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Theoretical Study of Al_nN_n, Ga_nN_n, and In_nN_n ($n = 4, 5, 6$) Clusters

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We report the results of a theoretical study of Al_nN_n, Ga_nN_n, and In_nN_n (with $n = 4, 5, 6$) clusters, focusing on their structural properties, stability, and electronic structure. For Al_nN_n clusters, the metal-nitrogen bond is found to dominate the lowest energy configurations, with a transition from planar to bulklike three-dimensional structures, as the cluster size increases from Al_4N_4 to Al_6N_6. However, for Ga_nN_n and In_nN_n clusters, the lowest energy configurations are mostly planar, and they are dominated either by N_3^- or N_2 subunits. It strongly suggests that N-segregation may occur during quantum dot or thin film deposition processes, due to the low atomic coordination and abundance of dangling bonds.

I. Introduction

Group III nitrides are well-known for their applications in the micro-electronic and optical industry[1] and have been the focus of several experimental and theoretical studies in the past decade. Although the nitride materials have been studied extensively in bulk and ordered surface forms, research in the cluster phase is still lacking. The knowledge of the physical and chemical properties of these materials at the molecular level can be vital in improving the device preparation processes, such as the sputtering process by which the surface layers of the electronic devices are generally constructed.[2] The absence of periodicity in the clusters may help uncover the existence of localized surface features due to the unsaturated valences, absent in periodic calculations.

Aluminum and gallium nitride clusters have been the focus of a few experimental and theoretical studies, but in a limited way. In a recent experimental study, gas-phase AlN clusters were observed, during Chemical Vapor Deposition (CVD) of AlN thin films from $AlCl_3$ and NH_3.[3] For GaN clusters, experimental studies were conducted on the organometallic precursors for chemical vapor deposition process (CVD) of GaN heterostructures.[4] On the theoretical front, the reported work on AlN and GaN clusters is limited to a multireference configuration interaction (MRCI) study performed on the AlN monomer,[5] calculations of AlN_3, Al_3N, and Al_2N_2 using the second-order Moller−Plesset (MP2) perturbation theory,[6] a study based on Density Functional Theory (DFT) calculations on $(AlN)_n$ and $(GaN)_n$ ($n = 2-4$)[7,8] and another DFT study on $(AlN)_n$ ($n = 1, 2, 4, 6, 12$) clusters.[9] A time dependent Hartree−Fock study on polarizabilities on GaN clusters in tetrahedral geometry ($Ga_3N_3H_{12}$ and $Ga_4N_4H_{18}$) reported their nonlinear optical properties suggesting that GaN cluster-based materials can be considered for efficient photonic systems.[10] Finally, experimental as well as theoretical (DFT) results for the vibration spectra of small clusters, both stoichiometric (AlN, GaN, and Al_2N_2) and nonstoichiometric, of AlN, GaN, and InN have been recently published.[11,12]

Aiming to understand the emergence of bulklike properties, starting from nano scale, our research group has initiated a theoretical study of Group-III nitride clusters in the framework of Density Functional Theory. Our results[13] show a strong preference for N−N multiple bonds in the most stable isomers of triatomic and dimer configurations. The strength of the metal-nitrogen bond decreases in going from Al to Ga and In, whereas, the weak metal−metal bond increases its strength from Al to Ga and In. In the case of trimers, the most stable isomer of Al_3N_3 was found to be an alternate-bond hexagonal ring, but a different trend was observed in Ga_3N_3 and In_3N_3.[14] Isomers containing N_3 subunits were found to have lower energies than the six-member ring isomer in Ga_3N_3 and In_3N_3. It was then expected that the lowest energy isomers of GaN and InN clusters with greater coordination numbers should have a dominance of the metal-nitrogen bond over the nitrogen−nitrogen bonds.

As a continuation to the above-mentioned work, in the present article, we report the geometric structures, stabilities, and electronic properties of M_nN_n ($n = 4-6$, M = Al, Ga, and In) clusters. It is to be noted here that Ga_4N_4 was studied previously,[8] but in a limited way, ignoring several probable structural isomers. No theoretical study has been devoted to Ga_nN_n ($n = 5, 6$) and In_nN_n ($n = 4, 5, 6$), to the best of our knowledge. Moreover, the use of same computational method for Al, Ga, and In nitride clusters will allow us to assess the differences and similarities in the structural properties of these clusters together with their variations with the size of the cluster.

The rest of the paper is organized as follows. In section II, we give a brief description of the computational method used in this work. In section III, the results and discussion for M_nN_n ($n = 4-6$, M = Al, Ga, and In) clusters, starting with a description of the different isomers considered and the lowest energy configurations. Then, we will discuss the stability of the clusters with respect to fragmentation, and their electronic properties. We will also discuss the role of relativistic effects in predicting the lowest energy isomers of Ga_nN_n and In_nN_n clusters. Finally, our conclusions will be given in section IV.

II. Computational Method

All electron calculations were performed on M_nN_n ($n = 4-6$, M = Al, Ga, and In) clusters, in the framework of DFT, using the DMol Program.[15] The gradient corrected Becke exchange[16] and Perdew−Wang correlation[17] functionals were employed here. Double numeric basis sets, supplemented with *d* polarization functions (DNP), were used for all atoms (Al, Ga, In, and N) in the cluster. The reliability of the DNP basis sets has been

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confirmed by previous studies of oxide[18,19] and GaAs[20,21] clusters, the excellent agreement with the experiment in the AlN monomer,[13] the direct comparison with the results of the good quality 6-31G* basis sets,[22] and the consistency of our predictions along a series of increasingly larger group III nitride clusters.[13,14] All of the calculations were performed in spin-unrestricted conditions, allowing the electron configuration to change and select the lowest energy spin state according to the aufbau principle. However, all of the lowest energy configurations were found to be singlet spin states.

In the SCF calculations, the density tolerance was set to 10^{-4} e/bohr^3. The geometric parameters were fully optimized under the given symmetry, with a convergence criterion for gradient component set to 10^{-3} hartree/bohr and energy tolerance set to 10^{-5} hartree. In previous studies on small nitride clusters,[13,14] a further re-optimization with tighter SCF convergence criteria has helped to eliminate spurious minima with imaginary frequencies. Hence, in the present study, we have conducted such a re-optimization for the three lowest-energy configurations of each compound, using a SCF density convergence criterion fixed at 10^{-6} e/bohr^3. This re-optimization will also facilitate the comparison of this study with our previous studies. To test the importance of relativistic effects, scalar mass-velocity and Darwin correction terms were included in a re-optimization of the lowest-energy isomers of Ga_nN_n and In_nN_n clusters. The stability of the clusters against fragmentation into smaller clusters and molecules, and electronic properties were studied for the predicted lowest energy isomers of these clusters.

III. Results and Discussion

A. M_4N_4 Clusters. On the basis of our previous results for M_3N_3,[14] several planar and nonplanar configurations were considered for the geometry optimization in M_4N_4. We have also considered various structural configurations, similar to those of the stable isomers of Al_4P_4[23] and Ga_4As_4[20,21,24] clusters as initial configurations for calculations. Some of the lowest-energy isomers considered in this study are given in Figure 1.[1] A complete list of the isomers, optimized geometries, and energies computed in this work can be obtained from the authors (mblanco@mtu.edu).

