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# Nano Science and Nano Technology

*An Indian Journal*

*Full Paper*

NSNTAJI, 2(2-3), 2008 [77-82]

## Study of Ga<sub>7</sub>As<sub>7</sub> cluster and its ions

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Received: 31<sup>st</sup> May, 2008 ; Accepted: 5<sup>th</sup> June, 2008

### ABSTRACT

We have investigated the structures and stabilities of Ga<sub>7</sub>As<sub>7</sub> cluster and its ions in detail using full-potential linear-muffin-tin-orbital molecular-dynamics (FP-LMTO-MD) calculations. The lowest energy structure for neutral cluster is found. Our calculations suggest that some ionic structures are different from that of the corresponding neutral cluster. They depend on the amount of charge. The structural distortions of the ion clusters result from the electrostatic repulsion among the charged atoms.

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### KEYWORDS

Cluster ions;  
Ground-state structure;  
Binding energy.

### INTRODUCTION

The semiconductor industry is a highly developing industry, which has a worth of billions of dollars. The arsenic and the gallium play important roles in this industry. It is necessary to make theoretical<sup>[1-3]</sup> and experimental researches on GaAs crystal and clusters<sup>[4,5]</sup>. In fact, for the mixed clusters like GaAs, the theoretical investigation on them is comparatively difficult because of the computational difficulties associated with the structural and permutational variations resulting from the presence of more than one element even though they contain a few atoms. However, due to their scientific and technological applications<sup>[6]</sup>, a great effort has been devoted to the investigation on their properties. Up to now, some development has already been obtained both experimentally and theoretically.

Experimentally, laser vaporization followed by supersonic expansion is used to produce the GaAs clusters and their ions<sup>[7-9]</sup>. Theoretically, some reports about

the GaAs clusters can be found. For neutral Ga<sub>4</sub>As<sub>4</sub> cluster, Mohammad et al. considered three structures with T<sub>d</sub>, C<sub>i</sub>, and D<sub>2d</sub> symmetries using an ab initio molecular-orbital method<sup>[10]</sup>, and Song et al. examined six structures<sup>[11]</sup> which are a rhombic prim structure, a planar octahedron structure, an edge-capped pentagonal pyramid structure, an edge-tricapped rhombus structure, a double bicapped rhombus structure, and a double rhombus structure using ab initio method<sup>[11]</sup>.

Vasiliev et al. studied the absorption spectra of two Ga<sub>4</sub>As<sub>4</sub> structures using a time-dependent density-functional formalism within the local density approximation<sup>[12]</sup>. In Song's report, the rhombic prism structure is regarded as the ground-state structure for the Ga<sub>4</sub>As<sub>4</sub> cluster<sup>[11]</sup>. Wei Zhao et al. calculated the Ga<sub>4</sub>As<sub>4</sub> cluster using full-potential linear-muffin-tin-orbital molecular-dynamics method (FP-LMTO-MD)<sup>[13]</sup>. They found a new edge-capped pentagonal bipyramid structure as its ground state structure. Its binding energy is much larger than that of the C<sub>i</sub> symmetry structure<sup>[13]</sup>. For

## Full Paper

**TABLE 1:** Calculated total binding energy ( $E_t$ , in eV), cohesive energy ( $E_c$ , in eV), scaled cohesive energy ( $E_s$ , in eV) and the measured cohesive energy ( $E_{exp}$ , in eV) by Knudsen mass spectrometers. The HF/6-31G\* and MP4/6-31G\* calculations are cited from Ref.<sup>[36]</sup>. The experimental results are quoted from Ref.<sup>[38-44]</sup>

Cluster	Si <sub>2</sub>	Si <sub>3</sub>	Si <sub>4</sub>	Si <sub>5</sub>	Si <sub>6</sub>	Si <sub>7</sub>	Si <sub>8</sub>
$E_t$ (HF/6-31G*)	1.47	2.96	5.90	7.24	9.90	12.08	13.20
$E_t$ (MP4/6-31G*)	2.60	6.34	10.57	13.74	18.02	22.16	24.31
$E_t$ (FP-LMTO-MD)	4.05	9.97	15.81	21.30	26.97	32.61	36.34
$E_c$ (HF/6-31G*)	1.30	2.11	2.64	2.75	3.00	3.17	3.04
$E_c$ (FP-LMTO-MD)	2.02	3.32	3.95	4.26	4.50	4.66	4.54
$E_s$ (MP4/6-31G*)	1.56	2.54	3.17	3.30	3.60	3.80	3.65
$E_s$ (FP-LMTO-MD)	1.56	2.54	3.05	3.28	3.47	3.59	3.50
$E_{exp}$	1.66	2.44	2.99	3.24	3.43	3.53	3.54

