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Structures and polarizabilities of medium-sized Ga_nAs_m clusters

Yuewen Mu [a], Jianrong Li [b], Jian-guo Wan [a,*], Fengqi Song [a], Guanghou Wang [a]

[a] National Laboratory of Microstructures, Department of Physics, Nanjing University, Nanjing 210093, PR China
[b] Department of Physics, Qujing Normal University, Qujing 655000, Yunnan, PR China

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ABSTRACT

Density functional theory calculations on medium-sized Ga_nAs_m clusters ($n + m = 17$–24, $n - m = 0, \pm 1$) are reported. The total polarizabilities of Ga_nAs_m clusters exhibit a linear dependence on their volumes despite of different composition, giving a way to predict the polarizabilities of larger clusters. The polarizabilities are also strongly correlated to ionization potentials and composition. Isomerization may be the main reason why the even–odd oscillation of polarizabilities disappears in this size from experiment. Ultra stability of Ga_9As_{10} and unusual electronic properties of $Ga_{10}As_{11}$ are found due to their special structures.

1. Introduction

The research of semiconductor clusters has become active for the past few decades due to their fundamental importance and potential application. Gallium arsenide clusters, as an important semiconductor material, can be widely used in various fields such as medical diagnostics [1], quantum computing [2], nonlinear optics [3,4] and so on. To understand the structures and physical properties of GaAs clusters is important for the application of low-dimensional GaAs nanostructures.

So far, a lot of experimental work has been done on gallium arsenide clusters. Laser photoionization of Ga_nAs_m clusters ($n + m = 5$–25) suggested an even–odd oscillation of ionization properties and this group revealed that the dominant species in Ga_nAs_m cluster beam are the clusters with the ratio of n/m close to 1 [5]. The polarizabilities of Ga_nAs_m clusters ($n + m = 4$–30) exhibited an even–odd oscillation for $n + m < 18$ at 38 and 300 K [6]. The effective optical band gaps of Ga_nAs_m clusters ($n + m = 4$–80) were studied by photoabsorption spectra [7]. On the theoretic side, the investigations mainly focused on very small Ga_nAs_m clusters ($n + m \leqslant 10$) [8–10], Ga_nAs_m clusters ($m + n = 2, 4, \ldots, 16$) [11] and larger stoichiometric clusters $(GaAs)_n$ ($n \leqslant 16$) [3,12–14], though there were a lot of experimental studies on both odd-numbered and even-numbered clusters. In addition, odd-numbered clusters may exhibit better properties (e.g., higher polarizabilities [6]) than even-numbered clusters, therefore systematical study on gallium arsenide clusters of both kinds is in demand. On the other hand, Schäfer et al. [6] suggested that the polarizabilities of gallium arsenide clusters were inversely correlated to their HOMO–LUMO gaps with a hypothesis about donorlike and acceptorlike states by perturbation theory, but the calculations on Ga_nAs_m ($n + m \leqslant 8$) clusters by Vasiliev et al. [8] did not conform this hypothesis to explain the polarizabilities of odd-numbered Ga_nAs_m clusters, and they predicted that the polarizabilities of Ga_nAs_n clusters were close to the average of the polarizabilities of Ga_nAs_{n-1} and $Ga_{n-1}As_n$ clusters. Therefore, what determines the polarizabilities of Ga_nAs_m clusters is still unclear. We investigate the structural, electronic properties and polarizabilities of medium-sized Ga_nAs_m clusters ($n + m = 17$–24, $n - m = 0, \pm 1$). The dependence of stability and electronic properties on composition and size for the lowest energy structures is analyzed. And the influences of isomerization, cluster volume, ionization potential and HOMO–LUMO gap on the polarizability are also discussed.