Among the three lowest-lying Al_4N_4 isomers, presented in Figure 2, the planar eight-member ring configuration with D_{4h} symmetry is found to be the lowest energy isomer with metal-nitrogen distance at 1.75 Å (isomer 2a). This octogonal ring is closely followed by a three-dimensional cubic configuration (isomer 2b) which is 0.8 eV higher in energy than the planar ring configuration. This trend is similar to the one found in trimers and different to those in GaN and InN, as also shown for trimers.

The three lowest energy isomers of Ga_4N_4 and In_4N_4 are given in Figures 3 and 4, respectively. Here, the isomers containing either N_3 or N_2 subunits are found to be the lowest energy isomers. For Ga_4N_4, the most stable isomer 3a is not an alternate-bond ring, but a configuration containing a N_3 subunit. The N−N distance in the N_3 subunit of the isomer 3a is 1.18 Å, about the same as in the N_3^- ion (1.20 Å). Moreover, the Mulliken charge analysis of the isomer 3a reveals a charge of $-1.11e$ on its N_3 subunit. Hence, this isomer can be viewed as a N_3^- ion bonded to a Ga_4N^+ ion with tetrahedral configuration. The alternate-bond ring isomer, the lowest-energy configuration in Al_4N_4, is 2.67 eV higher in energy. The isomer 3a is closely followed by the isomer 3b, having two N_2 subunits and D_{2h} symmetry, and a ring structure 3c with C_{2v} symmetry. A bulklike (tetrahedral) coordination for the nitrogen atom is seen in the isomer 3a, whereas no such coordination is seen in isomers 3b and 3c. The preference of six Ga−N bonds (in the isomer 3a) over four Ga−N and two Ga−Ga bonds (in the isomer 3c) in stabilizing the Ga_4N_4 is also seen here. Also, the calculated results show that the isomer 3c, a planar ring structure with strong N−N bonds, is stabilized by about 1.84 eV when compared to the octogonal planar ring configuration shown in Figure 2a. Hence, it is concluded that in Ga_4N_4, the N−N bonds still play a crucial role in stabilizing the cluster, and the metal-nitrogen bond is still not strong enough to replace the N−N bond in the lowest-energy isomers.

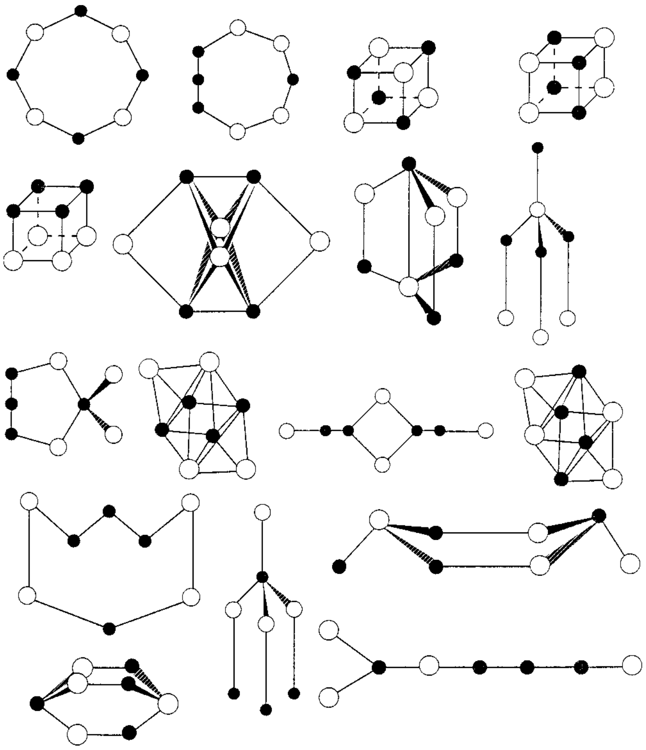

Figure 1. Some of the isomers of M_4N_4 (M = Al, Ga, In) considered in this study. Nitrogen and metal atoms are represented by small filled and large empty circles, respectively.

Our calculated results are not in agreement with the previously reported results[8] for Ga_4N_4 clusters. This contradiction can be explained by the fact that, in ref 8, few structural isomers were considered for the geometry optimization, overlooking the stability of N_3 subunits in the nitride clusters. However, ref 7 provides the ring structure as the lowest energy one for Al_4N_4, in agreement with the present results.

In In_4N_4, the configuration having two N_2 subunits and D_{2h} symmetry is the lowest energy structure (isomer 4a). It is closely followed by the isomer 4b, having a N_3 subunit. The planar alternate-bond ring structure is 5.8 eV higher in energy, when compared to the isomer 4a. Hence, in In_4N_4, the metal-nitrogen bond is not strong enough to replace the N−N bond in the lowest-energy isomers. The isomers, which were predicted to be the lowest energy structures for Ga_4As_4 and Al_4P_4, are much higher in energy than the 4a isomer of In_4N_4. Hence, the structural differences between the most stable isomers of AlN and those of GaN and InN are observed for tetramers, as they were for trimers.[14]

B. M_5N_5 Clusters. For M_5N_5, we considered several structural configurations (Figure 5) based on our results for M_nN_n (n = 3−4) and those for Ga_5As_5.[20,21,24]

In Al_5N_5, the planar alternate-bond ring (isomer 6a) is found to be the lowest energy isomer (Figure 6). Here, the Al−N

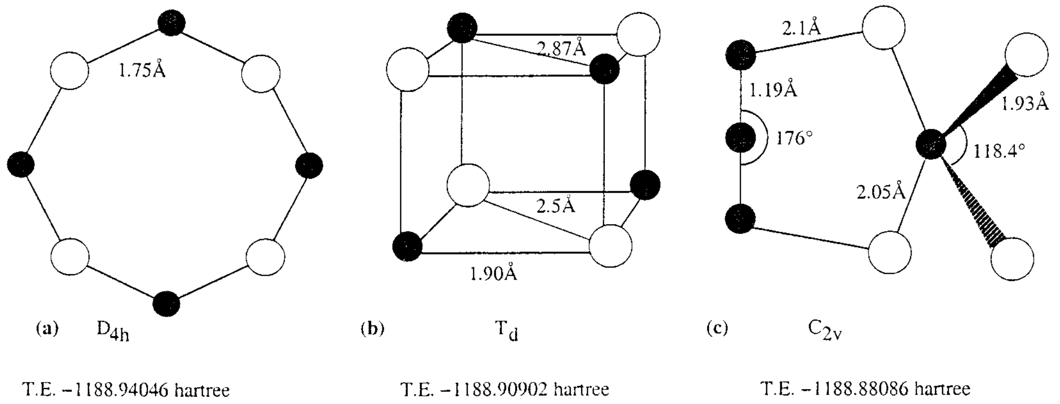

Figure 2. Structure, symmetry, and total energy (in hartree) for the three lowest-energy isomers of Al_4N_4. Nitrogen and metal atoms are represented by small filled and large empty circles, respectively.

