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Density-functional study of structural and electronic properties of Ga_nN ($n=1-19$) clusters

Bin Song,* Chang-Hong Yao, and Pei-lin Cao
Department of Physics and State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, China

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The lowest-energy geometries and electronic-structure properties have been obtained for Ga_nN ($n=1-19$) clusters within the density-functional theory using the generalized gradient approximation for the exchange-correlation potential. The resulting geometries show that the nitrogen atom tends to occupy an inside position for $n \leq 10$, but prefers a peripheral position with a bulklike coordination beyond $n=10$. The stability has been investigated by analyzing the binding energy per atom and the second difference in energy. The results indicate that Ga_3N, Ga_7N, and $Ga_{15}N$ exhibit particularly higher stability. The bonding property has been analyzed by calculating the Mulliken charges and Ga-N distances. The results show that the N in Ga_nN clusters is less ionic than that in bulk GaN (wurtzite phase). The calculated energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital, the vertical ionization potential, and the vertical electron affinity form an even-odd alternating pattern with increasing cluster size. In general, the vertical ionization potential tends to lower as the cluster size increases, while the vertical electron affinity tends to increase as the cluster size increases.

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I. INTRODUCTION

The study of the physics and chemistry of atomic clusters has become an increasingly active research field in recent years.[1] Apart from serving as prototypes for nanoscaled materials, clusters are expected to possess unique properties different from their extended bulk states or from the atomic state. Thus, the study of the size evolution of their properties, such as equilibrium geometries, stability, bonding nature, ionization potential, and electron affinity, is an interesting and challenging topic.

GaN is an important wide band-gap semiconductor, and has recently emerged as the material of choice for applications in the microelectronic and optical industry.[2] This has led to numerous theoretical and experimental studies on structural, electronic, and optical properties of both surface and bulk phases of GaN. However, there is still a lacking for research of GaN clusters. With the rapid advancement in science and technology, electronic devices have been reduced in size and the behavior of semiconductor surface properties has thus gained more attention. For example, in order to prepare electronic devices, GaN nanoclusters were made by using the sequential ion implantation in a dielectric matrix[3] or by rinsing the sample in a solution of a donor-stabilized galliumtriazid.[4] This may be viewed as nanoclusters of GaN adsorbed over the surface of a thin film. GaN bulk phases involving two elements occur only for certain stoichiometries, however, GaN clusters can be synthesized by mixing two kind of atoms in a wide range of compositions. It is even possible to synthesize clusters of different elements that normally are immiscible in the solid phase.[5] Therefore, a detailed knowledge of the physical and chemical properties of GaN clusters can be vital in understanding the properties of a material and improving the device preparation processes.

Previous experimental studies of GaN clusters are scarce. Zhou and Andrews[6] have studied the reactions of laser-ablated gallium atoms with nitrogen atoms and molecules. Very recently, Himmel and Hebben[7] have performed matrix-isolation experiments to study the interaction between Ga atoms and N_2 by using Raman and UV/Vis spectroscopies for detection and analysis. On the theoretical side, some calculations, which are mainly concerned with small stoichiometric clusters of GaN, have been performed. A notable theoretical contribution came from Kandalam and co-workers.[8–11] Kandalam *et al.* calculated the geometrical and electronic structures of Ga_nN_m ($n,m=1-2$) (Ref. 8) and Ga_nN_n ($n=3-6$) (Refs. 9 and 10) clusters based on the nonlocal density approximation to the density functional theory. Belbruno[12] investigated the geometrical and electronic structures of Ga_nN_n ($n=2-4$) clusters using the density functional theory. Costales and Pandey[13] calculated the electronic structures of small Ga_nN_n($n=1-3$) anionic clusters based on density functional calculations. Recently, the present authors have reported the structures of Ga_nN_n ($n=3-6$) (Refs. 14–17) and Ga_nN_m ($n+m=3-8$) (Ref. 18) by using full-potential linear-muffin-tin-orbital molecular-dynamics (FP-LMTO-MD) method. Very recently, Wang and Balasubramanian[19] have calculated the low-lying electronic states of Ga_2N, GaN_2, and the corresponding anions and cations. However, theoretical studies aimed at understanding the equilibrium geometries and electronic structure of large nonstoichiometric GaN clusters are very scarce.

In this paper, we present a systematic theoretical investigation of the Ga_nN system. To this end, we have carried out extensive investigations of the equilibrium geometries, stability, bonding nature, highest-occupied and lowest-unoccupied molecular orbital (HOMO-LUMO) gap, ionization potential, and electron affinity for Ga_nN ($n=1-19$) clusters using the density-functional theory (DFT) with a generalized gradient approximation (GGA). In the following section, we present the essentials of the computational methods, which is then followed by the results and a discussion.