2. Computational methods

We performed a genetic algorithm [15,16] (GA) global search with an empirical Stillinger–Weber potential [17,18] to get low-lying structures. A number of candidate structures (between 30 and 40) were obtained after 4000 steps matting. Furthermore we searched cage structures by basin hopping method [19] in the polar coordinates system, and the initial structures were taken from the results of the genetic algorithm search. All-electron density functional theory calculations with a DMOL3 Program [20] were performed to optimize the acquired isomers and to compute the electronic properties. The generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) [21] exchange–correlation function was chosen. Frequency analysis has been applied to the low-lying structures to make sure that they are real local minima. The dipole moments and polarizabilities of the low-lying structures of each size were calculated using the GAUSSIAN 03 Program [22] with BPW91 approach and 6-311+G* basis set [23]. The validity and efficiency of the combined scheme of empirical GA search

* Corresponding author. Fax: +86 25 8359 5535.
E-mail address: wanjg@nju.edu.cn (J.-g. Wan).

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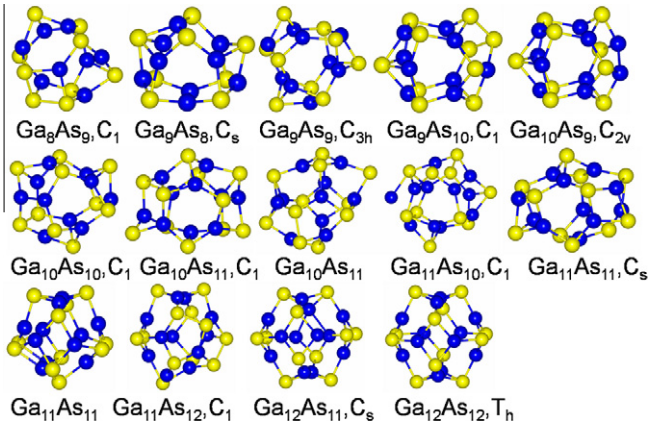

Figure 1. The lowest energy structures of Ga_nAs_m clusters ($n + m = 17–24$, $n - m = 0, \pm1$). The blue (yellow) balls stand for Ga (As) atoms. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

and DFT optimization were demonstrated in previous works [12,16].

3. Results and discussion

3.1. Structures and electronic properties

The lowest energy structures of Ga_nAs_m clusters ($n + m = 17–24$, $n - m = 0, \pm1$) are displayed in Figure 1. It is found that all the lowest energy structures and most of other low-lying isomers are hollow cages, which implies that hollow cages are still energetically preferred to stuffed cages in this size. Similar lowest energy structures of $(GaAs)_N$ clusters ($N = 9–12$) are obtained by Gutsev et al. [13]. By further comparing these lowest energy structures (especially $Ga_{10}As_{11}$ and $Ga_{11}As_{11}$ from different sides as shown in Figure 1), we find that most of the lowest energy structures can be seen as the derivatives from the smaller clusters by capping atoms on the surface. The binding energies per atom (E_b) of the lowest energy structures are listed in Table 1 and plotted in Figure 2a. As shown in Figure 2a, the binding energies per atom of stoichiometric, As-rich and Ga-rich clusters basically increase with increasing the cluster size respectively for corresponding average bond length decreases. The As–As bond is stronger than Ga–As bond, while Ga–Ga bond is much weaker than the former two bonds in small Ga_nAs_m clusters ($n + m = 2, 4, \ldots, 16$) clusters [11]. The total number of bonds of Ga_nAs_m clusters ($n + m = 17–24$, $n - m = 0, \pm1$) is $2n + m$ except Ga_9As_{10} and $Ga_{11}As_{10}$. When an As atom is added to a stoichiometric cluster, one more As–As bond appears, while two more Ga–As bond and Ga–Ga bond are formed in the case of Ga adding. The sum of the binding energy of a Ga–As bond and a Ga–Ga bond is smaller than that of an As–As bond, therefore the Ga_nAs_{n+1} cluster is more stable than $Ga_{n+1}As_n$ cluster. When a Ga atom and an As atom are added to a stoichiometric cluster, three more Ga–As bonds are formed, that is, one and a half Ga–As bonds for each added atom on average, whose binding energy is larger than that of an As–As bond. It brings about that the stoichiometric clusters are most stable. Ga_9As_{10} with more than $2n + m$ bonds is more stable than its neighboring stoichiometric clusters, while $Ga_{11}As_{10}$ with less than $2n + m$ bonds is just as stable as the smaller cluster $Ga_{10}As_9$.