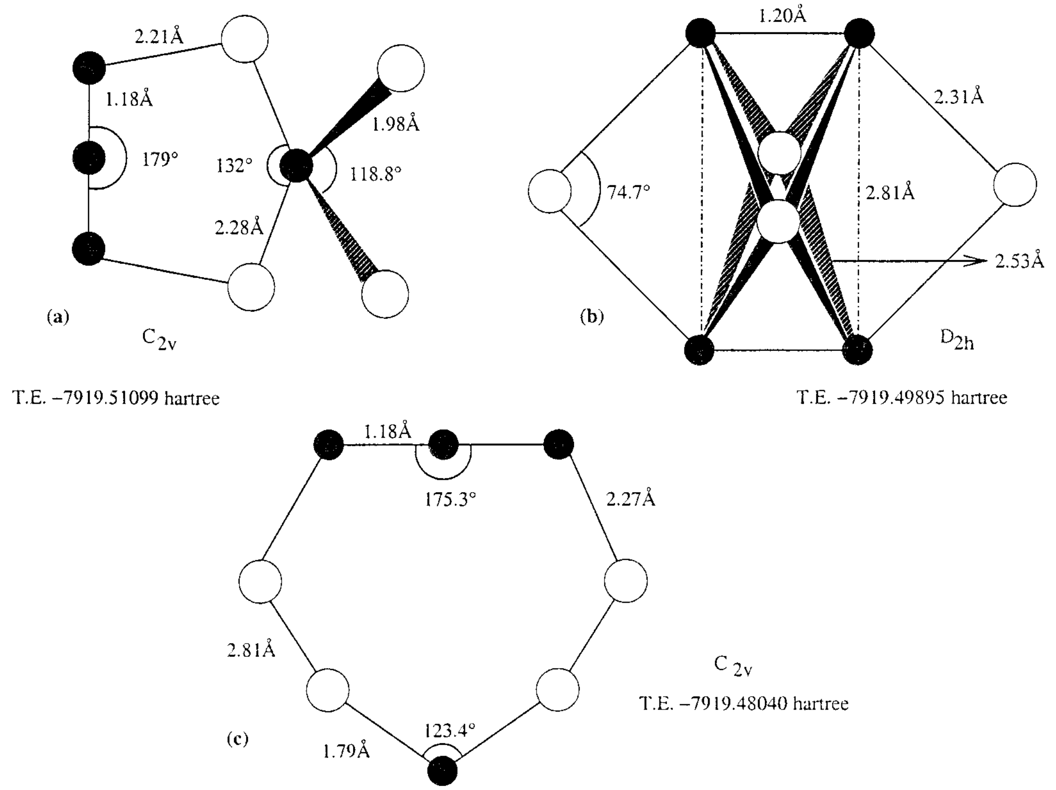

Figure 3. Structure, symmetry, and total energy (in hartree) for the three lowest-energy isomers of Ga_4N_4. Nitrogen and metal atoms are represented by small filled and large empty circles, respectively.

separation is the same as that in Al_4N_4, 1.75 Å. Hence, the Al−N bond strength remains almost the same in both Al_4N_4 and Al_5N_5. The Mulliken charge analysis also shows a charge of −0.595*e* on the N atom in both Al_4N_4 and Al_5N_5, indicating a close similarity in the nature of the Al−N bond in both cases. The isomer 6a is closely followed by a three-dimensional cubic configuration, with an Al−N cap on one of the cube edges (isomer 6b), and a planar fused-ring configuration (isomer 6c). The energy difference between the decagonal ring and the capped cube in Al_5N_5 (0.39 eV) is half the energy difference between the ring and the cubic configuration in Al_4N_4 (0.85 eV). This decrease in the energy difference between the planar ring and cubic configurations can be viewed as an attempt by AlN clusters to move away from the planar configurations to prefer three-dimensional bulklike structures with the increase in the cluster size.

For Ga_5N_5, the three lowest energy configurations are mostly planar structures (see Figure 7), containing strong N−N bonds. The planar ring structure with a N_3 subunit is again favored as the lowest energy configuration (isomer 7a). The N−N distance in the N_3 subunit is 1.19 Å, very close to that in the N_3^- ion. As in Ga_4N_4, the Mulliken charge analysis shows a charge transfer of −1.11*e* onto the N_3 subunit from the Ga_5N_2 unit. Here, the alternate-bond ring configuration is 2.7 eV higher in energy. It is to be noted here that strong N−N bonds are observed in all of the three lowest energy configurations of Ga_5N_5. Moreover, these isomers are energetically almost degenerate, with a very small energy difference of about 0.1 eV. The average N−N distance in all these isomers is approximately 1.13 Å, almost that of the N_2 molecule (1.12 Å). In fact, isomers 7a and 7c can be viewed as a N_3^- subunit weakly bonded to a $Ga_5N_2^+$ unit with 3-fold coordinated nitrogens, whereas the isomer 7b can be regarded as a N_2 molecule loosely bonded to Ga_5N_3. The central N−N bond of the latter isomer has a somewhat larger distance (1.31 Å), due to the coordination with four metal atoms. Overall, the lowest-

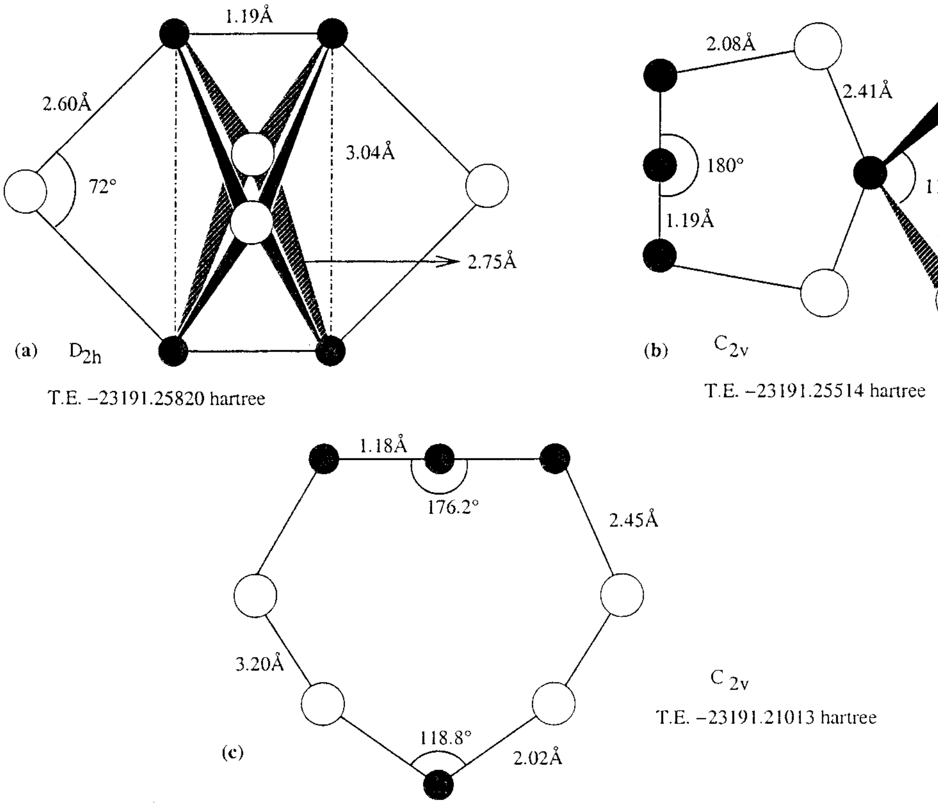

Figure 4. Structure, symmetry, and total energy (in hartree) for the three lowest-energy isomers of In_4N_4. Nitrogen and metal atoms are represented by small filled and large empty circles, respectively.

