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***Ab initio* band structure calculations of Mg₃N₂ and MgSiN₂**

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Abstract. *Ab initio* band structure calculations were performed for MgSiN₂ and Mg₃N₂. Calculations show that both nitrides are semiconductors with direct energy gaps at Γ . The valence bands are composed mainly of N 2p states hybridized with s and p characters of the metals. The bottom of the conduction band consists of the s characters of Mg and N for Mg₃N₂, as well as for MgSiN₂, while the characters of Si are higher in energy. The optical diffuse spectra show an energy gap of about 2.8 eV for Mg₃N₂ and 4.8 eV for MgSiN₂, in agreement with the calculated values.

1. Introduction

In recent years nitrides have become an important subject of research [1, 2]. Some binary nitrides, such as AlN and Si₃N₄, are used as high-performance engineering materials and substrate materials in the semiconductor industry [1]. MgSiN₂ is noted as an alternative ternary compound for high temperature application, showing properties such as a reasonable thermal conductivity, a rather good fracture toughness and hardness, and a good oxidation resistance up to 920 °C [3, 4]. MgSiN₂ is also promising as a substrate material with an electrical resistivity at room temperature comparable to and at high temperature higher than that of AlN [4]. Gaido *et al* showed that (Eu-doped) MgSiN₂ has not only similar luminescence properties to AlN, but also a quantum yield for the green band as high as 40%, as compared to 8% for AlN [5].

MgSiN₂ crystallizes in an orthorhombic structure, which is derived from the wurtzite structure. The hexagonal structure is distorted because of the presence of two metal atoms and displacement of the nitrogen atoms from the ideal positions in the wurtzite structure [6, 7]. The study for MgSiN₂ has been concentrated on preparation, characterization [3, 4, 6–8], mechanical and thermal properties [3, 4, 9], as well as the luminescence properties of the rare earth doped materials [5, 10]. There has been almost no work performed for the electronic properties, except the optical reflectance experiments, which showed MgSiN₂ has an energy gap of about 4.8 eV [5].

Mg₃N₂ is widely used as a catalyst in the preparation of some nitrides, such as silicon nitride ceramics and cubic boron nitride [11]. It was found in 1933 that some alkaline earth metal nitrides M₃N₂ (M = Be, Mg, Ca) have the anti-bixbyite structure [12–14]. Partin *et al* for the first time refined fully the structure for Mg₃N₂ from neutron time-of-flight diffraction data [15]. In this structure the Mg atoms are at the tetrahedral sites of an approximately cubic close packed array of N atoms (MgN₄).

In this paper we report in detail the results of *ab initio* calculations for the electronic structure of the ternary nitride MgSiN_2 using the local spherical wave (LSW) approach. For comparison calculations are also performed for the binary nitride Mg_3N_2 . The bond valences in the ternary nitrides are discussed. The electronic structure of the ternary nitride is compared to those of the binary nitrides Mg_3N_2 and Si_3N_4 .

2. Structure and bond valences

MgSiN_2 was first prepared by David and Lang using either (nitridation of) Mg_2Si and/or a mixture of the binary nitrides [16]. Wintenberger *et al* refined the structure of MgSiN_2 from neutron and x-ray diffraction data [17]. For the purpose of our band structure calculations the accurate structure of the compound was obtained from neutron diffraction data. MgSiN_2 was prepared directly from the binary nitrides Mg_3N_2 and Si_3N_4 , as described in [3]. Neutron diffraction determinations and refinements were performed at Intense Pulsed Neutron Source, Argonne National Laboratory (US). The former structure [6, 16, 17] was confirmed. The details of the preparation, structure determination and thermal expansion properties will be published elsewhere [18]. MgSiN_2 is orthorhombic, with lattice parameters: $a = 5.2708 \text{ \AA}$, $b = 6.4692 \text{ \AA}$ and $c = 4.9840 \text{ \AA}$. All the atoms are at general positions 4a of the space group $Pna2_1$. Both Mg and Si atoms are tetrahedrally coordinated by N (see figure 1 and table 1). The average Mg–N distance is 2.090 \AA , which is shorter than that in Mg_3N_2 (2.141 \AA). The Si–N distances range from 1.728 to 1.766 \AA . The average Si–N distance is 1.752 \AA , longer than that in Si_3N_4 (1.732 for $\beta\text{-Si}_3\text{N}_4$ [19], 1.738 \AA for $\alpha\text{-Si}_3\text{N}_4$ [20]). The Mg–Mg distances are about 3.09 to 3.11 \AA , which are also longer than those in Mg_3N_2 , but shorter than those (about 3.20 \AA) in the Mg metal. The shortest N–N distance is about 2.829 \AA , larger than that in $\beta\text{-Si}_3\text{N}_4$ (2.77 \AA) [19].

