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Ab initio study of the electronic properties of the planar Ga_5N_5 cluster*

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The first-principles, all-electron, *ab initio* calculations have been performed for an the amazing stable planar structure of Ga_5N_5 cluster based on the density functional theory. Electronic structure, electron affinity, ionization potential, and binding energy are obtained. No spin magnetic moment is found. The results show that the planar structure of the Ga_5N_5 cluster is stable. It is found that for the planar structure of Ga_5N_5 cluster, three nitrogen atoms in the N_3 subunit bind together with large electron transfer although no free N_3 can exist. This may be important to the stability of the planar structure of the Ga_5N_5 cluster which has the lowest ground-state energy.

Keywords: Ga_nN_n cluster, electronic structure
PACC: 3640, 7115A, 3120A

1. Introduction

GaN is an important wide band-gap semiconductor, which can be used in the micro-electronic and optical industry.[1] This has led to many theoretical and experimental studies on structural and electronic properties of both surface and bulk phases of GaN. We have studied the electronic structure of crystalline GaN using the self-consistent cluster-embedding calculation.[2] The obtained band-gap and relative positions of N 2p, N 2s and Ga 3d valence bands are in agreement with the experimental data.

Recently, Ga_nN_n clusters engaged theoretical and experimental attention.[3−13] The theoretical study on different structural geometries, relative stabilities, and electronic properties of Ga_nN_n cluster ($n \leq 6$) have been reported. An amazing stable planar structure of the Ga_5N_5 cluster, having the lowest ground-state energy among all possible structures of the Ga_5N_5 cluster, has been reported by Song and Cao.[7] It is declared that an azide-like N_3 subunit in the Ga_5N_5 cluster plays an important role in the cluster's stability.[4,7] But no detailed information, such as electronic structure, ionization potential, etc, is given. On the other hand, Costales *et al* have reported a totally different stable planar-like structure of the Ga_5N_5 cluster, which contains two N_2 subunits instead of one N_3 subunit.[5,13] They find that an azide-like N_3 subunit exists only in an anionic $Ga_5N_5^-$ cluster with significantly changed planar-like structure. The electronic properties of both Ga_5N_5 and $Ga_5N_5^-$ clusters have been given by Costales *et al*. Up to now, there have been no direct experimental data to show which structure is real, and we are not going to make a judgement here. In this paper, we only discuss the electronic properties of the planar structure of the Ga_5N_5 cluster reported by Song and Cao. The electronic structure of the Ga_5N_5 cluster is obtained using the first-principles, all-electron, *ab initio* calculation. It is confirmed that the planar structure of the Ga_5N_5 cluster reported in Ref.[7] is stable, and three nitrogen atoms in the N_3 subunit bind together with large electron transfer although no free N_3 can exist.

2. Results and discussion

We use the free cluster calculation method to solve the Kohn–Sham equation based on the density functional theory. The program package used in our calculations was developed and used by the research group of Callaway, Louisiana State University, USA.[14−20]

The optimized Gaussian basis set of Ga and N atoms is the same as that used in the calculation

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of crystal GaN.[2] They are originally taken from Refs.[21-23]. Several diffuse bases have been added. In order to reduce the size of the Hamiltonian matrix, one nitrogen s and one nitrogen p base remain as contracted bases. All other bases are uncontracted. Each nitrogen atom is assigned to 30 bases (9s7p), and each gallium atom is assigned to 77 bases (14s11p6d). The basis set has been tested in the calculation of crystal GaN, and can be considered being adequate.[2] The exchange-correlation potential is the same as that used in the calculation of crystal GaN.[2]

2.1. Electronic structure of the Ga_5N_5 cluster

The planar structure of the Ga_5N_5 cluster is shown in Fig.1, which has the lowest energy according to the Ref.[7]. Table 1 gives its atomic coordinators. The shortest bond, with a length of 0.1162 nm, is between N atom 6 and N atom 8.

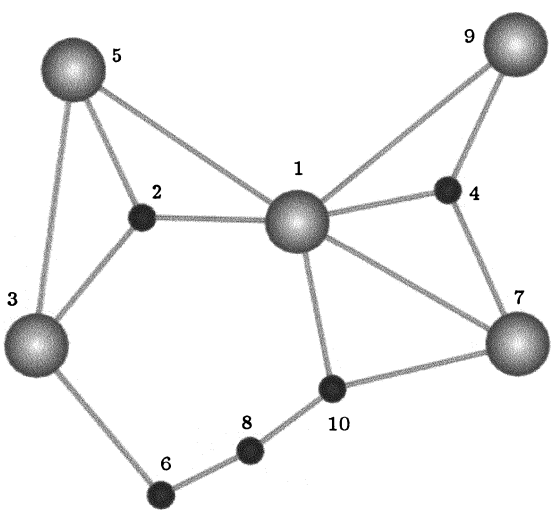


Fig.1. Structure of the Ga_5N_5 cluster. Gallium and Nitrogen are represented by large and small balls, respectively.