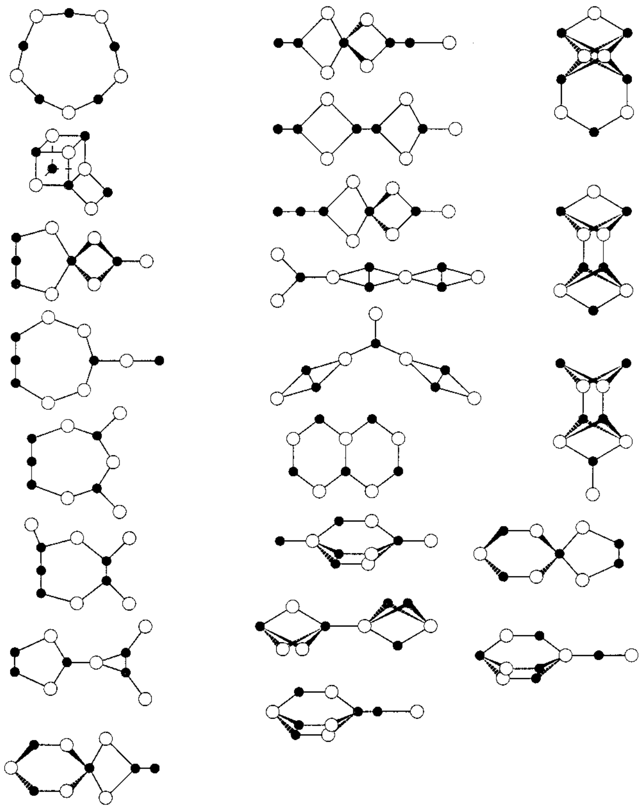

Figure 5. Some of the isomers of M_5N_5 (M = Al, Ga, In) considered in this study. Nitrogen and metal atoms are represented by small filled and large empty circles, respectively.

energy isomers of Ga_5N_5 prefer N−N bonds over Ga−N bonds, and the N_3^- subunit plays a significant role in stabilizing these clusters.

The lowest-energy configurations (Figure 8) of In_5N_5 are similar to those of Ga_5N_5, with planar configurations and N_2 or N_3 subunits, but the order of the two lowest-lying isomers is interchanged. The isomer 8a, containing two N_2 units, is here the most stable, followed by two planar ring structures with N_3 subunits (isomers 8b and 8c). The alternate-bond ring configuration is about 6.25 eV higher in energy than the isomer 8a. The isomers 8b and 8c are energetically very similar, with an energy difference of 0.036 eV, and they are 0.42 eV above the lowest-lying 8a. The N−N distance in all the three isomers is approximately 1.18 Å, similar to that observed in Ga_5N_5 and in the N_3^- ion. The elongation (its N−N distance is 1.28 Å) of the central N_2 unit is due to the higher metal coordination in the isomer 8a.

Hence, in Al_5N_5, the metal-nitrogen bond is the dominant bond, with the alternate-bond ring structure forming the lowest energy configuration. Moreover, it shows a tendency to move away from the planar configurations toward three-dimensional configurations as the cluster size increases. However, in Ga_5N_5 and In_5N_5, isomers having N−N bonds are still found to be the preferred lowest energy configurations. In Ga_5N_5, as in Ga_4N_4, the lowest energy isomer contains a N_3 subunit, whereas in In_5N_5, as in In_4N_4, the lowest energy configuration displays two N_2 subunits. In these clusters, the N−N bond is still dominant and plays a crucial role in stabilizing the cluster.

C. M_6N_6 Clusters. The various structural configurations of M_6N_6 (Figure 9) clusters considered here are based on our results for M_5N_5 clusters.

The three lowest energy configurations of Al_6N_6 are given in Figure 10. Here, the lowest energy isomer is a hexagonal prism with D_{3d} symmetry (isomer 10a): two alternate-bond hexagonal rings with bond distances of 1.84 Å, separated by a distance of 1.94 Å by Al−N bonds, also. Hence, two different (nonequivalent) metal-nitrogen bonds are seen here. The first

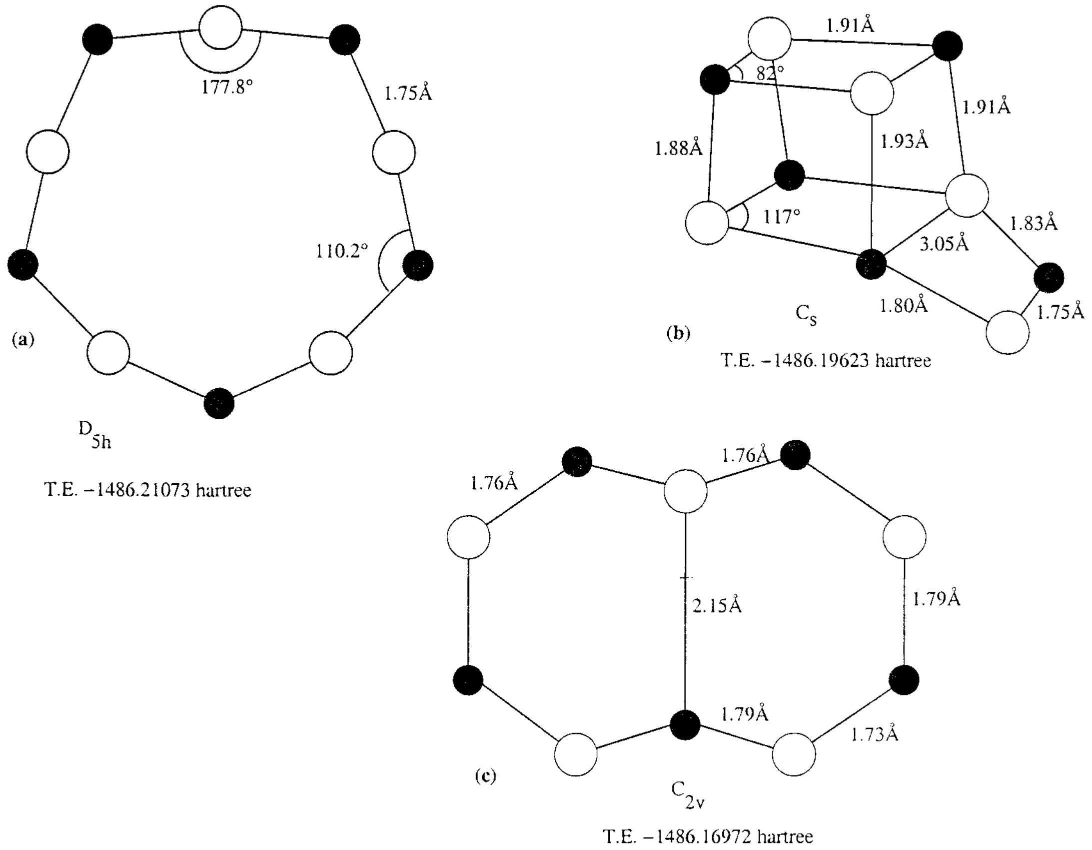

Figure 6. Structure, symmetry, and total energy (in hartree) for the three lowest-energy isomers of Al_5N_5. Nitrogen and metal atoms are represented by small filled and large empty circles, respectively.