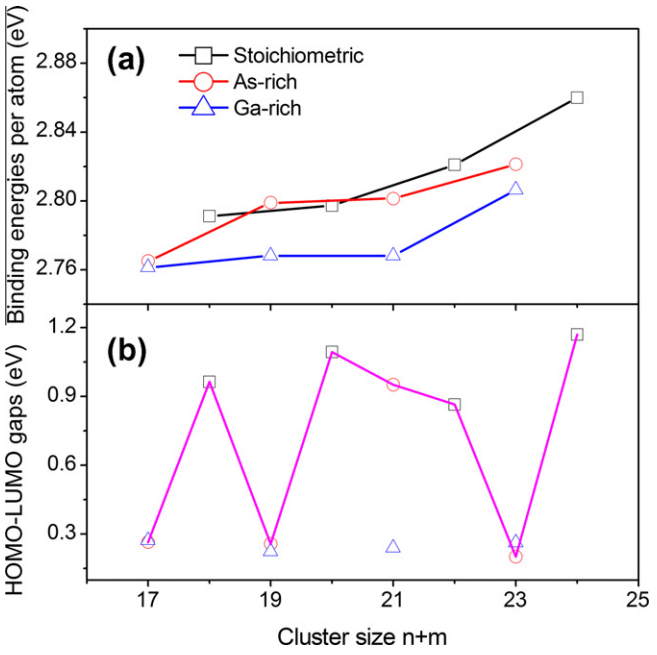

Figure 2. (a) The binding energies per atom of the lowest energy structures of Ga_nAs_m clusters. (b) The HOMO–LUMO gaps of the lowest energy structures of Ga_nAs_m clusters.

Some other electronic properties of the gallium arsenide clusters are further calculated. As shown in Figure 2b, obvious even–odd oscillation of HOMO–LUMO gaps is observed except $Ga_{10}As_{11}$. The HOMO–LUMO gaps of As-rich clusters for odd $n + m = 17, 19, 23$ are only about 0.25 eV while the gaps for even-numbered clusters ($n + m = 18, 20, 22, 24$) reach about 1.0 eV. Such even–odd oscillation of the gaps should be attributed to the electron-pairing effect. We take As-rich clusters as the ground state structures for

Table 1
Binding energies per atom (E_b, eV), HOMO–LUMO gaps (△, eV), vertical ionization potentials (VIP, eV), adiabatic ionization potentials (AIP, eV), vertical detachment energies (VDE, eV), static dipole moments (μ, debye), polarizabilities per atom ($\bar{\alpha}$, Å^3), average mulliken charges (e) at the Ga site (q_{Ga}) and As site (q_{As}) of the lowest energy structures of Ga_nAs_m clusters.

Cluster	E_b	△	VIP	AIP	VDE	μ	$\bar{\alpha}$	q_{Ga}	q_{As}
Ga_8As_9	2.765	0.264	5.988	5.922	2.62	0.922	4.815	0.497	−0.442
Ga_9As_8	2.761	0.273	6.227	6.141	2.821	0.532	4.803	0.45	−0.506
Ga_9As_9	2.791	0.964	6.919	6.832	2.873	0.000	4.756	0.526	−0.526
Ga_9As_{10}	2.799	0.257	6.068	6.043	2.793	0.714	4.747	0.524	−0.472
$Ga_{10}As_9$	2.768	0.226	6.132	6.087	2.885	0.991	4.818	0.472	−0.524
$Ga_{10}As_{10}$	2.797	1.094	6.751	6.568	2.682	0.430	4.802	0.504	−0.504
$Ga_{10}As_{11}$	2.801	0.952	6.781	6.626	2.674	0.154	4.818	0.561	−0.510
$Ga_{11}As_{10}$	2.768	0.239	5.808	5.682	2.666	0.933	4.933	0.455	−0.50
$Ga_{11}As_{11}$	2.821	0.866	6.711	6.576	2.938	0.213	4.785	0.527	−0.527
$Ga_{11}As_{12}$	2.821	0.202	5.563	5.526	2.55	1.158	4.865	0.551	−0.505
$Ga_{12}As_{11}$	2.806	0.264	6.161	5.874	3.064	0.393	4.866	0.512	−0.560
$Ga_{12}As_{12}$	2.86	1.169	6.827	6.813	2.879	0.001	4.730	0.584	−0.584