Ga<sub>5</sub>As<sub>5</sub> cluster, Lou et al. presented two structures using Dmol method. Their binding energies were comparatively low. The ground-state energy structure is a tetracapped trigonal prism (TTP) structure<sup>[14]</sup>. Andreoni considered three structures<sup>[15]</sup>, while Yi considered one structure (a cube-based structure) using cp method<sup>[16]</sup>. Vasiliev et al. also studied the absorption spectra of two Ga<sub>5</sub>As<sub>5</sub> structures<sup>[12]</sup>. Zhao et al. also studied the Ga<sub>5</sub>As<sub>5</sub> cluster using the FP-LMTO-MD method<sup>[17]</sup>. They presented 27 stable structures for the neutral Ga<sub>5</sub>As<sub>5</sub> cluster. A two-capped cube structure was regarded as its ground-state structure. They also investigated 9 stable structures for neutral Ga<sub>6</sub>As<sub>6</sub> cluster<sup>[18]</sup>. Recently, Zhao et al. investigated the Ga<sub>8</sub>As<sub>8</sub> cluster<sup>[19]</sup>. 10 stable structures were obtained including the ring structure presented by Sun et al. We have studied Ga<sub>n</sub>As<sub>n</sub> (n=4, 5, 6) cluster ions in detail<sup>[20]</sup>. It's found that gallium atoms are more easily on capped atomic positions than arsenic atoms in the negative Ga<sub>n</sub>As<sub>n</sub> clusters. Among those studies, the calculations are confined to the neutral Ga<sub>n</sub>As<sub>n</sub> clusters. In fact, on charging the neutral clusters, their structures and properties change significantly.

In this paper, we investigate neutral and ionic Ga<sub>7</sub>As<sub>7</sub> cluster using FP-LMTO-MD method. Our main aim is to investigate its neutral ground state structure and the influence of charge on the neutral cluster.

## METHOD

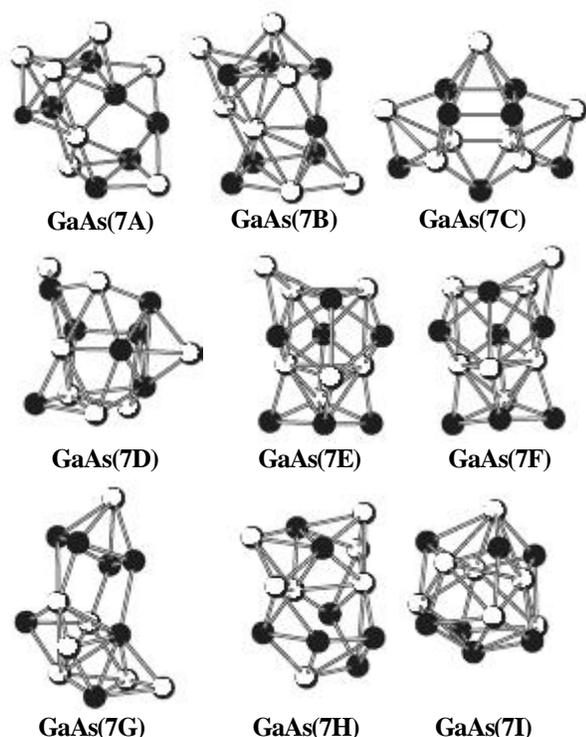
The full-potential linear-muffin-tin-orbital molecular-dynamics method (FP-LMTO-MD) is a self-consistent implementation of the Kohn–Sham equations in

the local density approximation<sup>[21-24]</sup>. During the molecular dynamics calculations, space is divided into two parts: non-overlapping muffin-tin (MT) spheres centered at the nuclei, and the remaining interstitial region. LMTOs are augmented Hankel functions inside the MT spheres, but not in the interstitial region<sup>[25-28]</sup>. Self-consistent calculations are carried out with convergence criteria of 10<sup>-5</sup> a.u. on the total energy and 10<sup>-3</sup> a.u. on the force. The details of how the molecular dynamics method can be performed are described in references<sup>[25-29]</sup>.