II. METHODS

All calculations were performed using the $DMOL^3$ program (Accelrys Inc.) based on DFT.[20] The generalized gradient approximation using Perdew-Burke-Ernzerhof's exchange-correlation functional was employed.[21] Double numeric basis sets, supplemented with d polarization functions were used for all atoms in the cluster. All-electron calculations were used. For accurate calculations, we chose an octupole scheme for the multipolar fitting procedure (the maximum angular momentum of the fitting function was set to be 3) on the charge density and Coulomb potential, and a fine grid scheme for numerical integration (about 1500 integration points per atom). Self-consistent field procedures were done with a convergence criterion of 10^{-6} a.u. on the energy and electron density. The geometric parameters were fully optimized without symmetry constraints. We used a convergence criterion of 10^{-3} a.u. on the gradient and displacement and 10^{-5} a.u. on the total energy in the geometry optimization. All the calculations were carried out allowing for spin polarization. It is to be noted here that calculations were not performed for each spin state of the given cluster but the Aufbau principle as implemented in the DMOL^3 program was used to obtain the optimal spin state of the cluster.

For each specific cluster size, an exhaustive search for minimum energy structures was performed by using a combination of FP-LMTO-MD (Refs. 22–24) search and GGA minimization. The FP-LMTO method is a self-consistent implementation of the Kohn-Sham equations in the local density approximation. In this method, space is divided into two parts: nonoverlapping muffin-tin (MT) spheres centered at the nuclei and the remaining interstitial region. The electron wave functions are expanded in terms of MT orbitals.[25] The LMTOs are augmented Hankel functions, and are augmented only inside the MT spheres rather than in the interstitial region.[25–27] Its potential and density are expressed as a linear combination of Hankel functions. In the present study, all MT sphere radii for Ga and N were taken as 2.10 and 1.00 a.u., respectively. The LMTO basis sets included s, p, and d functions on all spheres. Geometry optimization was carried out by using the forces on the nuclei. Each calculation was considered to be converged when the maximum of the forces was less than 0.001 (Ry/bohr), and the variation in total energy was less than 10^{-4} Ry. The details of how the molecular dynamics can be performed are described in Ref. 24. The accuracy of the FP-LMTO-MD method for investigating the cluster structures has been confirmed by previous studies (for example, Refs. 17, 18, and 28–30) on small Si_n, $\mathrm{Ga}_n\mathrm{N}_n$, Ge_n clusters, etc. In order to perform the systematic search for the equilibrium structures of$\mathrm{Ga}_n\mathrm{N}$ ($n=1-19$) clusters, we first used the FP-LMTO-MD method to calculate the structures and energies in a global wide search. Large numbers of initial geometric configurations as seeds were relaxed until the local minimum of the total energy was found. For small $\mathrm{Ga}_n\mathrm{N}$ (n up to 4) clusters, all possible connectivities have been used as seeds. For larger $\mathrm{Ga}_n\mathrm{N}$, the main initial atomic configurations were set up by random selections of atomic positions in three-dimensional space. The separation of Ga-Ga and Ga-N atoms was confined in a range. The range for Ga-Ga and Ga-N was 2.51–3.32 Å and 1.76–2.40 Å, respectively. The separation of any pair of atoms was set randomly when the seed structures were carried out. Depending on the cluster size, we selected 80–120 initial geometry configurations for geometry optimization. Then, the low-lying energy structures for each cluster size obtained by FP-LMTO-MD calculations were further optimized by using DMOL^3 with GGA. No significant rearrangement occurred during the DMOL^3 optimization process. In addition, we considered several other structures, which were generated by removing and adding gallium andnitrogen atoms to the nearest gallium clusters,[31] as our starting structures for straightforward geometry optimization. We also considered several other structures, usually with high symmetry, as our starting structures for straightforward geometry optimization. To make sure the obtained lowest-energy structures are real local minima, normal-mode vibrational analysis were applied. All of the energy minima obtained for the most stable $\mathrm{Ga}_n\mathrm{N}$ clusters had no imaginary frequencies.

III. RESULTS AND DISCUSSION

A. Lowest-energy structures

The calculated lowest-energy structures for $\mathrm{Ga}_n\mathrm{N}$ ($n=1-19$) clusters are shown in Figs. 1 and 2. Their symmetries and spin multiplicities are given in Table I. "Bonds" are generally shown for atomic separations less than 3.33 Å for Ga-Ga and 2.43 Å for Ga-N. It is found that the N atom occupies an inside position for $n \leq 10$. This can be understood on the basis of atomic radii of constituent atoms and the relative strength of the bond between them. The pauling ionic radii of Ga atom is much larger than that of N. For a corresponding diatomic system, the Ga-Ga bond is weaker than the Ga-N bond. So the N atom prefers to remain inside the small $\mathrm{Ga}_n\mathrm{N}$ clusters in order to improve the stability of system. Whereas, beyond $n=10$, the N atom prefers a peripheral position, and the N atom with a bulklike coordination emerges. The structures evolve on a base of a decahedral and/or icosahedral structure, except $\mathrm{Ga}_{13}\mathrm{N}$. Such a positional change of N atoms is reasonable because the pauling ionic radii of the N atom is substantially smaller than that of the Ga atom. This means that the N atom cannot become centrally located to form a Ga-Nbond due to its too long bond length.