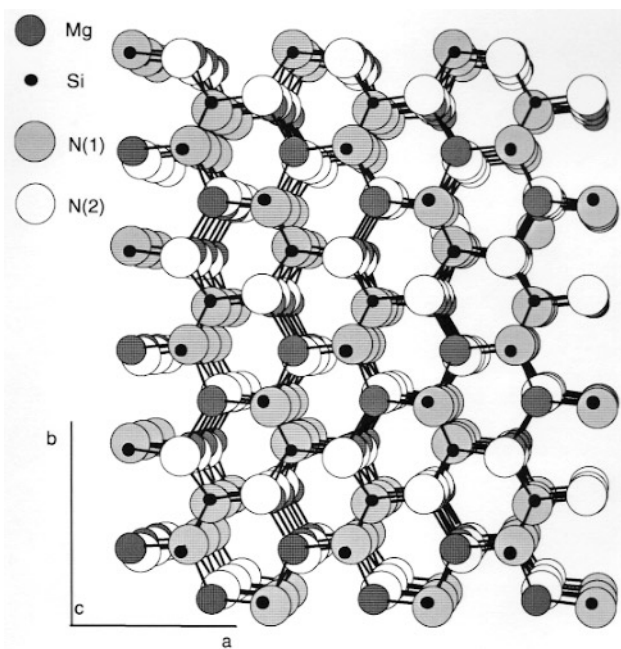


Figure 1. The projection of the structure of MgSiN_2 along $[001]$.

Table 1. Interatomic distances (d_i , Å) and bond valences (V , vu) in the compounds Mg₃N₂ and MgSiN₂, and compared to that of β -Si₃N₄.

d_i (Å)	V (vu)	d_i (Å)	V (vu)
a. Mg ₃ N ₂ [15]			
Mg–N(1) 2.145	2.03	N(1)–Mg 2.145 (6×)	3.00
–N(2) 2.084		N(2)–Mg 2.084 (2×)	
–N(2) 2.160		–Mg 2.160 (2×)	
–N(2) 2.179		–Mg 2.179 (2×)	
b. MgSiN ₂ [18]			
Mg–N(1) 2.0630	2.33	N(1)–Mg 2.0630	3.20
–N(1) 2.0707		–Mg 2.0707	
–N(2) 2.1240		–Si 1.7458	
–N(2) 2.1019		–Si 1.7284	
Si–N(1) 1.7458	3.78	N(2)–Mg 2.1019	2.91
–N(1) 1.7284		–Mg 2.1240	
–N(2) 1.7660		–Si 1.7657	
–N(2) 1.7657		–Si 1.7660	
c. β -Si ₃ N ₄ [19]			
Si–N(1) 1.730	3.98	N(1)–Si 1.730 (3×)	3.00
–N(1) 1.728		N(2)–Si 1.728	
–N(2) 1.704		–Si 1.704	
–N(2) 1.767		–Si 1.767	

The lattice parameter and coordinates of Mg₃N₂ were obtained from the recent structure determination by Partin *et al* [15]. Mg₃N₂ is cubic with lattice parameter $a = 9.9528$ Å. The metal (Mg) atoms are in general positions 48e of space group $Ia\bar{3}$ (x, y, z). There are two crystallographically different kinds of N atom, as shown in tables 1 and 2. N1 is in positions 8b (1/4, 1/4, 1/4), and N2 in positions 24d ($x, 0, 1/4$). In the structure the N arrays are fairly close to ideal cubic close packing. The 12 shortest N–N distances are in the range from 3.31 to 3.72 Å. Each nitrogen atom is coordinated by six Mg atoms. N1 has six Mg neighbours with a distance of 2.145 Å, while N2 is coordinated by six Mg with different N–Mg distances ranging from 2.084 to 2.179 Å. There are Mg–Mg distances of 2.72 Å.