The method is suitable for investigating the geometrical and electronic structures of semiconductor. Our calculated results are in good agreement with other advanced methods<sup>[30-35]</sup>. In order to compare with those obtained by 6-31G\* and MP4/6-31G\* calculations<sup>[36&-37]</sup> and the experimental values<sup>[38-44]</sup>, our results for small Si<sub>2-8</sub> clusters are presented in TABLE 1. The calculated Si-Si bond lengths are expected to be reliable to within 1-2%<sup>[36]</sup>. In MP4/6-31G\* calculations, electron correlation effects were included by means of complete fourth order Moller–Plesset perturbation theory with the 6-31G\* basis set (MP4/6-31G\*). This theory has contributions from single, double, triple, and quadruple substitutions from the starting HF determinant and gives reliable binding energies for many calculations. However, comparison with the corresponding experimental values suggests that about 80-85 % of the true binding energy is obtained. A scale factor of 1.2 empirically corrects for the under-estimations, and yields binding energies in good agreement with experiment<sup>[37]</sup>. Using the FP-LMTO-MD method, we have also obtained the same ground state structures for Si<sub>2-8</sub> clusters. The geometrical parameters are in consistent with those obtained by other LDA methods. We haven't listed the values repeatedly here. Although the calculated cohesive energies (binding energy per atom) are larger than the corresponding experimental values, we find that a scale factor of 0.77 empirically corrects for the overestimations, and yields binding energies in excellent agreement with experiment values.

The use of such a single uniform scale factor does not bias the relative comparisons of the different clusters.

In this paper, we obtain a number of new isomers for Ga<sub>7</sub>As<sub>7</sub> cluster and its ions by means of the FP-



**Figure 1:** The stable structures with large binding energies for the  $\text{Ga}_7\text{As}_7$  cluster. White spheres and black spheres refer to Ga atom and As atom, respectively

**TABLE 2:** The relative energies ( $E_b$ , in eV) for the stable structures of  $\text{Ga}_7\text{As}_7$  clusters with respect to the lowest energy structures, which is set to 0 eV.  $E_g$ s (in eV) are the gaps between the highest-occupied molecular orbital and the lowest unoccupied molecular orbital (HOMO-LUMO)

Structure	GaAs(7A)	GaAs(7B)	GaAs(7C)	GaAs(7D)	GaAs(7E)
$E_b$	0.00	1.09	1.12	1.15	1.29
$E_g$	1.30	1.41	0.68	1.19	1.12
Structure	GaAs(7F)	GaAs(7G)	GaAs(7H)	GaAs(7I)	
$E_b$	1.30	1.35	1.42	1.43	
$E_g$	1.12	1.10	0.79	0.85	

LMTO-MD method. But, only some representative structures are presented below in order to stress the essentials of the cluster.

## STRUCTURES AND DISCUSSIONS

In order to search for the equilibrium structures of the  $\text{Ga}_7\text{As}_7$  cluster systemically, we need many initial geometric configurations as seeds. There are hundreds of possibilities of arranging two kinds of atoms to form a  $\text{Ga}_7\text{As}_7$  cluster. In our calculations, the main initial atomic configurations are set up by random selections of atomic positions in three-dimensional space. The separation of the atoms is confined in some range. In

addition, some initial ionic configurations are selected from the stable structures of its corresponding neutral cluster. A number of final stable structures are obtained after hundreds of initial geometrical configurations were relaxed. In some cases, the geometrical optimization of several different initial configurations is found to give one and the same structure. Because we adopt enough initial geometric configurations including almost all the arrangement of two kinds of atoms, we have good reason to say that the structure with the largest binding energy in this Letter is the ground state structure of the  $\text{Ga}_7\text{As}_7$  cluster.

For the  $\text{Ga}_7\text{As}_7$  cluster, we present 9 stable structures with large binding energies, which are shown in figure 1. Their relative energies ( $E_b$ ) with respect to the lowest energy structure and gaps  $E_g$  between the highest-occupied molecular orbital and the lowest unoccupied molecular orbital (HOMO-LUMO) are listed in TABLE 2.