For the GaN monomer, the binding energy and vibration frequency are obtained as 2.56 eV and 591.3 cm^{-1}, respectively. There are no experimental values available. The present GGA Ga-N bond length for the GaN monomer is predicted to be 1.87 Å. Our calculated bond length of GaN monomer agrees well with the calculation of Zhou (1.87 Å) (Ref. 6) and Das (1.88 Å),[32] and is somewhat shorter than the result of BelBruno[12] (2.01 Å) and Kandalam[8] (2.06 Å). Note that the nearest distance between Ga and N in the wurtzite crystalline GaN is 1.95 Å,[32]our predicted Ga-N bond length for the GaN monomer is slightly smaller than that in wurtzite crystalline GaN. For $\mathrm{Ga}_2\mathrm{N}$, the present calculations indicate that the lowest-energy form is a linear Ga-N-Ga chain with a Ga-N bond length of 1.80 Å. The Ga-N bond distance is 0.06 Å shorter than that in the GaN monomer. Our structure for $\mathrm{Ga}_2\mathrm{N}$ is in agreement with a very recent calculation of Wang.[19] For $\mathrm{Ga}_3\mathrm{N}$, as shown in Fig. 1(c), the lowest-energy structure is an equilateral triangle in which a central N binds to three Ga atoms. The