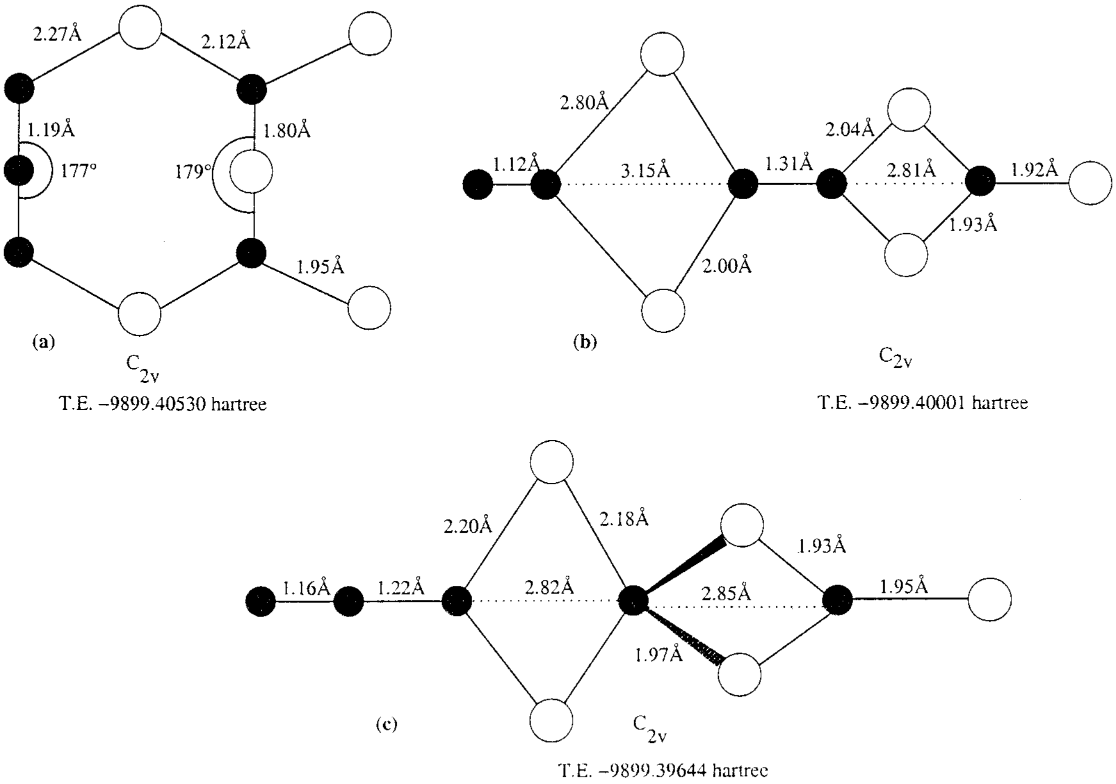

Figure 7. Structure, symmetry, and total energy (in hartree) for the three lowest-energy isomers of Ga_5N_5. Nitrogen and metal atoms are represented by small filled and large empty circles, respectively.

kind of bond is between Al and N atoms in the same hexagonal ring, whereas the second kind is between the metal and nitrogen of two different hexagonal rings, with the latter being a longer, and thus weaker, bond. The isomer 10a is followed by a double cube (isomer 10b) and a two-dimensional ring configuration (isomer 10c). The competition between the planar ring configurations and the three-dimensional structures, dominated by the former in Al_4N_4 and Al_5N_5, is reversed in Al_6N_6. The three-

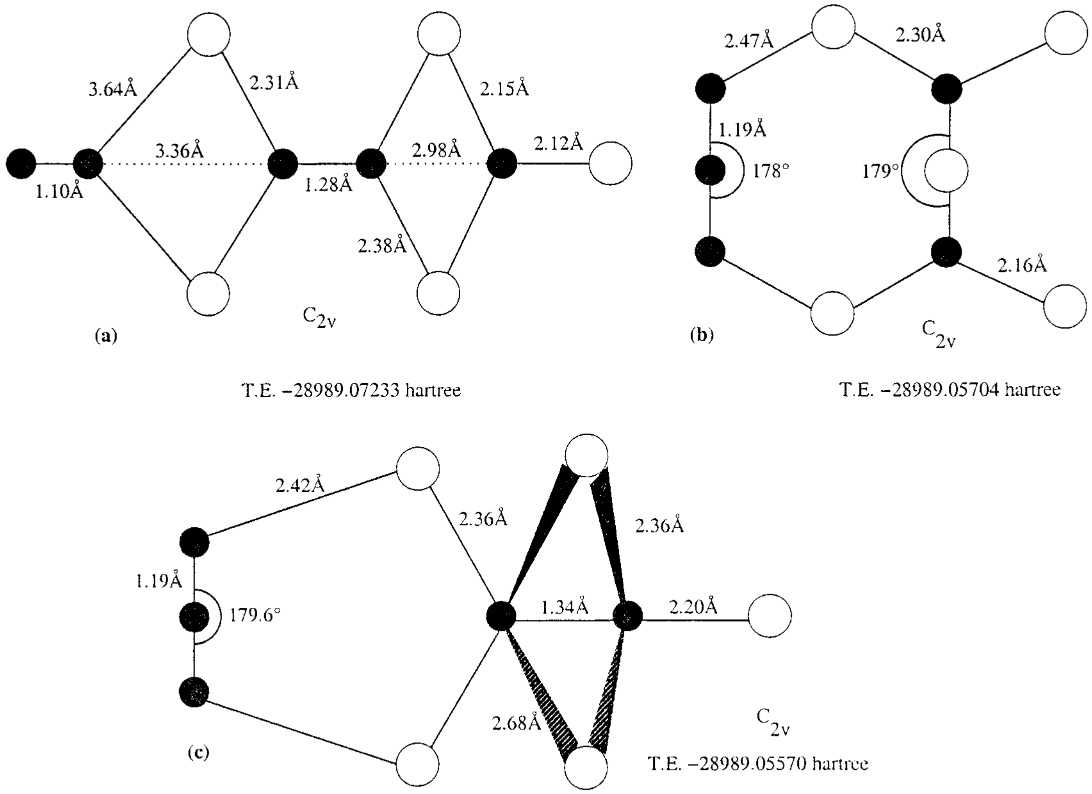

Figure 8. Structure, symmetry, and total energy (in hartree) for the three lowest-energy isomers of In_5N_5. Nitrogen and metal atoms are represented by small filled and large empty circles, respectively.

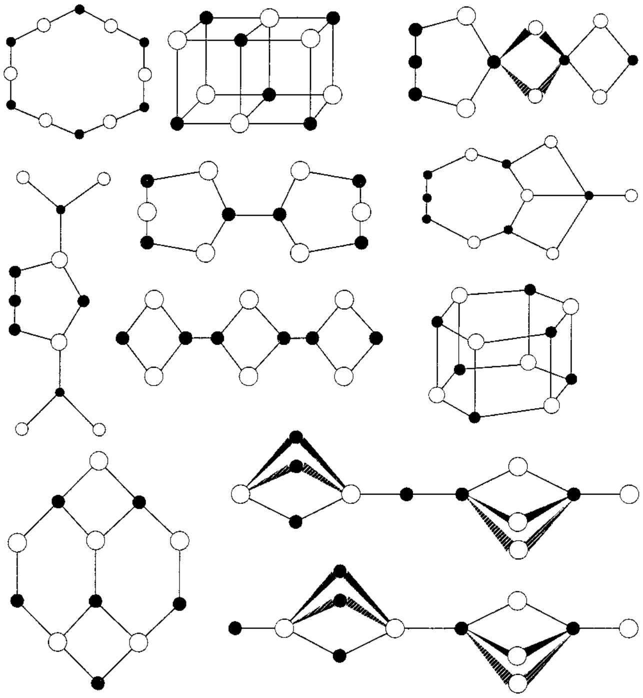

Figure 9. Some of the isomers of M_6N_6 (M = Al, Ga, In) considered in this study. Nitrogen and metal atoms are represented by small filled and large empty circles, respectively.

