0.18 \text{ \AA}^3$  than the wurtzite one, in our calculations the volumes are essentially the same.

For all III–V nitrides the calculations yield a stable wurtzite structure as experimentally observed. The energy differences are significantly larger than the one for SiC, which clearly indicates that no polytypism exists for the III–V nitrides. The most stable compound in wurtzite structure is AlN, followed by InN and then GaN. For the latter two systems it was also possible to epitaxially grow the zinc-blende structure [20, 21]. In comparison with the

**Table 4.** Cohesive energies per unit cell in hartrees; their ratio to the corresponding experimental values is given in parentheses; for comparison, literature data from LDA calculations are also reported.

	SiC	AlN	GaN	InN
$E_{\text{coh}}^{\text{HF}}$	-0.329 (70%)	-0.287 (67%)	-0.185 (56%)	-0.132 (45%)
$E_{\text{coh}}^{\text{HF+corr}}$ (basis A)	-0.418 (89%)	-0.380 (89%)	-0.288 (86%)	-0.236 (81%)
$E_{\text{coh}}^{\text{HF+corr}}$ (basis B)	-0.440 (93%)	-0.400 (93%)	-0.307 (92%)	-0.257 (88%)
$E_{\text{coh}}^{\text{LDA}}$	-0.622 [7] (132%)	—	-0.397 [27] (119%) -0.478 [28] (144%)	—
$E_{\text{coh}}^{\text{exp}}$	-0.471	-0.429	-0.333	-0.293

LDA results given by Yeh *et al* [2], our energy differences are larger again, by about a factor of two, but the trends reproduced are the same. A possible explanation is the following: the LDA gets the long-range interaction right, because the latter can be well described in a mean-field approach, and thus yields the right structure. But the short-range correlations, which can only be described with a many-body theory, have a substantial influence on the total energy and on the energy differences as well.

#### 4.2. The lattice parameter

In order to find the minimum of the total energy we calculated the optimized Hartree–Fock geometries for both the zinc-blende and wurtzite structures. The results are listed in table 3. The experimental values [22] are measured at room temperature. The extrapolation to zero degrees Kelvin changes the measured value for SiC by 0.001 Å. In table 3 we listed for comparison the range of the room-temperature experimental values where available and some other theoretical values obtained within the LDA.

For SiC the lattice constants of both structures are slightly too large (by 0.5%), but the ratio  $c/a$  of the wurtzite structure agrees perfectly with experiment. This ratio is somewhat larger than the ideal one, which indicates that the zinc-blende structure is more stable than the wurtzite one. The internal-cell parameter  $u$  only marginally differs from the ideal one. The LDA results underestimate the lattice constants (Karch *et al*: 0.2%–0.3%; Käckell *et al*: 0.7%–1.8%). Their  $c/a$  ratio is in good agreement with experiment, too. Karch *et al* did not allow for an internal-cell relaxation and Käckell *et al* found it even closer to the ideal one than we did.

The III–V nitrides are stable in the wurtzite structure. The  $c/a$  ratio is smaller than the ideal one, i.e. the bonds in the direction of the  $c$ -axis (figure 1(b),  $b_1$ ) are shorter than those ((figure 1(b),  $b_2$ ) of the buckling plane.

Our calculated lattice parameters for the wurtzite structure of AlN agree well with experiment, the  $c/a$  ratio slightly differs from experiment, and a larger deviation from the ideal  $u$  occurs than for SiC. For the zinc-blende structure no experimental data are available, but our result lies in the same region as the various LDA results.

For GaN the Hartree–Fock calculation overestimates the lattice constants by  $\sim 1.3\%$ , although the  $c/a$  ratio agrees well with experiment. This fact can partly be explained with the missing electron correlation (cf. the discussion below). The  $u$ -parameter is smaller than

that of AlN but still larger than the ideal one, which indicates that the wurtzite structure of GaN is not as stable as that of AlN.

For InN all lattice parameters are close to the experimental values. The  $u$ -parameter lies between those of AlN and GaN; the same holds true for the  $c/a$  ratio.

The influence of correlations on the lattice parameters has been discussed in detail for various cubic III–V compounds, applying the method of increments, by Kalvoda *et al* [23]. Here, we checked this influence for SiC only, where we calculated the cubic lattice constant at the correlated level with basis A. Virtually no change to the Hartree–Fock value is seen (an increase of  $\leq 0.1\%$ ). This can be understood by considering the opposing effects of inter- and intra-atomic correlations. The inter-atomic correlation that dominates for the lighter elements such as C and N increases the lattice constant, while intra-atomic correlations that become more important for heavier elements decrease it. Thus the net effect of correlation cancels for SiC and probably, to a great part, for AlN, too. GaN is an exception: there the core–valence correlation yields an important contribution to the reduction of the lattice constant, because the fully occupied 3d shell of Ga is easily polarizable. Simulating this effect with a core polarization potential reduces the lattice constant by about 1% (e.g. for GaAs by 0.9% [23]).