Table 1. Atomic coordinators of the Ga_5N_5 cluster.

No	Atom	X/nm	Y/nm	Z/nm
1	Ga	–0.0152	–0.0133	0.0000
2	N	–0.0092	0.1674	0.0000
3	Ga	–0.1568	0.2914	0.0000
4	N	0.0209	–0.1888	0.0000
5	Ga	0.1618	0.2464	0.0000
6	N	–0.3303	0.1473	–0.0002
7	Ga	–0.1576	–0.2694	0.0000
8	N	–0.2796	0.0428	0.0001
9	Ga	0.1885	–0.2686	0.0000
10	N	–0.2085	–0.0534	0.0003

The calculation shows that the ground-state energy of the Ga_5N_5 cluster is E_{Ga5N5}=–268838.8739eV. Using the same Gaussian bases, the ground-state energy of a single Ga atom is calculated as E_{Ga}=–52283.87 eV; and the ground-state energy of a single N atom is E_N=–1472.65eV. So the total binding energy of the Ga_5N_5 cluster is 56.27eV, i.e. smaller than 58.11eV reported in Ref.[7].

Table 2 gives the eigenvalues and the Mulliken populations of spin-up orbitals. The spin-down orbitals are the same as the spin-up orbitals. The Mulliken population analysis shows that orbitals 82, 88–90 and 93 are mainly for nitrogen 2p electrons. Orbitals 91, 92, 94 and 95 are hybridized states containing gallium 4*s*, gallium 4p and nitrogen 2p electrons. Above the Fermi energy, orbitals 96 and 98 are hybridized states with gallium 4p and nitrogen 2p electrons, orbital 97 is for gallium 4p electron; orbital 99 is for gallium 4*s*and 4p electrons. Figure 2 shows the orbitals from 81 to 99.

Table 2. Eigenvalues and Mulliken populations of the Ga_5N_5 cluster in ground state (spin up).

Orbital No	Energy/eV	Ga s	Ga p	Ga d	N s	N p
81	–14.5153	0.0467	0.0333	0.0264	0.2318	0.6619
82	–14.0844	0.0000	0.0070	0.0028	0.0000	0.9901
83	–12.9681	0.1252	0.0174	0.0117	0.4040	0.4416
84	–11.3791	0.3268	0.0973	0.0193	0.0373	0.5193
85	–10.4458	0.4318	0.0705	0.0213	–0.0039	0.4802
86	–10.3967	0.4748	0.0604	0.0297	0.0530	0.3822
87	–9.8780	0.3053	0.1309	0.0188	–0.0121	0.5571
88	–8.6676	0.0516	0.1391	0.0101	–0.0911	0.8903
89	–8.2544	0.0000	0.1016	0.0066	0.0000	0.8919
90	–7.4546	0.0000	0.1873	0.0130	0.0000	0.7997
91	–7.3327	0.8377	0.1346	0.0029	–0.0755	0.1002
92	–6.9017	0.6417	0.2015	0.0051	0.0045	0.1471

Table 2. (*Continued*)

Orbital No	Energy/eV	Ga s	Ga p	Ga d	N s	N p
93	–6.8198	0.0000	0.1109	0.0292	0.0000	0.8599
94	–6.1540	0.6137	0.2266	0.0116	–0.0094	0.1576
95	–6.0202(E_F)	0.5581	0.2569	0.0068	0.0004	0.1778
		— the followings are unoccupied orbitals —				
96	–3.2640	0.0562	0.3282	0.0074	–0.0399	0.6481
97	–3.0601	0.0410	0.9604	0.0192	–0.0606	0.0401
98	–2.8351	0.0000	0.3972	0.0073	0.0000	0.5954
99	–2.4318	0.4277	0.7048	0.0166	–0.3144	0.1652

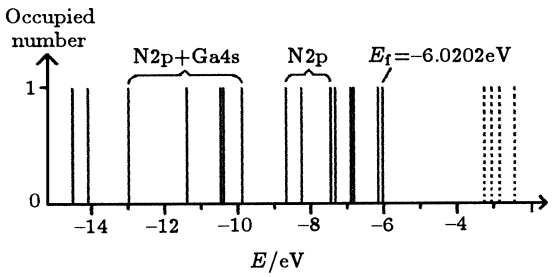


Fig.2. Schematic diagram of orbitals 81 to 99. Full lines represent the occupied orbitals, dashed lines represent the unoccupied orbitals.

Total Mulliken populations (spin-up electrons) of atoms in the Ga_5N_5 cluster are shown in Table 3. The values for the spin-down are similar to those for the spin-up. Please pay special attention to the N_3 subunit containing nitrogen atoms 6, 8 and 10, because the most stable planar structure of the Ga_5N_5 cluster is preferred for N_3 subunit according to the Ref.[7]. The Mulliken populations show that the central nitrogen atom 8 has lost 0.971 electrons, while the side atoms 6 and 10 have acquired 0.358 and 0.815 electrons, respectively. Such a kind of charge transfer in the N_3 subunit has not been reported before. We think that the charge transfer is important to the stability of the lowest energy structure of the Ga_5N_5 cluster.