In MgSiN₂ both Mg and Si are in tetrahedral coordination by N, the same as Si in Si₃N₄. The coordination of N by Mg and/or Si is different: N in Mg₃N₂ has six nearest Mg neighbours, and N in MgSiN₂ is coordinated to four neighbours (two Mg and two Si), while in Si₃N₄ every N is coordinated to three tetrahedral Si [19, 20].

Some insight into the bonding of Mg and Si in MgSiN₂ can be obtained using the concept of bond valence [21]. The bond V_i is calculated from the relations: $V_i = \exp[(d_0 - d_i)/b]$, where d_i is the distance between the atoms of bond i , and $b = 0.37$ is the universal constant. If the ionic model is used for Mg₃N₂ and β -Si₃N₄, then d_0 is 1.889 Å for Mg–N and 1.730 Å for Si–N. The bond valence or oxidation state V of an atom is calculated by summing over all neighbouring atoms $V = \sum V_i$. The calculated bond valences are given in table 1. In MgSiN₂, the bond valence of Mg is 2.33 valence units (vu), larger than 2.03 vu in Mg₃N₂, while Si have the valence of 3.78 vu, smaller than that in β -Si₃N₄. That is due to the fact that Si is more electronegative than Mg.

3. Calculations and results

Ab initio band structure calculations were performed with the localized spherical wave (LSW) method [22] using a scalar-relativistic Hamiltonian. We used local-density

Table 2. Input for the calculations (space group, lattice parameter, position and Wigner–Seitz radius (R_{WS}) of atoms and empty spheres), and some calculated results (electronic configurations) of Mg_3N_2 [15] and $MgSiN_2$ [18].

a. Mg_3N_2 : space group $Ia\bar{3}$ (No 206), $a = 9.9528 \text{ \AA}$					
	WP	Coordinates	R_{WS} (\AA)	EC(N 2s)	EC(N 3s)
Mg	48e	(0.3890, 0.1520, 0.3823)	1.101	$[Ne]3s^{0.20}3p^{0.24}3d^{0.06}$	$[Ne]3s^{0.19}3p^{0.23}3d^{0.05}$
N1	8b	(1/4, 1/4, 1/4)	1.363	$[He]2s^{1.82}2p^{4.45}3d^{0.02}$	$([He]2s^2)3s^{0.03}2p^{4.38}3d^{0.02}$
N2	24d	(0.9695, 0, 1/4)	1.342	$[He]2s^{1.81}2p^{4.48}3d^{0.02}$	$([He]2s^2)3s^{0.03}2p^{4.40}3d^{0.02}$
Va1	8a	(0, 0, 0)	1.363	$1s^{0.33}2p^{0.30}3d^{0.11}$	$1s^{0.34}2p^{0.28}3d^{0.09}$
Va2	16c	(1/8, 1/8, 1/8)	1.220	$1s^{0.26}2p^{0.22}3d^{0.07}$	$1s^{0.26}2p^{0.19}3d^{0.05}$
Va3	24d	(0.7394, 0, 1/4)	1.148	$1s^{0.26}2p^{0.15}3d^{0.04}$	$1s^{0.27}2p^{0.15}3d^{0.03}$
Va4	48e	(0.2531, 0.1543, 0.6109)	0.536	$1s^{0.08}2p^{0.01}3d^{0.00}$	$1s^{0.07}2p^{0.01}3d^{0.00}$
b. $MgSiN_2$: space group $Pna2_1$ (No 33), $a = 5.2708$, $b = 6.4692$ and $c = 4.9840 \text{ \AA}$ [18]					
	Coordinates	R_{WS} (\AA)	EC(N 2s)	EC(N 3s)	
Mg	(0.0844, 0.6228, 0.9869)	1.168	$[Ne]3s^{0.20}3p^{0.27}3d^{0.13}$	$[Ne]3s^{0.18}3p^{0.23}3d^{0.10}$	
Si	(0.0694, 0.1242, 0.0000)	0.743	$[Ne]3s^{0.19}3p^{0.21}3d^{0.02}$	$[Ne]3s^{0.17}3p^{0.17}3d^{0.02}$	
N1	(0.0486, 0.0957, 0.3476)	1.260	$[He]2s^{1.77}2p^{4.69}3d^{0.04}$	$([He]2s^2)3s^{0.03}2p^{4.66}3d^{0.03}$	
N2	(0.1087, 0.6552, 0.4102)	1.310	$[He]2s^{1.79}2p^{4.76}3d^{0.04}$	$([He]2s^2)3s^{0.04}2p^{4.73}3d^{0.04}$	
Va1	(0.8156, 0.6272, 0.7011)	1.274	$1s^{0.36}2p^{0.44}3d^{0.24}$	$1s^{0.32}2p^{0.37}3d^{0.19}$	
Va2	(0.2618, 0.3767, 0.6389)	1.222	$1s^{0.32}2p^{0.36}3d^{0.18}$	$1s^{0.29}2p^{0.30}3d^{0.14}$	