The LDA results agree on average quite well with experiment, but are not systematically better than our results. With LDA, there is a small underestimation of the lattice constants, which is a well-known shortcoming of this method. Moreover, the LDA results spread quite a lot.

#### 4.3. Cohesive energies

The cohesive energy per unit cell is calculated as difference between the total energy of the zinc-blende structure and that of the free atoms:  $E_{\text{coh}} = E_{\text{zb}} - \sum_i E_{\text{atom},i}$ . For the Hartree–Fock calculation, we use the enlarged [3s3p1d] (Ga and In: [3s3p2d]) basis, although the changes with respect to the [2s2p1d] basis are small. The Hartree–Fock results together with the experimental data are listed in table 4.

The energy differences between the zinc-blende and wurtzite structure are so small that they could not be measured so far. We take the experimental cohesive energies from Harrison [24] and correct them by the phonon zero-point energies  $\frac{9}{8}k_B\Theta_D$  (derived from the Debye model [25];  $\Theta_D$  from reference [22]) as well as by atomic spin–orbit splittings [26]. Both effects increase the cohesive energy. For SiC and AlN the phonon zero-point energy dominates by about 0.004 au and 0.003 au, respectively, over the spin–orbit splitting of the free atoms (by about a factor of 10). For GaN both effects are nearly equal ( $\sim 0.002$  au); for InN the spin–orbit splitting clearly dominates ( $\sim 0.007$  au). In all cases, the total effect is larger than the energy difference between the two structures. According to Harrison [24] an experimental error due to measuring the heat of formation and the heat of atomization at different temperatures can be estimated to be about 0.0015 au which leads to an experimental error bar of less than 1% of the cohesive energy.

At the Hartree–Fock level, we reach between 70% (SiC) and 45% (InN) of the experimental cohesive energy. At the correlated level, we performed calculations with two different basis sets. With basis A we reach 89% of the experimental cohesive energy for SiC and AlN, and 86% and 81% for GaN and InN, respectively (table 4). The improved basis set (basis B) yields much better results especially for the heavier compounds: whereas the improvement due to the basis set is only 4% for SiC and AlN, for GaN and InN it is up to 7% (table 4). This shows that excitations from the  $sp^3$  bonds into unoccupied d and f shells are becoming more and more important. Overall we reach on average 91% of the

experimental cohesive energy. For comparison, LDA results are listed in table 4, too. They clearly overestimate the cohesive energies (by up to 44%).

#### 4.4. Bulk moduli

For cubic structures the bulk modulus  $B = V \partial^2 E / \partial V^2$  can be easily derived from the curvature:

$$B = \left( \frac{4}{9a} \frac{\partial^2}{\partial a^2} - \frac{8}{9a^2} \frac{\partial}{\partial a} \right) E(a). \quad (5)$$

Calculation of the bulk modulus for the wurtzite structure would require full geometry optimization at every volume point. Only thus would the correct relaxation behaviour to a homogeneous pressure be obtained. We have not performed this time-demanding procedure and restrict ourselves to the bulk moduli of the zinc-blende structure here. The latter have been determined for the optimized Hartree–Fock lattice constant, so that the second term in (5) is zero. The results are listed in table 5.

**Table 5.** Bulk moduli in Mbar for the zinc-blende structure; deviations from the average experimental values (reference [7] and [5] and references therein) are given in parentheses; for comparison, literature data from LDA calculations are also reported.

		SiC	AlN	GaN	InN
$B_{\text{HF}}$	zb	2.54 (+13%)	2.18 (+10%)	2.54 (+17%)	1.59 (+27%)
$B_{\text{HF+corr}}$	zb	2.44 (+9%)			
$B_{\text{LDA}}$	zb	2.22 [7]	2.03 [5]	2.01 [5]	1.39 [5]
	w	2.10 [7]	2.02 [5]	2.07 [5]	1.46 [5]
$B_{\text{exp}}$	zb	2.24	—	—	—
	w	2.23	1.85–2.12	1.88–2.45	125

The Hartree–Fock approximation leads to an overestimation of the bulk moduli by between 10% and 27%. Electron correlations reduce the bulk moduli by allowing an instantaneous response of the electrons to an homogeneous pressure. For a detailed analysis and a discussion of the errors, see reference [23]. Here we performed correlated calculations for zinc-blende SiC in basis A only, where electron correlations reduce the bulk modulus only slightly (see table 5). A further improvement of the one-particle basis set is expected to yield a further reduction. The LDA results are in better agreement with experiment than ours. In table 5, we list LDA results for both zinc-blende and wurtzite structure in order to show that the structural influence on the bulk moduli is small. Kim *et al* [5] even claim that the uncertainty of their calculations is larger than the difference between the bulk moduli of the two structures.