Table 3. Total Mulliken population of atoms in the Ga_5N_5 cluster (spin up).

No.	Atomic species	s	p	d	total
1	Ga	3.450	6.712	5.069	15.2315
2	N	1.721	2.071	0.000	3.7924
3	Ga	4.009	6.352	5.020	15.3809
4	N	1.717	2.021	0.000	3.7378
5	Ga	4.040	6.350	5.015	15.4052
6	N	2.111	1.568	0.000	3.6790
7	Ga	4.095	6.314	5.017	15.4265
8	N	1.276	1.739	0.000	3.0147
9	Ga	4.058	6.353	5.013	15.4244
10	N	2.159	1.749	0.000	3.9077

The electron affinity of the Ga_5N_5 cluster is calculated: one electron is added, and the negative charged $Ga_5N_5^-$ cluster is fully relaxed during the calculation. The result is E_{aff}=–1.2679 eV. In the rearranged structure of the $Ga_5N_5^-$ cluster, nitrogen atoms 6 and 10 move away from the cluster centre compared with the original structure of neutral cluster. The Mulliken population now shows that for the N_3 subunit, the central nitrogen atom 8 has lost more (1.062) electrons, while the side atoms 6 and 10 have acquired 0.561 and 1.003 electrons, respectively. Similarly, the ionization potential of the Ga_5N_5 cluster is calculated: one electron is removed, and the positive charged $Ga_5N_5^+$ cluster is fully relaxed during the calculation. The result is E_{ion}=7.9552eV. The Mulliken population shows that for the N_3 subunit, the central nitrogen atom 8 has lost less (0.828) electrons, while the side atoms 6 and 10 have obtained 0.175 and 0.718 electrons, respectively.

2.2. Electronic structure of free N_3 cluster

The electronic structure of a free N_3 cluster, for which the coordinates of three nitrogen atoms are the same as those of nitrogen atoms 6, 8 and 10 in the Ga_5N_5 cluster, is calculated with the same Gaussian bases. The ground-state energy and Mulliken popula-

tion are given in Table 4 (No.4). Now the distances between the central atom and two side atoms of the N_3 cluster are changed, and the electronic structure of the cluster is recalculated. In Table 4, the larger the number is, the smaller the distance between central atom and side atom is.

Table 4. Ground-state energies and Mulliken population of N_3 clusters with different sizes.

No.	Distance-1*/nm	Distance-2**/nm	Energy/eV	Atom-1 (total)	Atom-2 (total)	Atom-3 (total)
1	0.1395	0.1435	–4436.7016	6.9367	7.1026	6.9608
2	0.1320	0.1413	–4437.3922	6.9835	7.0047	7.0118
3	0.1278	0.1316	–4438.4623	7.0811	6.8391	7.0798
4	0.1162	0.1196	–4439.1481	7.2610	6.4893	7.2497
5	0.1104	0.1271	–4438.5574	7.3282	6.3397	7.3321
6	0.1093	0.1088	–4438.0117	7.4196	6.1650	7.4154

*Distance-1 is the distance between atom-1 (nitrogen atom 6) and atom-2 (nitrogen atom 8).

**Distance-2 is the distance between atom-2 (nitrogen atom 8) and atom-3 (nitrogen atom 10).

Table 4 shows that the structure with minimum N–N distance has the largest charge transfer from central nitrogen atom to two side nitrogen atoms. Besides, it is clear that the N_3 cluster with the same atomic coordinates of the Ga_5N_5 cluster has the lowest ground-state energy, so is the most stable structure. But this does not mean that a free N_3 molecule can exist. The ground-state energy of the most stable N_3 cluster is E_{N3}=–4439.1481eV. The ground-state energy of molecular N_2 (nitrogen gas) is E_{N2}=–2961.4977eV. Consider $2\times E_{N3} - 3 \times E_{N2}$=–8878.2962eV –(–8884.4931eV)=+6.1969eV, the free N_3 cluster is less stable than the nitrogen gas and cannot exist independently.

Finally, we check the stability of the planar-structure Ga_5N_5 cluster. The electronic structure of fully relaxed Ga_5N_3 cluster, with two nitrogen atoms 6 and 8 removed, is calculated. The ground-state energy is –265873.7525eV. The total energy of the Ga_5N_3 cluster and molecular N_2 is –268835.2502eV, higher than the ground-state energy –268838.8739eV of the Ga_5N_5 cluster. Consider the result of last paragraph, this shows that the amazing planar structure of the Ga_5N_5 cluster is really stable. However, the planar-structure Ga_5N_5 cluster has not been confirmed experimentally. So whether this amazing cluster exists is still an open question.

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