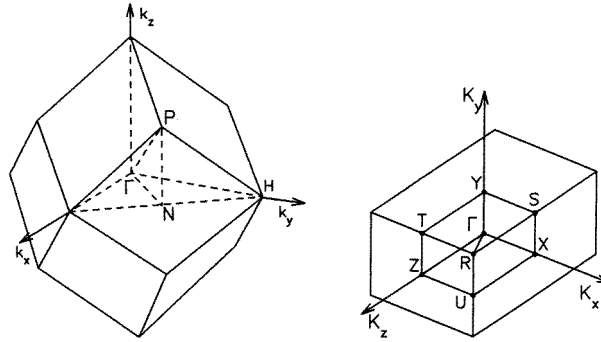
exchange–correlation potentials [23] inside space-filling, and therefore overlapping spheres around the atomic constituents. The self-consistent calculations were carried out including all core electrons. We performed iterations with about 245 k -points for Mg_3N_2 and 1290 k -points for $MgSiN_2$ distributed uniformly in an irreducible part of the Brillouin zone (BZ), corresponding to a volume of the BZ per k -point of less than $1 \times 10^{-6} \text{ \AA}^{-3}$. Self-consistency was assumed when the changes in the local partial charges in each atomic sphere decreased to the order of 1×10^{-5} .

Recently it was found that in ionic compounds, such as alkali chlorides and alkaline earth metal oxides, it is important to include the empty s states in a complete basis set [24–26]. It is an interesting question to what extent the empty anion states influence the conduction bands in nitrides, where the anionic $3s$ level is positioned higher in energy as compared with the oxides and halides. In order to investigate this question two sets of calculations were performed: one with N 2s states as valence states and one with N 3s states. In the construction of the LSW basis [22, 27], the spherical waves were augmented by solutions of the scalar-relativistic radial equations indicated by the atomic symbols $2p$, $3s$ with $2s$ as core level for N, and $3s$, $3p$ for Mg and Si. The internal l summation used to augment a Hankel function at surrounding atoms was extended to $l = 2$, resulting in the use of $3d$ orbitals for all the atoms. We also performed calculations for the N without the N 3s states but N 2s in the basis set for the sake of comparison, as mentioned before. Because the crystals are not very densely packed, it is necessary to include empty spheres (Va) in the calculations. The functions $1s$, $2p$ and $3d$ as an extension were used for the empty spheres. The input parameters for calculations are listed in table 2.

For a better understanding of the electronic structure of $MgSiN_2$, it is useful to compare with the electronic structure of the binary nitrides Si_3N_4 and Mg_3N_2 . Si_3N_4 has two modifications (α and β) with the β -form the stable one at room temperature [19, 20]. Xu and Ching performed band structure calculations for α - and β - Si_3N_4 using the self-consistent

Table 3. Comparison of calculated electronic structure of Mg₃N₂, MgSiN₂ and Si₃N₄. Data in parentheses represent the calculated energy gaps with nitrogen 2s orbitals in the basis set.