dimensional configuration (isomer 10a) clearly overtakes the planar configuration (isomer 10c), with the latter being 3.5 eV higher in energy than the former. However, the bulk configuration displays six-member rings as in the 10a isomer, these rings adopt a chairlike configuration in the solid, with tetrahedral coordination. The hexagons of two consecutive layers are displaced so that, although three of the atoms (i.e., the three upper N) sit on top of three opposite atoms (i.e., three Al) of the lower layer, the other three atoms (i.e., the three upper Al) are over the center of the lower layer hexagon, forming bonds with the next layer above them instead. Our results for Al_6N_6 are in good agreement with previously reported DFT calculations.[9]

In Ga_6N_6 and In_6N_6, the trend is different from that observed in Al_6N_6. The planar configurations, either with N_3 or N_2 subunits, are found again to be the lowest energy isomers (Figure 11 for Ga_6N_6, Figure 12 for In_6N_6). The isomer 11a, the lowest energy isomer of Ga_6N_6, is a planar configuration with a N_3 subunit of 1.19 Å N−N bond length. This configuration can be viewed as two Ga_2N units bonded to each of the metal atoms in Ga_2N_4 unit. The hexagonal prism isomer, the lowest-energy configuration in Al_6N_6, is 3.53 eV higher in energy in the case of Ga_6N_6. The planar ring and the double cube structures are also higher in energy. The isomer 11a is followed by two almost degenerate configurations, isomers 11b and 1c. The isomer 1b appears to be an extension of the lowest energy configuration of Ga_5N_5 (isomer 7a).

The three lowest-energy configurations of In_6N_6 are similar to those of in Ga_6N_6. The isomer 12a, the lowest-energy isomer, is a planar structure with a N_3 and a N_2 subunits. Although there exists a tetrahedral coordination for two of the N atoms, one of them is involved in a strong N−N bond. The remaining two lowest energy isomers also show the presence of N_3 subunits. The hexagonal prism structure with alternate bonds is 5.58 eV higher in energy here. This large energy difference again emphasizes the fact that there exists a distinct structural difference between the AlN clusters, on one hand, and the GaN and InN clusters, on the other hand. Again, it is a N_3 dominated structure the one having the lowest energy for the GaN cluster, and the lowest energy configuration of the InN cluster contains a N_2 unit. However, the latter one also has a N_3 unit, showing how it seems necessary to have a 4-fold coordination to have N atoms bonded to In atoms instead of forming strong N−N

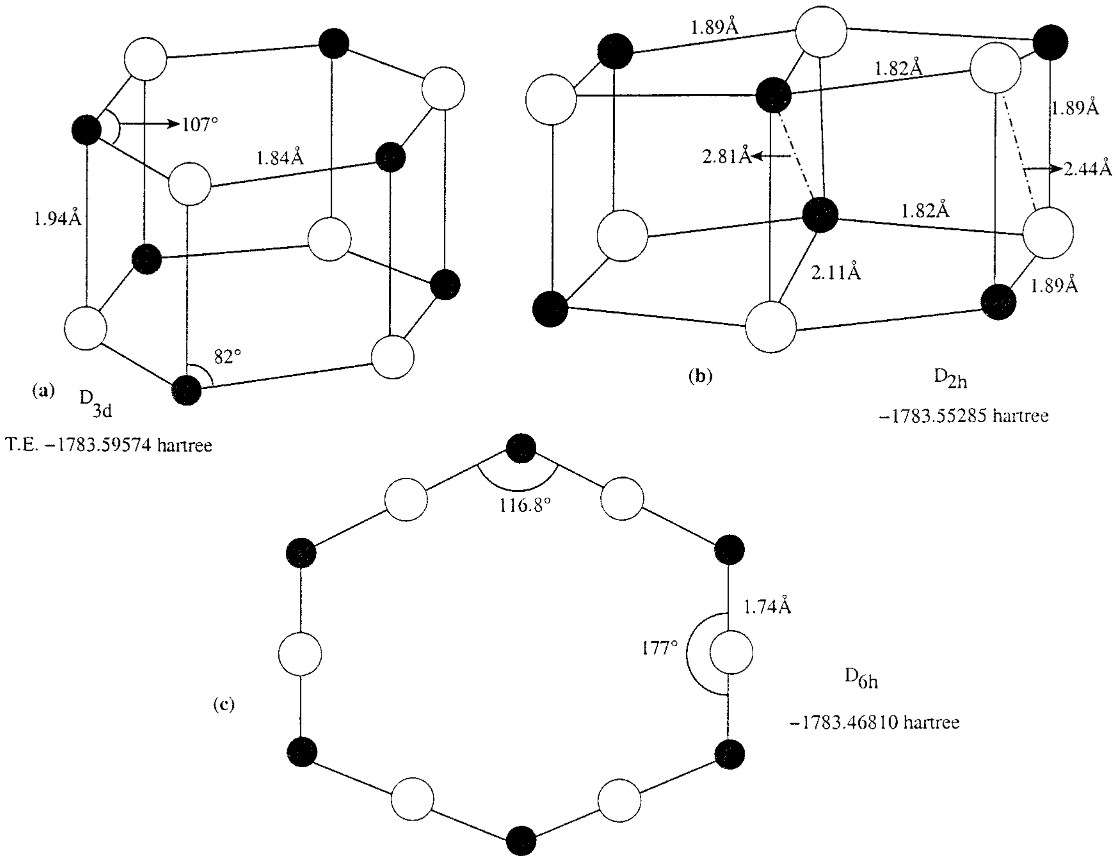

Figure 10. Structure, symmetry, and total energy (in hartree) for the three lowest-energy isomers of Al_6N_6. Nitrogen and metal atoms are represented by small filled and large empty circles, respectively.