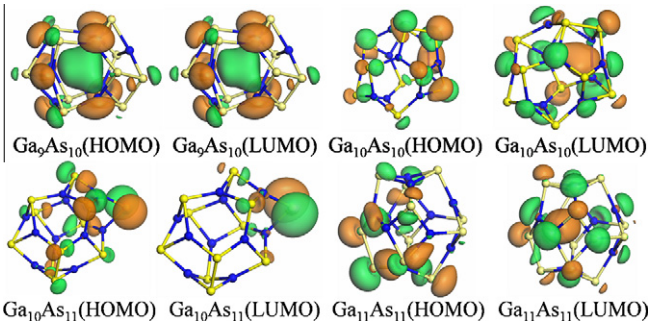

Figure 3. The HOMO and LUMO orbits of Ga_9As_{10}, $Ga_{10}As_{10}$, $Ga_{10}As_{11}$ and $Ga_{11}As_{11}$ clusters. The isovalue is 0.03.

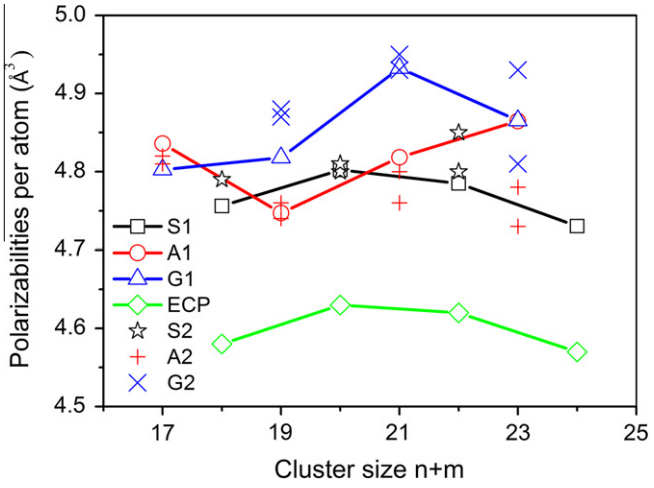

Figure 4. The polarizabilities per atom of the low-lying structures of Ga_nAs_m clusters. S1, A1 and G1 represent lowest energy structures of stoichiometric, As-rich and Ga-rich clusters respectively and S2, A2 and G2 represent other low-lying structures of stoichiometric, As-rich and Ga-rich clusters observable at 38 K. ECP stands for BPW91/ECP (Ref. [13]) results for stoichiometric Ga_nAs_m clusters.

odd-numbered clusters due to their larger binding energy than Ga-rich ones, though the HOMO–LUMO gaps of Ga-rich clusters are similar to that of As-rich ones. More stability is expected for stoichiometric clusters for their large gaps and vice versa. Basically, the vertical ionization potentials of Ga_nAs_m clusters also exhibit similar even–odd oscillation (listed in Table 1), which agrees with earlier experimental results [5]. The differences between vertical ionization potentials and adiabatic ionization potentials of the lowest energy structures are very small, suggesting that their geometries will change little when losing an electron.