Crystal	Mg ₃ N ₂	MgSiN ₂	β -Si ₃ N ₄ [28, 29]	α -Si ₃ N ₄ [28]
Top of VB	Γ , H	Γ	Γ -A	M
Bottom of CB	Γ	Γ	Γ	Γ
E_g min (eV)	1.10(2.35)	4.35(6.45)	4.96 [28] 4.20 [29]	4.63
E_g (direct Γ)	1.10(2.35)	4.35(6.45)	5.25 [28]	4.67
Width of VB (eV)	4.40	6.50	9.79 [28] 10.1 [29]	10.15
Position of N 2s	(-13.1 to -11.3)	(-15.5 to -12.3)	-18.2 to -14.0 [29]	-18.4 to -14.3
Experimental E_g (eV)	2.8	4.8 4.8 [5]	4.6-5.5 [29]	

**Figure 2.** BZ and high symmetry points of Mg₃N₂ (a, left) and MgSiN₂ (b, right).

orthogonalized linear combination of the atomic orbitals (OLCAO) method [28]. They found that the electronic structures of α -Si₃N₄ and β -Si₃N₄ are similar, and their results for β -Si₃N₄ are also in agreement with the calculations by Liu and Cohen using the first-principles pseudo-potential total energy approach within a localized orbital formalism [29]. The main features of the electronic structure of the nitrides are listed in table 3.

First calculated results for Mg₃N₂ are presented. Figure 2(a) shows the Brillouin zone (BZ) of Mg₃N₂. Some calculated results are given in tables 2 and 3. There are about 0.5 electrons in the sphere of Mg and about 6.3 electrons in the sphere of a nitrogen atom (table 2). There are few electrons in the N 3s orbitals. We remark that not too much significance should be attributed to differences in charge and orbital configurations, as these numbers are dependent on the Wigner-Seitz radii, and the presence of empty spheres.

The partial and total densities of states (DOSs) and the energy bands along the high-symmetry directions in the BZ are shown in figures 3 and 4, respectively. The valence band has a width of about 4.4 eV, and is composed mainly of N 2p. Other states have a density at least one magnitude lower. However, there are characteristics of Mg 3s, 3p states in the valence band, which indicates strong interactions between N 2p and Mg 3s, 3p states. The Mg 3s states are mainly at the bottom of the valence band. The Mg 3p states are all over the valence band. The calculations show that Mg₃N₂ has a direct energy gap of 1.10 eV, as both the bottom of the conduction band and the top of the valence band are at Γ point. The conduction band is mainly composed of Mg 3s and N 3s states. The major part of the Mg 3p states lies about 3 eV above the Fermi level.

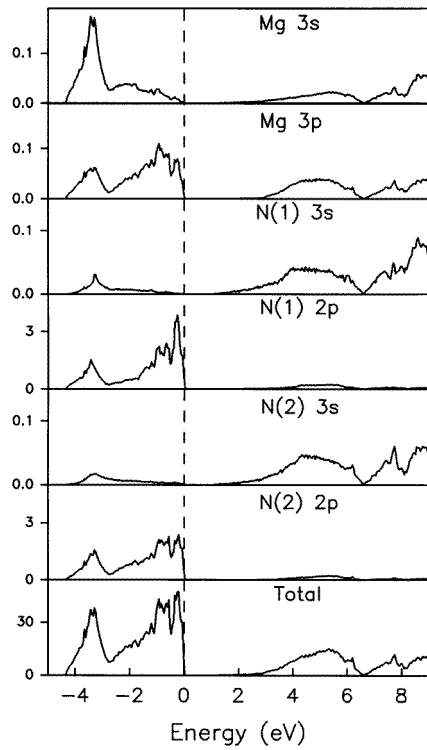


Figure 3. Partial and total density of states for Mg_3N_2 . The Fermi level is at zero eV, the same as in figures 5 and 6.

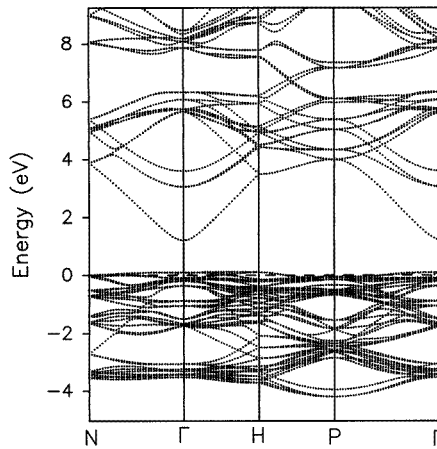


Figure 4. Dispersion of the energy bands for Mg_3N_2 .