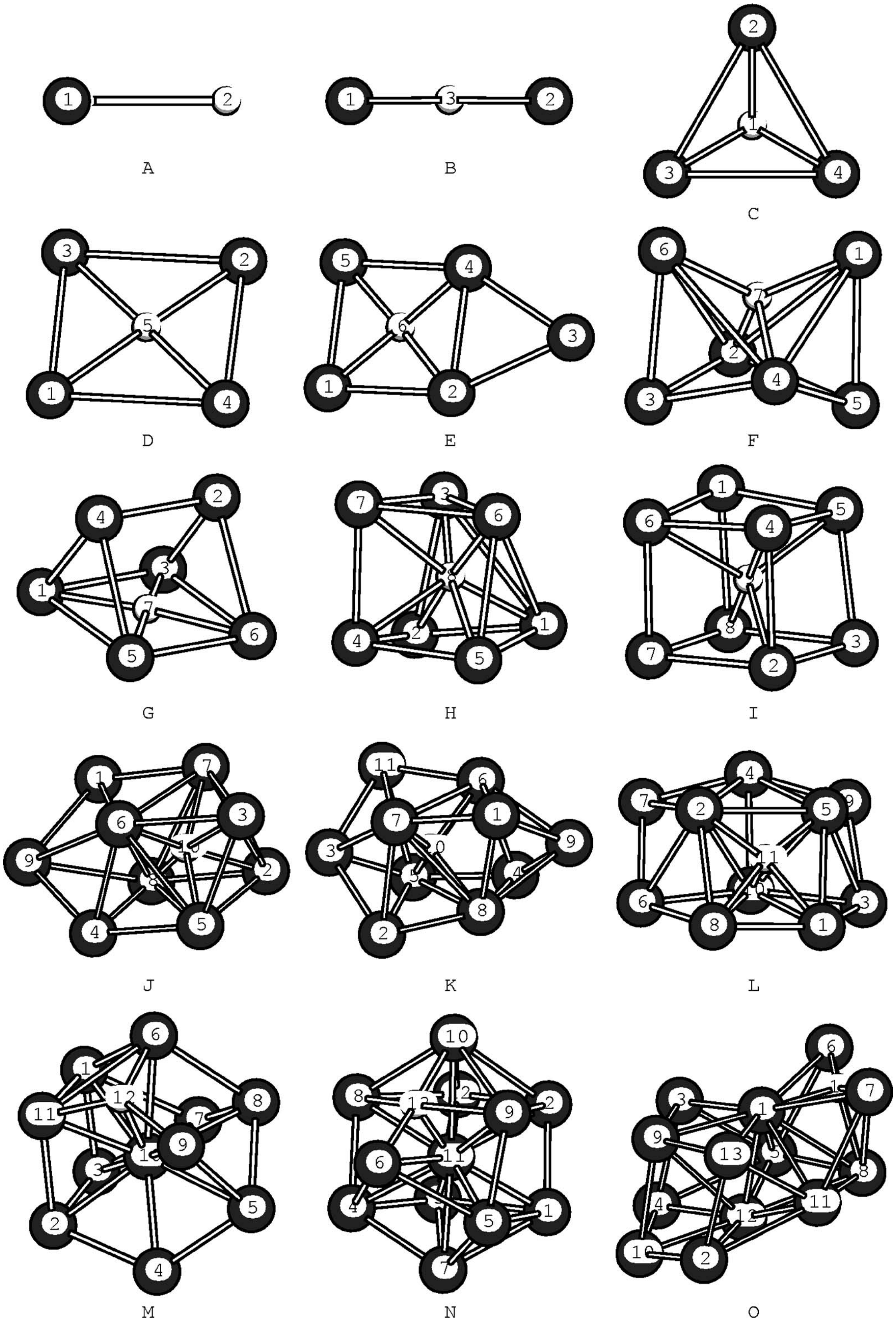

FIG. 1. The calculated lowest-energy structures for Ga_nN ($n=1-13$) clusters. Small circles represent N atoms, and large circles represent Ga atoms.

Ga-Ga bond length is 3.32 Å, while the Ga-N bond length is 1.94 Å. For Ga_4N, the lowest-energy structure we found is a planar structure with a central N surrounded by four Ga atoms forming a square [Fig. 1(d)]. The N atom binds to four Ga atoms with the bond length 2.06 Å. Comparing with Ga_3N clusters [Fig. 1(c)], we can find that the Ga-N bond length becomes larger. This is due to the larger coordination of N atoms. In the case of Ga_4N, nitrogen has fourfold coordination while it has threefold coordination in the case of Ga_3N. In the case of Ga_5N, the geometry could be envisioned as a Ga_4N cluster with a Ga atom attached to one side.