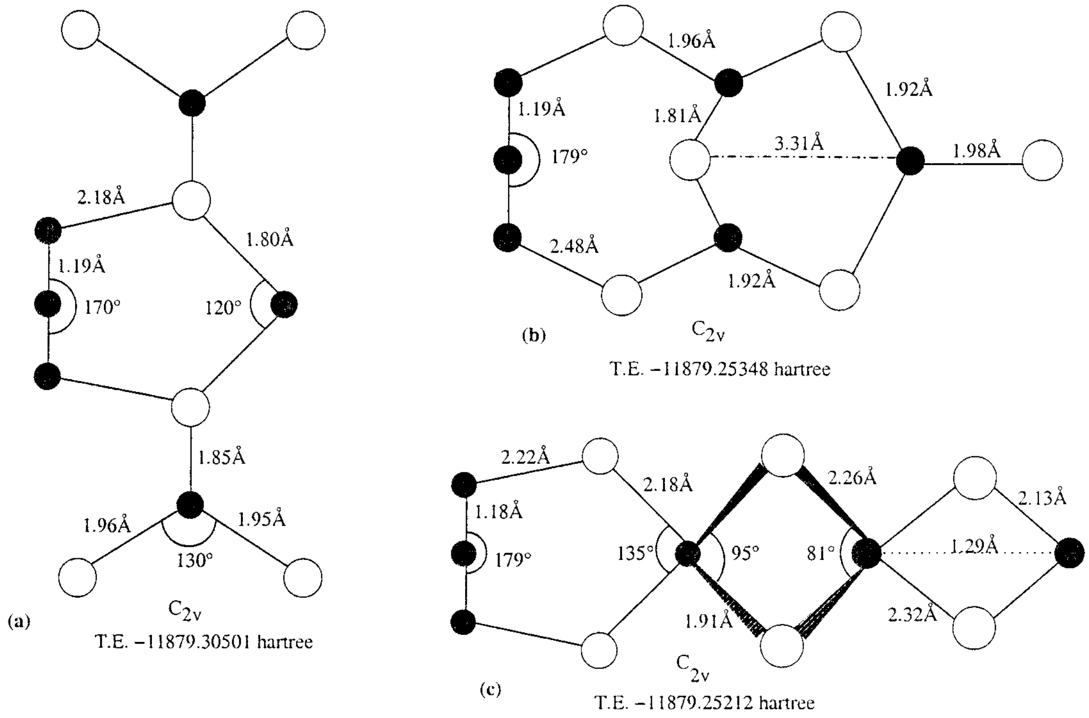

Figure 11. Structure, symmetry, and total energy (in hartree) for the three lowest-energy isomers of Ga_6N_6. Nitrogen and metal atoms are represented by small filled and large empty circles, respectively.

bonds, whereas 3-fold coordination seems sufficient enough for GaN clusters, and 2-fold for AlN clusters.

D. Stability. The stability of the lowest isomers of the M_nN_n clusters was investigated by studying the binding energy per atom (energy required to separate the molecule into atoms, divided by the number of atoms) and also the dissociation energy of the clusters with respect to various possible products. The calculated results for these energies are given in Table 1.

The binding energy per atom is very similar for Al_4N_4 and Al_5N_5, and it shows a large increase in Al_6N_6. In the first two,

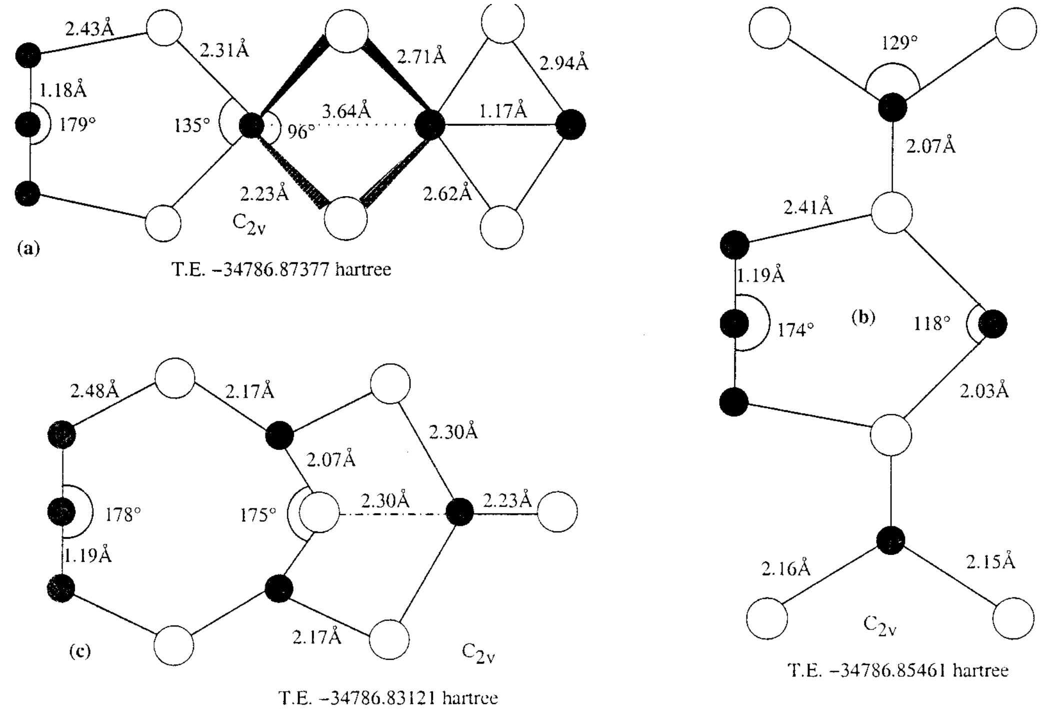

Figure 12. Structure, symmetry, and total energy (in hartree) for the three lowest-energy isomers of In_6N_6. Nitrogen and metal atoms are represented by small filled and large empty circles, respectively.

TABLE 1: Binding Energy Per Atom (in eV) and Dissociation Energies (in eV) into Different Products for Al_nN_n, Ga_nN_n, and In_nN_n with ($n = 4 - 6$)

	Al	Ga	In
M_4N_4 - - B. E. per atom	3.63	3.16	3.09
$M_4N_4 \rightarrow 2\ M_2N_2$	4.47	2.21	2.93
$M_4N_4 \rightarrow M_3N_3 + MN$	6.65	5.36	5.68
$M_4N_4 \rightarrow 2\ M_2N + N_2$	3.31	2.01	3.84
$M_4N_4 \rightarrow 2\ MN_2 + M_2$	6.88	3.66	3.49
$M_4N_4 \rightarrow M_2N + MN_2 + MN$	8.11	6.05	7.11
M_5N_5 - - B. E. per atom	3.73	3.21	3.06
$M_5N_5 \rightarrow M_4N_4 + MN$	5.47	4.32	4.04
$M_5N_5 \rightarrow M_3N_3 + M_2N_2$	5.33	3.05	3.08
$M_5N_5 \rightarrow M_2N_2 + 3\ MN$	16.74	13.16	13.61
$M_5N_5 \rightarrow 2\ M_2N + N_2 + MN$	8.78	6.33	7.88
$M_5N_5 \rightarrow 2\ MN_2 + MN + M_2$	12.35	7.98	7.54
$M_5N_5 \rightarrow 2\ M_2N + MN_2 + N$	11.10	8.51	9.85
M_6N_6 - - B. E. per atom	4.05	3.25	3.09
$M_6N_6 \rightarrow M_4N_4 + M_2N_2$	7.27	2.16	1.10
$M_6N_6 \rightarrow 2\ M_3N_3$	9.30	4.03	2.90
$M_6N_6 \rightarrow 2\ M_2N + M_2 + 2\ N_2$	11.34	4.36	4.68
$M_6N_6 \rightarrow 2\ M_2N + M_2N_2 + N_2$	10.59	4.16	4.93
$M_6N_6 \rightarrow 2\ MN_2 + M_2N_2 + M_2$	14.15	5.81	4.59
$M_6N_6 \rightarrow 3\ M_2N_2$	11.74	4.37	4.02
$M_6N_6 \rightarrow M_5N_5 + MN$	8.60	4.47	3.70

TABLE 2: Energy Separation (in eV) of the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) for the Lowest-energy Isomers of the M_nN_n Clusters with n = 4, 5, 6 W and M = Al, Ga, In

M	Al	Ga	In
M_4N_4	2.07	1.67	0.98
M_5N_5	2.25	2.31	0.64
M_6N_6	1.55	2.60	0.42
MN bulk (DFT-LDA) (ref 26)	4.2	1.7	
MN crystal (ref 25)	6.28	3.44	2.05

The DFT band gap for the *M*N crystals is included for comparison.

there is one bond for each atom, on average because they share a common alternate bond ring structure with 2-fold coordination, being the bond angles the only difference between them. On the other hand, Al_6N_6 prefers a three-dimensional structure, with 3-fold coordination and a larger number of bonds per atom (1.5 on average) that provides it with its increased stability. However, the binding energy per atom for Ga_nN_n and In_nN_n clusters remains almost constant for n going from 4 to 6, and is clearly lower than that in Al_nN_n clusters. This is what we expected because the lowest energy structures in Ga_nN_n and In_nN_n are all of them of a similar nature, dominated by strong N−N bonds on one part of the cluster, and having weak M−N bonds linking that part to the rest.