For the reason of comparison figure 5 shows the calculated partial and total DOS for Mg_3N_2 with N 2s as valence orbitals in the basis set. The N 2s band has a width of about 1.8 eV (from -13.1 to -11.3 eV). The 2s band of N1 has two features, with a single peak at the upper part of the band, while the N2 2s band has three peaks in the upper part of the band.

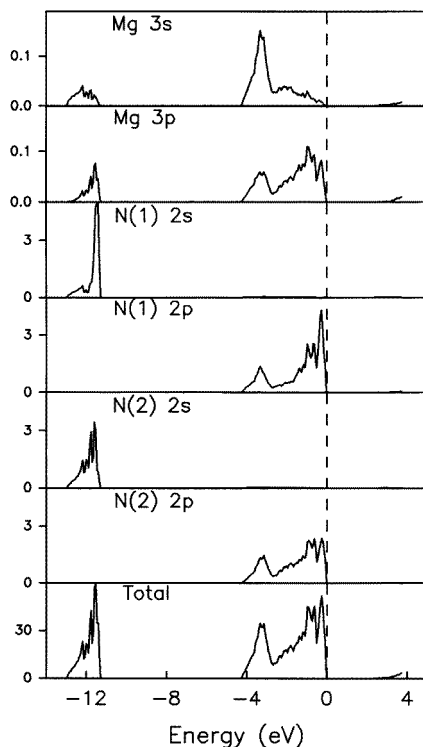


Figure 5. Partial and total density of states of Mg₃N₂ without N 3s states in the basis set.

That is mainly due to the N–Mg₆ cluster with a single N–Mg distance for N1, but three different N–Mg distances for N2, as shown in table 1. The influence from the N–N interactions may not be important due to large N–N distances (3.31 to 3.72 Å). Figure 5 also shows a larger energy gap, 2.35 eV. The bottom of the conduction band is mainly composed of Mg 3s characters.

The BZ for MgSiN₂ is included in figure 2(b). Calculated electronic configurations are given in table 2. The electronic configurations of Mg atoms are comparable to those in Mg₃N₂. The N atoms in MgSiN₂ have larger occupations in the 2p states, although they have smaller spheres than those in the binary nitride Mg₃N₂ (see table 2). Again, we remark that not too much significance should be attributed to differences in charge and orbital configurations. Figures 6 and 7 show the partial and total density of states, and the dispersion curve along the high symmetry lines in the BZ of MgSiN₂, respectively.

Table 3 lists the major features of the electronic structures of the ternary nitride MgSiN₂ and the binary nitrides Mg₃N₂ and Si₃N₄. For MgSiN₂ the bandwidth of the valence band, which is composed mainly of the N 2p state hybridized with some Mg 3s, 3p and Si 3s, 3p (figure 6), is about 6.50 eV, in between those of Mg₃N₂ and Si₃N₄. The Mg 3s bands are all over the valence band and are more delocalized as compared to that in Mg₃N₂. There is a feature at about –4.0 eV, corresponding to the Mg 3s peak in the partial density of states in Mg₃N₂ (figures 3 and 5). There are Mg 3p states all over the valence band. The Si 3s and 3p states in the valence band are similar to that of Si₃N₄ [28, 29]: a higher partial density of the Si 3s states at the lower part of the band, while the partial density of the Si 3p states is over all the band. The bandwidth of MgSiN₂ is narrower than that of Si₃N₄. The energy gap between the conduction band and the valence band is 4.35 eV. It is noted that the lower part

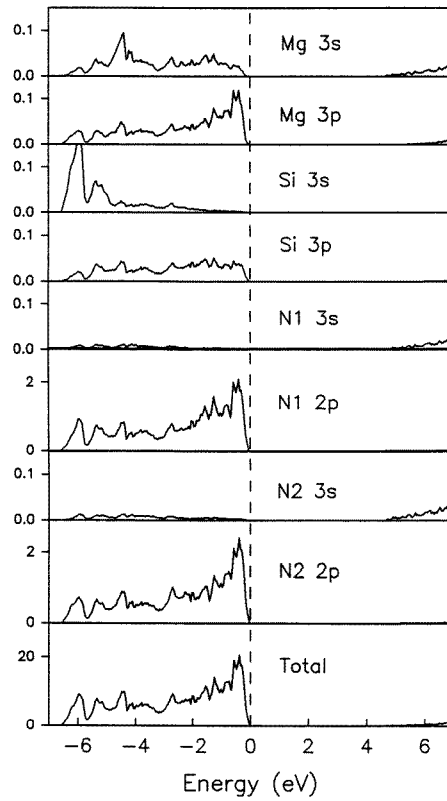


Figure 6. Partial and total density of states of MgSiN₂.