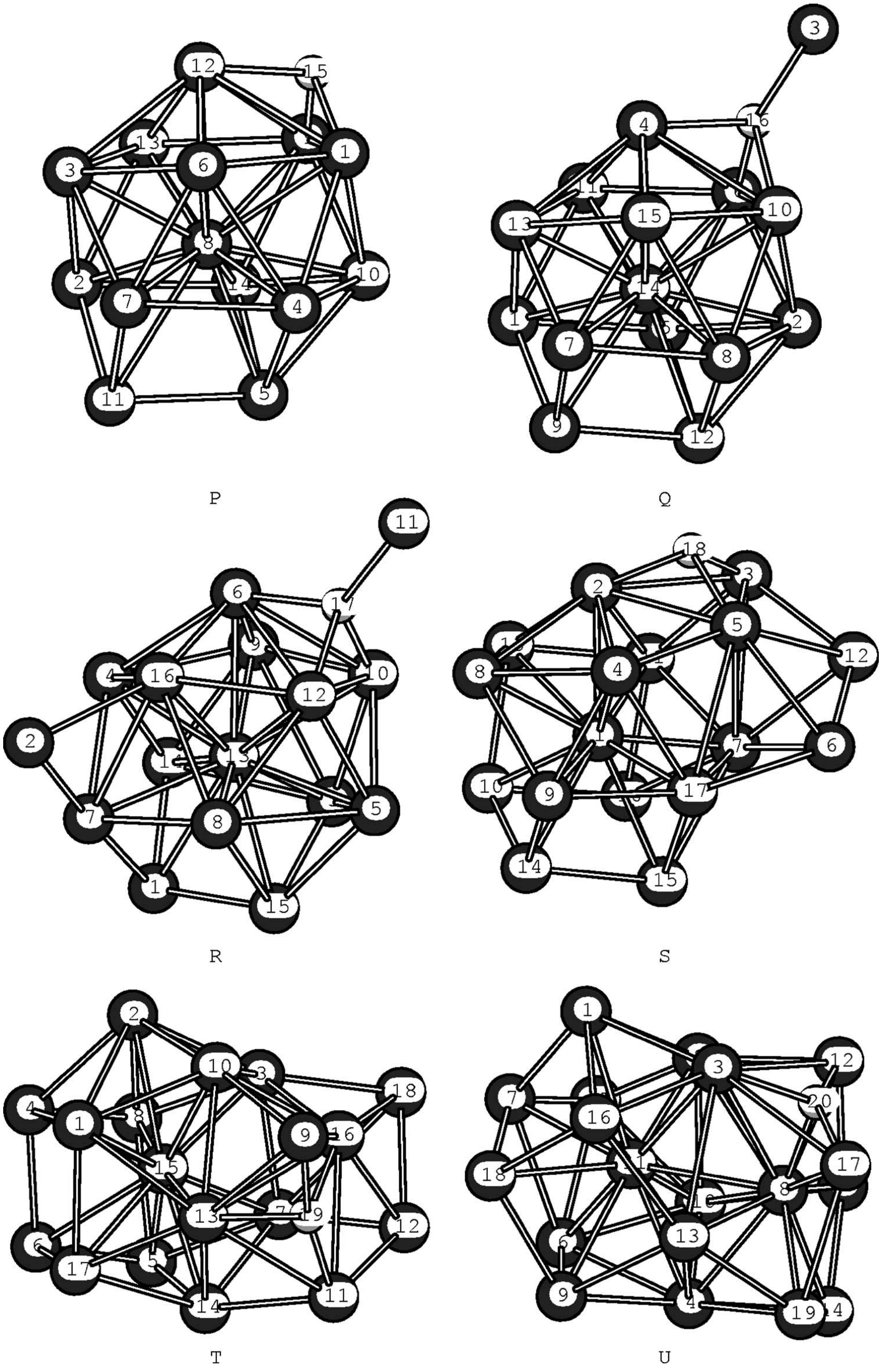

FIG. 2. The calculated lowest-energy structures for Ga_nN ($n=14-19$) clusters. Small circles represent N atoms, and large circles represent Ga atoms.

The Ga_6N is the first cluster in which a three-dimensional structure is adopted. For Ga_6N, two almost degenerate isomers [Figs. 1(f) and 1(g)] are obtained as the lowest-energy structure. Structure 1(g) lies only 0.01 eV above the structure 1(f). Both structures have a fourfold-coordinated N atom (similar to that in the lowest-energy structure of Ga_4N). For a Ga_7N cluster, the lowest-energy structure is shown in Fig. 1(h). This structure is composed of a Ga_6N structure that is attached to a Ga atom so that the five nearest Ga atoms form a tetrahedral pyramid. The lowest-energy structure of Ga_8N can be obtained by capping the ground state of the Ga_7N. Further cappings lead to Ga_9N and $Ga_{10}N$ structures in Figs. 1(j) and 1(k). The structure shown in Fig. 1(l) is another structure we obtained for a $Ga_{10}N$ cluster. It has C_s symmetry, and lies merely 0.01 eV above the structure 1 K. Therefore, the two structures should be viewed as nearly degenerate.

TABLE I. The symmetries, spin multiplicities, and electronic properties of the lowest-energy structures of Ga_nN clusters. E_b(eV): theoretical binding energy per atom. E_g(eV): theoretical HOMO-LUMO gap. E_i(eV): theoretical vertical ionization potential. E_a(eV): theoretical vertical electron affinity.

n	Symmetry	Multiplicity	E_b	E_g	E_i	E_a	Symmetry of HOMO	Symmetry of LUMO
1	$C_{\infty v}$	3	1.28	0.6	8.74	1.51	E	A_1
2	$D_{\infty h}$	2	2.30	0.83	8.15	2.0	A_{2u}	A_{2u}
3	D_{3h}	1	2.64	2.87	7.28	0.25	E'	E'
4	D_{4h}	2	2.43	0.63	6.80	1.74	B_{1g}	B_{1g}
5	C_{2v}	1	2.38	0.99	6.32	1.28	A_1	B_2
6	C_{2v}	2	2.37	0.44	6.35	1.93	A_1	A_1
7	C_{3v}	1	2.45	2.18	7.06	0.98	E	A_1
8	C_{3v}	2	2.39	0.42	6.24	1.89	A_2	A_2
9	C_{2v}	1	2.41	1.52	6.64	1.42	B_1	B_2
10	C_{2v}	2	2.39	0.45	5.93	1.96	A_1	A_1
11	C_1	1	2.40	1.20	6.38	1.75	A	A
12	C_s	2	2.41	0.29	5.97	2.29	A'	A'
13	C_s	1	2.46	1.16	6.30	1.90	A''	A''
14	C_{3v}	2	2.46	0.33	6.39	2.76	A_1	A_1
15	C_{3v}	1	2.51	1.60	6.46	1.70	A_1	E
16	C_1	2	2.47	0.20	5.50	2.22	A	A
17	C_1	1	2.47	0.94	5.98	1.98	A	A
18	C_1	2	2.47	0.23	5.52	2.32	A	A
19	C_1	1	2.48	0.87	5.83	2.02	A	A

The structural transition takes place at $n=11$. As mentioned in the above, the ground-state geometry of a $Ga_{11}N$ cluster [see Fig. 1(m)] is not a structure in which the N atom takes a central position. The N atom has already moved to the surface, and the central position is taken by a Ga atom. The lowest-energy structure of $Ga_{12}N$ is a decahedral-like structure with the N atom at the surface. It can be viewed as N replacing one Ga atom of the Ga_{13} decahedron. We optimized the geometry of a decahedral $Ga_{12}N$ cluster with the N atom occupying the central site. After relaxing the structure changed to an icosahedral $Ga_{12}N$ structure with a radial bond length of 2.59 Å. The icosahedral structure is above the lowest-energy structure of $Ga_{12}N$ [Fig. 1(n)] by 0.16 eV. The lowest-energy structure of $Ga_{13}N$ that we obtained is a C_s structure. The $Ga_{14}N$ geometry results by capping two trigonal faces of the icosahedron by one Ga atom and one N atom, respectively. The lowest-energy structure of $Ga_{15}N$ is formed by capping a Ga atom on the top of the N atom of $Ga_{14}N$. Capping one more Ga atom on the ground state of $Ga_{15}N$, it becomes the structure of $Ga_{16}N$. Further cappings lead to $Ga_{17}N$, $Ga_{18}N$, and $Ga_{19}N$ structures. As compared with those structures of Ga_nN ($n=15-19$), it can be seen that generally the ground-state structures of Ga_nN can be obtained by capping a Ga atom on the structure of $Ga_{n-1}N$.