It is interesting that the lowest energy structure of $Ga_{10}As_{11}$ cluster has an unusual HOMO–LUMO gap (0.952 eV) which is much larger than that of other nonstoichiometric clusters and comparable to that of stoichiometric clusters. We notice that for two other low-lying isomers of $Ga_{10}As_{11}$ the gaps are 0.205 and 0.200 eV respectively. This indicates that the unusual gap of the lowest energy $Ga_{10}As_{11}$ should be related to its special structure. Generally, Ga-rich (As-rich) clusters have several Ga–As bonds and one Ga–Ga (As–As) bond, while the stoichiometric clusters only have Ga–As bonds, which may also be an important reason for their large gap. $Ga_{10}As_{11}$ is a special structure with a bicoordinate As atom, which only has Ga–As bonds like stoichiometric clusters. So we can infer that the special structure of the lowest energy $Ga_{10}As_{11}$ cluster plays an important role in its unusual electronic properties, such as HOMO–LUMO gap and ionization potential.

The distribution of electron density of HOMO and LUMO orbits of lowest-energy Ga_9As_{10}, $Ga_{10}As_{10}$, $Ga_{10}As_{11}$ and $Ga_{11}As_{11}$ clusters is plotted in Figure 3. The HOMO and LUMO states of Ga_9As_{10} are mainly localized around Ga sites, similar to other nonstoichiometric clusters except $Ga_{10}As_{11}$, whose HOMO and LUMO states are localized around As sites. The HOMO states of $Ga_{10}As_{10}$ and $Ga_{11}As_{11}$ clusters, like other stoichiometric ones, are basically confined around As sites, while the corresponding LUMO states are near Ga sites. Similar to the stoichiometric clusters, the HOMO states of $Ga_{10}As_{11}$ cluster are localized around As sites, which have much stronger attraction to electrons than Ga sites. The special HOMO–LUMO electron density distribution of $Ga_{10}As_{11}$ may be the direct cause of its unusual electronic properties.

3.2. Dipole polarizabilities

The dipole polarizabilities per atom of Ga_nAs_m clusters are presented in Figure 4. The polarizabilities per atom of Ga_nAs_m clusters are higher than the bulk limit (4.14 Å^3) estimated from the Clausius–Mossotti relation. Generally, nonstoichiometric gallium arsenide clusters have higher polarizabilities per atom than stoichiometric ones, and the polarizabilities of Ga-rich clusters are higher than that of As-rich ones, suggesting the composition dependence of the polarizabilities. Such polarizability properties may be related to the two following reasons. Firstly, the polarizability of Ga atom is twice as high as that of As atom [24]. Secondly, larger binding energy means stronger binding of the nuclei to the electrons and smaller delocalization volume which tends to demote the polarizability magnitude. Ga_9As_{10} has smaller polarizability per atom than its neighboring stoichiometric clusters, which is presumably due to its larger binding energy. The polarizabilities of $(GaAs)_N$ clusters ($N = 9$–12) in our calculations are in agreement with early results using effective core potentials [13] as shown in Figure 4. Isomerization should be considered because any experimental measurement value of polarizabilities should be the thermal average of all possible isomers. The energy limit for higher energy isomer observable at temperature T can be estimated from $E_{GS} - (3n + 3m - 6)k_BT/2$, where E_{GS} is the total binding energy of the lowest energy structure and k_B is the Boltzmann constant. The polarizabilities per atom of low-lying Ga_nAs_m clusters observable at 38 K, just as the temperature in Ref. [6], are displayed in Figure 4. The polarizabilities of other low-lying isomers for As-rich clusters which dominate the odd-numbered clusters, are mostly lower than that of corresponding lowest energy structures, therefore measurement gives smaller polarizabilities for As-rich clusters, whereas the stoichiometric clusters are quite the opposite. This may be the main reason why the even–odd oscillation of the polarizabilities per atom disappears in the medium size from experiment.