## 5. Conclusion

We have performed correlated *ab initio* calculations for SiC and III–V nitrides in the zinc-blende and wurtzite structures. The mean-field part has been determined for the periodic solid using the program package CRYSTAL92. Correlation contributions have been evaluated using the coupled-cluster approach with single and double excitations, applying the methods of local increments. Pseudopotentials have been used in conjunction with valence basis sets

optimized for the solid. Results have been obtained for the ground-state energies of both structures with fully optimized geometries. For SiC the zinc-blende structure is slightly more stable, but the small energy difference from the wurtzite structure confirms the polytypism occurring. AlN, GaN and InN are stable in the wurtzite structure with a significant energy difference from the zinc-blende structure. The calculated lattice parameters agree well with experiment. The cohesive energies reach only 45% to 70% of the experimental values, at the Hartree–Fock level, but electron correlations increase these percentages to over 90%. Bulk moduli for the zinc-blende structure are overestimated by 10% to 30% at the Hartree–Fock level; electron correlations yield a reduction.

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## References

- [1] Davis R F 1993 *Physica B* **185** 1
- [2] Yeh C-Y, Lu Z W, Froyen S and Zunger A 1992 *Phys. Rev. B* **46** 10086
- [3] Min B J, Chan C T and Ho K M 1992 *Phys. Rev. B* **45** 1159
- [4] Miwa K and Fukumoto A 1993 *Phys. Rev. B* **48** 7897
- [5] Kim K, Lambrecht W R L and Segall B 1996 *Phys. Rev. B* **53** 16310
- [6] Karch K, Pavone P, Windl W, Schütt O and Strauch D 1994 *Phys. Rev. B* **50** 17054
- [7] Käckell P, Wenzien B and Bechstedt F 1994 *Phys. Rev. B* **50** 17037
- [8] Pisani C, Dovesi R and Roetti C 1988 *Hartree–Fock Ab initio Treatment of Crystalline Systems (Springer Lecture Notes in Chemistry 48)* ed G Berthier *et al* (Berlin: Springer)
- [9] Dovesi R, Saunders V R and Roetti C 1992 *Computer Code CRYSTAL92* Gruppo di Chimica Teorica, University of Torino, and United Kingdom Science and Engineering Research Council Laboratory, Daresbury
- [10] Stoll H 1992 *Phys. Rev. B* **46** 6700
- [11] Bergner A, Dolg M, Küchle W, Stoll H and Preuss H 1993 *Mol. Phys.* **80** 1431
- [12] Schwerdtfeger P, Fischer T, Dolg M, Igel-Mann G, Nicklass A, Stoll H and Haaland A 1995 *J. Chem. Phys.* **102** 2050  
Leininger T, Nicklass A, Stoll H, Dolg M and Schwerdtfeger P 1996 *J. Chem. Phys.* **105** 1052
- [13] Dolg M, unpublished results  
Leininger T, Berning A, Nicklass A, Stoll H, Werner H-J and Flad H-J 1997 *Chem. Phys.* at press
- [14] MOLPRO is a package of *ab initio* programs written by H-J Werner and P J Knowles, with contributions from J Almlöf, R D Amos, A Berning, C Hampel, R Lindh, W Meyer, A Nicklass, P Palmieri, K A Peterson, R M Pitzer, H Stoll, A J Stone and P R Taylor.  
Hampel C, Peterson K and Werner H-J 1992 *Chem. Phys. Lett.* **190** 1  
Knowles P J, C. Hampel and Werner H-J 1993 *J. Chem. Phys.* **99** 5219
- [15] Pandey R, Causà M, Harrison N M and Seel M 1996 *J. Phys.: Condens. Matter* **8** 3993
- [16] Paulus B, Fulde P and Stoll H 1995 *Phys. Rev. B* **51** 10572
- [17] Paulus B, Fulde P and Stoll H 1996 *Phys. Rev. B* **54** 2556
- [18] Foster J M and Boys S F 1960 *Rev. Mod. Phys.* **32** 296
- [19] Dunning T H 1989 *J. Chem. Phys.* **90** 1007
- [20] Lei T, Moustakas T D, Graham R J, He Y and Berkowitz S J 1992 *J. Appl. Phys.* **91** 4933
- [21] Strite S, Ruan J, Smith D J, Sariel J, Manning N, Chen H, Choyke W J and Morkoç H 1992 *Bull. Am. Phys. Soc.* **37** 346
- [22] *Physics of Group IV Elements and III–V Compounds; Landolt–Börnstein New Series* 1982 Group III, vol 17a, ed K-H Hellwege (Berlin: Springer)
- [23] Kalvoda S, Paulus B, Fulde P and Stoll H 1997 *Phys. Rev. B* at press

- [24] Harrison W A 1989 *Electronic Structure and the Properties of Solids* (New York: Dover)
- [25] Farid B and Godby R 1991 *Phys. Rev. B* **43** 14248
- [26] Moore C E 1958 *Atomic Energy Levels* NBS Circular No 467 (Washington, DC: US Government Printing Office)
- [27] Kim K, Lambrecht W R L and Segall B 1994 *Phys. Rev. B* **50** 1502
- [28] Jhi S-H and Ihm J 1995 *Phys. Status Solidi b* **191** 387