B. Stabilities and electronic properties

The stability of these clusters can be discussed on the basis of the binding energy per atom (E_b) and the second difference in energy ($\Delta_2 E$),

$$E_b[Ga_nN] = (nE[Ga] + E[N] - E[Ga_nN])/(n+1),$$

$$\Delta_2 E[Ga_nN] = E[Ga_{n+1}N] + E[Ga_{n-1}N] - 2E[Ga_nN],$$

where E is the total energy of the corresponding system. The calculated binding energy per atom E_b is shown in Fig. 3. Table I is a function of size n. It can be seen from Fig. 3 that the cluster binding energies increase with cluster size n rapidly up to $n=3$, then the binding energies reduce with the size increase of the Ga_nN ($n=3-6$). The binding energies of the clusters begin to slowly elevate from Ga_6N and contain two minor bumps at $n=7$ and 15 indicating their relative stabilities. The peak at $n=3$ shows that the Ga_3N cluster has a high stability, which is easy to understand from its equilat-

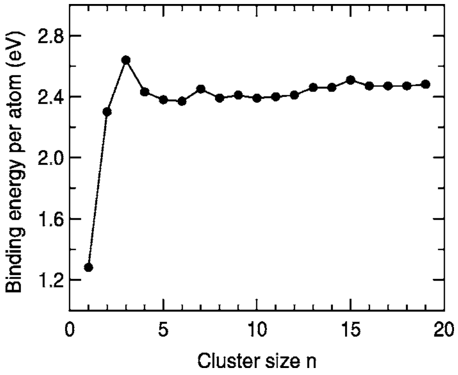

FIG. 3. Binding energy per atom as a function of size for Ga_nN ($n=1-19$) clusters.

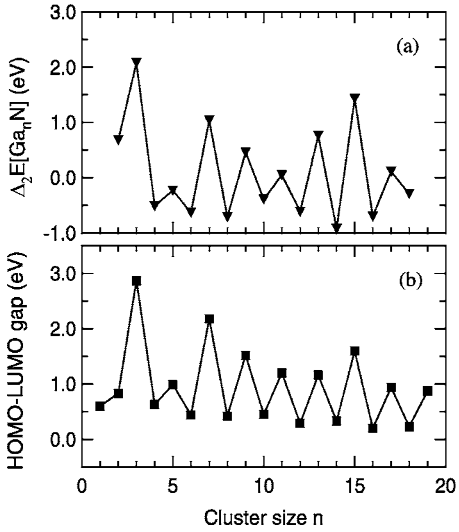

FIG. 4. (a) Second difference of cluster energies Δ_2E and (b) HOMO-LUMO gaps for Ga_nN ($n=1-19$) clusters.

eral triangle structure. A similar structure was reported for Al_3N clusters[33,34] as the lowest-energy structure. From theoretical calculations one can search for magic clusters by calculating the second difference in energy (Δ_2E). In cluster physics, the second difference of cluster energies $\Delta_2E$is a sensitive quantity that reflects the stability of clusters and can be directly compared with the experimental relative abundance.[35] Magic clusters are those that show unusually high stability as compared to their nearest two neighbors. In Figs. 4(a), we plot the second differences of cluster energies as a function of cluster size. It is found that the Δ_2E exhibits odd-even oscillations. The even-numbered Ga_nN clusters are relatively more stable than the neighboring odd-sized ones. It is found that the Ga_nN clusters with $n=3,7$, and 15 are particularly stable. These clusters can thus be considered as magic clusters. According to jellium model,[36] the magic numbers in metal clusters can be understood in view of the magic numbers of total valence electrons of $8,20,40,\ldots$. If we apply such a model to all Ga_nN clusters that we studied, the stability at $n=3,7$, and 15, which has 14, 26, and 50 electrons, respectively, cannot be explained.