All of the M_nN_n (n = 4, 5, 6) clusters of Al, Ga, and In are stable with respect to dissociation into smaller molecules or atoms. That is, all of the smaller size combinations of molecules or atoms with the same overall stoichiometry have a higher energy than the lowest energy configuration of tetramers, pentamers, and hexamers. For Al_4N_4 and Ga_4N_4, metal-excess triatomic clusters and nitrogen molecules are the most preferred dissociation products. However, for In_4N_4, dissociation into two dimer (M_2N_2) clusters, with a strong N−N bond each, is energetically favored. Hence, dissociation leading to either N_2 molecules (in Al_4N_4 and Ga_4N_4) or small clusters with a strong N−N bonding (In_4N_4 dissociation) is preferred for M_4N_4 clusters. The domination of the N−N bond in the preferred dissociation products of nitride clusters was also observed in M_2N_2 and M_3N_3 clusters.[13,14] In M_5N_5 and M_6N_6, dissociation into stoichiometric units, with M_2N_2 clusters containing strong N−N bonds as one of the products, is the one requiring the least energy.

E. Electronic Structure. Regarding the electronic structure of these clusters, we have focused on the HOMO−LUMO energy separation, which can be very valuable for the interpretation of photoelectron spectroscopy experiments. In Table 2, we present the HOMO−LUMO gap for the lowest-energy isomers of the M_nN_n (n = 4, 5, 6, M = Al, Ga, In) clusters, including the values of the band gaps of the wurtzite solid nitrides[25] for the sake of comparison.

The HOMO−LUMO gaps for Al and Ga nitride clusters are larger than those for In clusters. This may be explained by the dominance of alternate bonds in the case of Al. The distinction

TABLE 3: Energy Separation (in eV) with Respect to the Corresponding Lowest-energy Isomer (isomer a) of Ga_nN_n and In_nN_n Clusters with $n = 4, 5, 6$, the Scalar Relativistic Values Are Given in the Bracket

	M = Ga		M = In	
isomer	$E_b - E_a$	$E_c - E_a$	$E_b - E_a$	$E_c - E_a$
M_4N_4	0.33(0.25)	0.83(0.87)	0.08(0.23)	1.31(1.57)
M_5N_5	0.14(0.15)	0.24(0.31)	0.42(0.35)	0.45(0.10)
M_6N_6	1.40(0.82)	1.44(1.20)	0.52(1.04)	1.16(1.50)

between Ga and In is of a different nature: the N−N bonds in Ga clusters are always contained in the highly ionic azide-like N_3^- units, in which the charge-transfer fills a bonding orbital, whereas in the case of In clusters there is always at least one N_2 unit, in which the charge transfer will populate antibonding orbitals of higher energy. When comparing the respective band gaps in solids, we find that these clusters are still quite far from the bulk behavior and could be adscribed to the incomplete coordination of atoms in these clusters. This is also responsible for the apparently incorrect increasing trend of the gap in Ga clusters, which should decrease with increasing size were the trend extended to much larger clusters.

We have also computed the Mayer bond order for the lowest energy structures as a guide toward the understanding of the main trends of the bonding in these clusters. We find that the bond orders of the Al−N bond in the Al_4N_4 and the Al_5N_5 clusters are near 1.5, whereas the bond orders of the two different bonds of the Al_6N_6 cluster are close to 1, due to the higher coordination involved that prevents multiple bonds. In the case of the Ga_nN_n clusters, the N−N bonds show a bond order close to 2, very similar to that in the azide ion. Finally, the bond order of the N−N bonds in the In_nN_n clusters is also close to 2, both in azide-like and N_2-like configurations. Although the N−N bond order in the N_2 molecule should be close to 3, here it is much reduced because of the charge transfer from the In atom coordinated to the N_2 units.

F. Relativistic Effects. The relativistic effects on the structure and energies of the lowest-energy isomers of Ga_nN_n and In_nN_n were also studied in this work. The three lowest energy isomers obtained in the nonrelativistic calculations were chosen for scalar-relativistic calculations, including mass-velocity and Darwin terms in the otherwise nonrelativistic Hamiltonian, and were re-optimized in this context.

The structural parameters of the re-optimized configurations are very close to the nonrelativistic ones, and will be omitted here. The energy separation with respect to the most stable isomers, for both the nonrelativistic and the relativistic cases, is given in Table 3. It can be seen that the inclusion of relativistic terms does not change the energy order of these configurations, neither in Ga_nN_n nor in In_nN_n. The only exception is In_5N_5, for which isomers 8b and 8c swap their energy order when the relativistic effects are included.

IV. Conclusions

In Al_nN_n clusters, as the cluster size increases from Al_4N_4 to Al_6N_6, the lowest energy configuration moves away from the planar alternate-bond ring structure to a three-dimensional hexagonal structure, similar to the bulk one but with a different stacking. However, in Ga_nN_n and In_nN_n clusters, no such trend was observed. In fact, isomers with strong N−N bonds are preferred over the alternate-bond isomers (cyclic planar or three-dimensional), in Ga_nN_n and In_nN_n. The Ga isomers tend to prefer N_3^- units surrounded by high-metal-coordinated N atoms, whereas in the In clusters a tendency toward the formation of N_2 units is shown. It is only for In_6N_6, in which it reaches coordination four, that a non-N−N bonded N atom appears in the lowest energy isomer of the InN clusters studied here. The structural difference between the stable configurations of AlN and those of GaN and InN clusters can be attributed to the relative strengths of the metal-nitrogen bonds. It appears that, to have a N bonded only to metal atoms, its coordination needs to be at least four for InN clusters, three for GaN clusters, and only two for AlN clusters. The presence of the stable N_3^- subunit in Ga_nN_n and In_nN_n ($n = 3, 4, 5, 6$) suggests that the number and strength of the metal-nitrogen bonds is not yet large enough to replace the N−N bonds in these clusters. The segregation of N atoms within stoichiometric clusters indicates that the formation of N_2 and N_3 defects should play a major role during the thin film deposition processes, due to the low coordination exhibited in these materials. However, we have been unable to find any reference to this effect, and so further experiments can be devised to test our prediction.

The nitride clusters are stable against the various dissociation products considered here. In M_4N_4, dissociation leading to a nitrogen molecule and M_4N_2 clusters is the one requiring the least energy. In M_5N_5 and M_6N_6 clusters, dissociation into symmetric units with M_2N_2 as one of the products is favored.

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