It has been revealed that there are close relation between the polarizabilities of small molecules and their volumes [25] and close correlation between the polarizabilities and corresponding ionization energies for some small alkali clusters [26] and Au clusters [27]. What is the case for semiconductor clusters? The total polarizabilities of Ga_nAs_m clusters versus their volumes are plotted in Figure 5a. Interestingly, the plot yields a good linear relationship with a correlation coefficient of 0.991 despite of different composition, which implies that the cluster volume plays a dominant role in the determination of polarizabilities of Ga_nAs_m clusters. The cluster volume is calculated by integrating the space with electronic density greater than 0.001 a.u. as recommended by Bader [28]. Higher polarizabilities are associated with the clusters which have loosely bound charge density and relatively large volumes. This explains why stoichiometric clusters and Ga_9As_{10} possess lower polarizabilities. This is an important observation because this linear dependence can provide a way to calculate the polarizability of Ga_nAs_m clusters of larger size from their volumes.

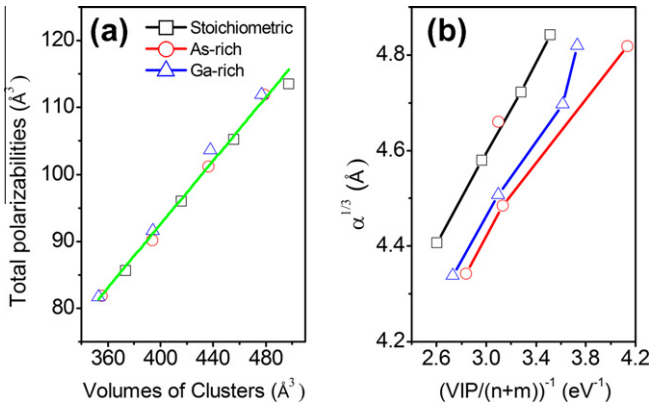

Figure 5. (a) The total polarizabilities of the lowest energy structures of Ga_nAs_m clusters as a function of their volumes. (b) The cube root of total polarizabilities of the lowest energy structures of Ga_nAs_m clusters as a function of the reciprocal of vertical ionization potential per atom of corresponding clusters.

In addition, the cube roots of the total polarizabilities ($\alpha^{1/3}$) as a function of the reciprocals of vertical ionization potentials per atom ($(\mathrm{VIP}/(n+m))^{-1}$) are depicted. As displayed in Figure 5b, the cube roots for stoichiometric, As-rich and Ga-rich clusters nearly linearly depend on the reciprocals respectively except $Ga_{10}As_{11}$ for its unusual electronic properties. The plot suggests that the polarizabilities are strongly related to ionization potential and composition. This inverse correlation between polarizabilities and ionization potential is due to that higher ionization potential means stronger binding of valence electrons, which suppresses the response of electronic cloud to the external electric field. The contribution from the HOMO–LUMO transition may constitute a large part of the polarizability which comes from all exited states [29] therefore an inverse correlation between them was proposed by Schäfer et al. [6]. The HOMO–LUMO gaps of stoichiometric clusters oscillate with increasing the cluster size, but the evolution of their polarizabilities per atom does not show obvious inverse correlation between them. Furthermore, the nonstoichiometric clusters do not possess much higher polarizabilities per atom than stoichiometric clusters for the big differences between their HOMO–LUMO gaps as excepted. Therefore this hypothesis fails in this size.

4. Conclusions

By using genetic algorithm, basin hopping method and density functional theory calculations, the geometries, electronic properties and polarizabilities of Ga_nAs_m clusters ($n+m=17$–24, $n-m=0, \pm1$) are investigated systematically. All the lowest energy structures are hollow cages with a total number of bonds of about $2n+m$. The total polarizabilities of Ga_nAs_m clusters exhibit a linear dependence on their volumes despite of different composition, indicating that the volumes are crucial in determining the polarizabilities. The polarizabilities are also strongly correlated to ionization potentials and composition. The odd-numbered clusters tend to possess higher polarizabilities than even-numbered ones, but this behavior will not be observed from experiment in this size due to isomerization. Ga_9As_{10} shows ultra stability for it has more than $2n+m$ bonds, and $Ga_{10}As_{11}$, seen as a fragment of $Ga_{12}As_{12}$, has special HOMO–LUMO electron density distribution which may account for its unusual electronic properties like stoichiometric clusters.

Acknowledgments

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