In Fig. 4(b), we plot the HOMO-LUMO gaps as a function of cluster size. The HOMO-LUMO gap is the equivalent of the energy gap in a bulk semiconductor and it is of considerable importance in the study of semiconductor materials. The results from the present calculation show that the HOMO-LUMO gaps display odd-even oscillations as a function of cluster size. Except for GaN monomers, the even-numbered clusters with closed shell singlet ground states have a larger gap. The odd-numbered clusters with a open shell have a smaller gap. This is due to the fact that even-numbered clusters have an even number of valence electrons and furthermore all the electrons are paired together in their respective molecular orbitals. Table I shows that the magnitude of the gaps changes from 0.20 to 2.87 eV. Hence, these clusters may still present semiconductorlike properties. The HOMO-LUMO gap is also a useful quantity for examining the stability of clusters. It is found that systems with larger HOMO-LUMO gaps are, in general, less reactive. The clusters with an even number of electrons, with the exception of a GaN monomer, have peaks indicating their enhanced stability with respect to their neighbors. The HOMO-LUMO gap is particularly large for Ga_3N, Ga_7N, and $Ga_{15}N$, indicating that these clusters have closed shell electronic configurations with enhanced stability.

To determine the nature of Ga-N bonding in clusters, we carried out a Mulliken population analysis of the resulting charge at each site. The charges at N site are given in Table II and plot in Fig. 5(a) as a function of cluster size. As expected, Ga is cationic and N is anionic in all of the clusters. It is found that there is a significant charge transfer from Ga to N site in all clusters. This indicates that the bonding in Ga_nN clusters has some ionic character. In fact, the electrostatic attraction between N and Ga in the GaN monomer, assuming that the Mulliken charges are localized at the sites, would be 1.18 eV compared to its binding energy of 2.56 eV. This shows that there is also a significant covalent contribution. It can be seen from Fig. 5(a) that the Mulliken charge at the N site increases with cluster size n rapidly up to $n=3$, then the Mulliken charge reduces with the size increase of the Ga_nN ($n=3-8$). The Mulliken charges at the N site begin to oscillate from $n=8$. In Ga_3N, the nitrogen atom carries one extra electron. This charge slightly diminishes with increasing cluster size indicating that the clusters take on an increasingly metallic character. It should be noted here that the Mulliken charges, although indicative, do not always describe the atomic or bond charges accurately as they display sensitivity to the atomic basis set. The values of the Ga-N bond length for each cluster are also given in Table II, and the average Ga-N bond length for each cluster is plotted in Fig. 5(b). It is found that the magnitude of the average Ga-N bond lengths charges from 1.80 to 2.24 Å. For comparison, we performed calculations on bulk GaN (wurtzite phase) using the same method but with a periodic boundary condition. The calculations for bulk GaN show that the Ga-N distance is 1.95/1.96 Å, and the Mulliken charge at the N site is $-1.13e$. Thus, the N in Ga_nN clusters is less ionic than that in bulk stoichiometric GaN.

The ionization potential and electron affinity of the clusters are also sensitive quantities to provide fundamental insight into the electronic structure. In this work, we calculate the vertical ionization potentials and vertical electron affinities of the lowest-energy structure of the Ga_nN clusters. The vertical ionization potential (vIP) was calculated as the energy difference between the neutral cluster and the corresponding positively charged cluster having the neutral geometry. The vertical electron affinity (vEA) was calculated as the energy difference between the neutral cluster and the corresponding negatively charged cluster having the neutral geometry. The theoretical results are given in Table I. Figure 6(a) and 6(b) display the calculated vIP and vEA as a function of cluster size. To our knowledge, no experimental ionization potential and electron affinity data are available for Ga_nN clusters. It can be seen from Fig. 6(a) that generally the vIP decreases as the cluster size increases. This can be explained on the basis of the metallic character of the cluster. The successive addition of a Ga atom increases the metallic character of the system. This leads to a decrease of the vIP

TABLE II. Mulliken charges at the N site and Ga-N distances for the lowest-energy structures of Ga_nN clusters. d_{Ga-N}(Å): theoretical Ga-N distance. q_N: Mulliken charge at the N site.

Species	Type	d_{Ga-N}	q_N	Species	Type	d_{Ga-N}	q_N
GaN	1–2	1.87	−0.42	$Ga_{13}N$	6–14	2.01	−0.86
Ga_2N	1–3	1.80	−0.81		1–14	1.96	
Ga_3N	2–1	1.94	−1.00	$Ga_{14}N$	12–15	1.96	−0.73
Ga_4N	1–5	2.06	−0.94	$Ga_{15}N$	3–16	1.96	−0.93
Ga_5N	4–6	1.97	−0.94		4–16	2.06	
	5–6	2.08		$Ga_{16}N$	6–17	2.03	−0.93
Ga_6N	1–7	1.99	−0.89		10–17	2.10	
	4–7	2.17			11–17	1.96	
Ga_7N	4–8	2.23	−0.85	$Ga_{17}N$	2–18	1.92	−0.74
	5–8	2.34			3–18	1.96	
	6–8	2.12			5–18	1.97	
Ga_8N	4–9	2.13	−0.75	$Ga_{18}N$	9–19	2.10	−0.84
	5–9	2.34			11–19	2.00	
	8–9	2.06			13–19	1.98	
Ga_9N	3–10	2.25	−0.87		16–19	2.07	
	5–10	2.19		$Ga_{19}N$	3–20	1.99	−0.86
	6–10	2.01			8–20	2.06	
$Ga_{10}N$	6–10	2.19	−0.70		12–20	2.06	
	7–10	2.11			17–20	2.01	
$Ga_{11}N$	9–12	1.97	−0.82	GaN bulk		1.95	−1.13
	11–12	2.02				1.95	
	6–12	2.04				1.95	
	10–12	2.22				1.96	
$Ga_{12}N$	6–13	1.99	−0.77				
	8–13	2.36					
	9–13	2.40					
	10–13	2.10					
	11–13	2.02					