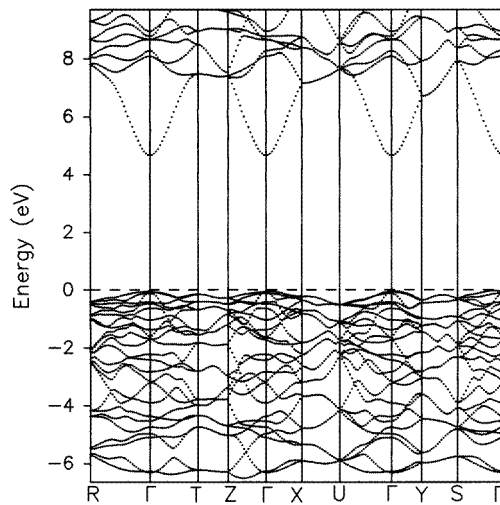


Figure 7. Dispersion of the energy bands for MgSiN₂.

of the conduction band is mainly composed of N 3s and Mg 3s states. The main parts of the Mg 3p and the Si 3s, 3p states are higher in energy. The dispersion curves of the energy bands

are very flat in the top of the valence band and sharp in the bottom of the conduction band. These features indicate heavy holes and light conducting electrons. The dispersion curves also show little anisotropy (figures 4 and 7).

Calculations with N 2s as valence orbitals in the basis set showed little changes for the valence band. The N 2s band has a width of about 3.2 eV, in between that of Mg₃N₂ (1.8 eV) and Si₃N₄ (about 4.1 eV). The N1 2s has a broader peak positioned at lower energy (about -12.80 eV) than that of N2 s (at about -12.30 eV), which corresponds to the larger bond valence (table 1). The calculations showed a larger energy gap (6.45 eV). Again, the bottom of the conduction band consists mainly of Mg 3s states.

For both MgSiN₂ and Mg₃N₂, there is little experimental data available. Optical diffuse-reflectance spectra were measured for Mg₃N₂ and MgSiN₂ by a Perkin-Elmer LS-50B spectrometer in the range of 250–630 nm (2.0–5.0 eV). The scanning speed is 100 nm min⁻¹. The splitting is 5 nm for excitation and 5 to 10 nm for emission, respectively. An energy gap of about 2.8 eV is obtained for Mg₃N₂. The measured energy gap for MgSiN₂ is 4.8 eV, in agreement with the former measurements [5, 10]. This value is also in line with that of CaSiN₂ (about 4.5 eV [30]). The calculated bandgaps (1.10 eV for Mg₃N₂, and 4.35 eV for MgSiN₂) are smaller than the experimental values (2.8 eV and 4.8 eV, respectively). It is known that the local density approximation employed in our calculations generally underestimates the energy gaps for semiconductors [31]. The inclusion of the N 3s states as valence states is important. Although the bandgap *without* them leads to a bandgap in closer agreement with experiment in the case of Mg₃N₂, this agreement is fortuitous: a calculation better than LDA would produce a much too large bandgap. This is best exemplified in the case of MgSiN₂, where the LDA calculation without the N 3s states leads already to a gap 1.65 eV in *excess* in the experimental value.

4. Conclusions

In conclusion, *ab initio* band structure calculations were performed for the binary nitride Mg₃N₂ and ternary nitride MgSiN₂. The calculations showed that both compounds are semiconductors with a direct energy gap of 1.1 eV for Mg₃N₂ and 4.35 eV for MgSiN₂, in line with the experimental data (2.8 eV and 4.8 eV, respectively). In both compounds the bottom of the conduction bands is mainly composed of Mg 3s and N 3s states, which is important to understand the optical transition.

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