with the addition of Ga. The vIP decreases monotonically up to Ga_5N, beyond which it exhibits an odd-even pattern with peaks for clusters with an even number of electrons. The vEA, shown in Fig. 6(b), increases as the cluster size increases, and also exhibits an odd-even pattern. This is again a consequence of the electron pairing effect. In the case of clusters with an even number of valence electrons, the extra electron has to go into the next orbital, which costs energy, resulting in a lower value of vEA. Note that all the even Ga atom clusters have higher electron affinity than the proximate odd clusters with Ga_3N being the lowest. Since there are few experimental results available for the GaN clusters, the present systematic theoretical results should provide strong motivation for further experimental studies for these important GaN clusters.

IV. CONCLUSIONS

In summary, using DFT and GGA, we have calculated the lowest-energy structures of Ga_nN ($n=1-19$) clusters. It is found that the nitrogen atom tends to occupy an inside posi-

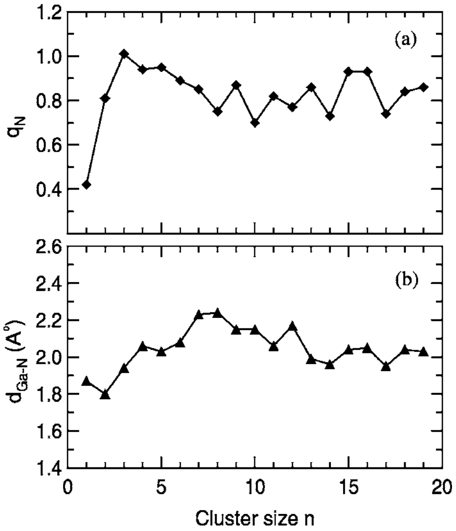

FIG. 5. (a) The Mulliken charge at N site (q_N) and (b) the average Ga-N bond length (d_{Ga-N}) for Ga_nN ($n=1-19$) clusters.

tion for $n \leq 10$, but prefers a peripheral position beyond $n = 10$. The N atom with a bulklike coordination emerges as the cluster size increases. The $\Delta_2 E$ exhibits odd-even oscillations, implying that the even-numbered Ga_nN clusters are relatively more stable than the neighboring odd-sized ones. It is found that the clusters Ga_3N, Ga_7N, and $Ga_{15}N$ exhibit particularly higher stability. The bonding property has been analyzed by calculating the Mulliken charges and Ga-N distances. The Mulliken charge and Ga-N distance depend on the cluster size. The results show that the N in Ga_nN clusters is less ionic than that in bulk GaN (wurtzite phase). The HOMO-LUMO gap, vIP and vEA have also been calculated. The calculated HOMO-LUMO gap, vIP and vEA form an even-odd alternating pattern with increasing cluster size. In general, the vIP tends to lower as the cluster size increases, while the vEA tends to increase as the cluster size increases.

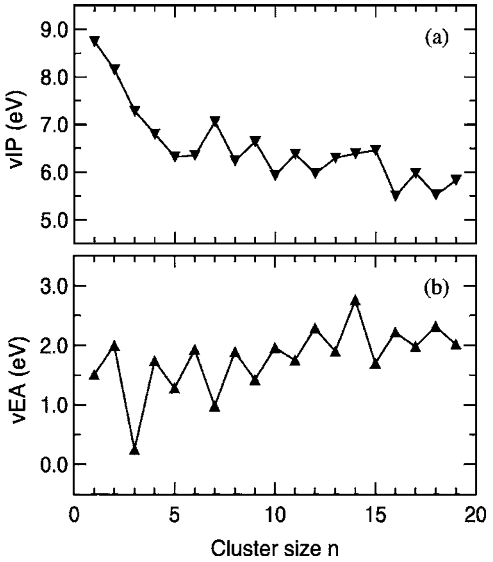

FIG. 6. (a) Vertical ionization potentials (vIPs) and (b) vertical electron affinities (vEAs) for Ga_nN ($n = 1-19$) clusters.

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*Electronic address: bzsong@css.zju.edu.cn

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