The structures rank in the sequence of stability. Structure GaAs(7A) is the most stable among the 9 structures, while structure GaAs(7I) is the least. GaAs(7B) and GaAs(7C) structures are found to be 1.09 and 1.12 eV less stable than GaAs(7A), respectively. The energy difference between GaAs(7A) and GaAs(7I) structures is 1.43 eV. In the GaAs(7A) structure, one of the two-capped Ga atoms is put on the triangular face of the triangular prism, and the other on the rectangular face of the prism. In addition, there are two Ga atoms on capping atom positions, which have only three bonds. The second most stable structure GaAs(7B) has three capped Ga atoms, and the third most stable structure GaAs(7C) has two capped Ga atoms. In the other six stable structures, Ga atoms more easily occupy the capping positions compared with As atoms. According to their valence bonding characteristics, it is easy to understand the property. The electronic configurations of arsenic atom and gallium atom are  $4s^24p^3$ , and  $4s^24p^1$ , respectively. Arsenic atom can adopt  $sp$ ,  $sp^2$ ,  $sp^3$  or  $sp^3d^1$  hybrid, whereas gallium atom usually has only  $sp$  or  $sp^2$  hybrid. In addition, both of them can form  $\sigma$  bonds, or  $\pi$  bonds with neighbor atoms. Therefore, in the mixed clusters, the gallium atoms are easily on the capping atom positions, which need fewer bonds. The result agrees well with the discussions considered in Ref.<sup>[17-20]</sup>. The energy gaps in

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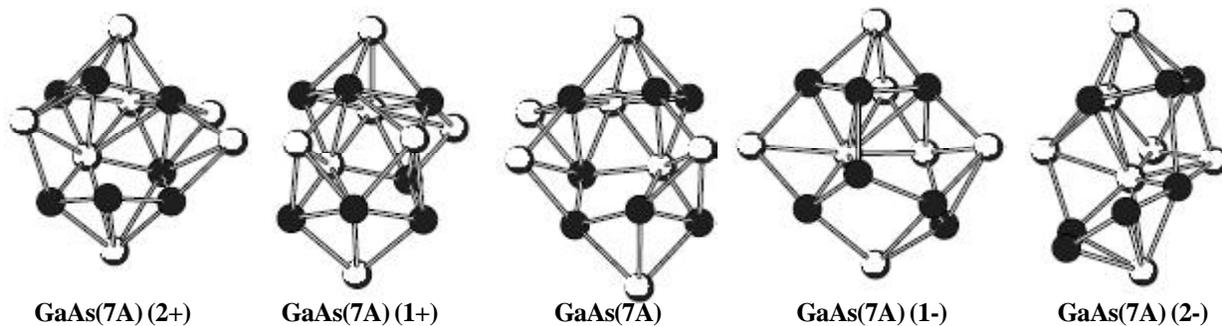


Figure 2: The stable structures of neutral GaAs(7A) and its corresponding positive and negative ions. White spheres and black spheres refer to Ga atom and As atom, respectively

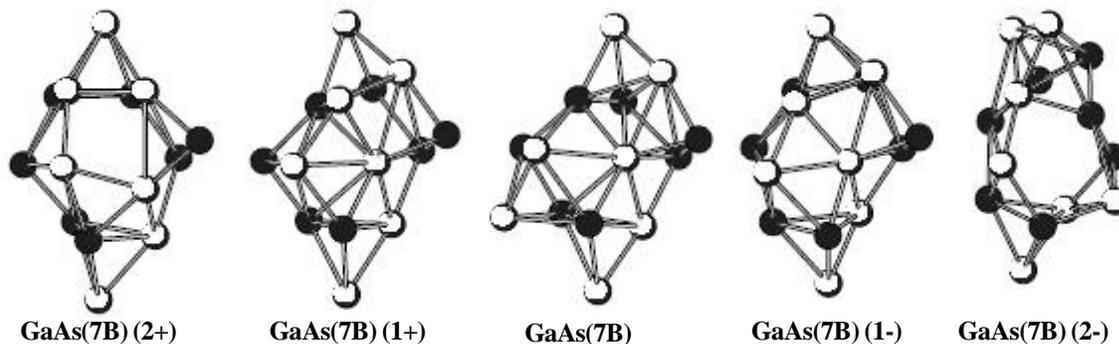


Figure 3: The stable structures of neutral GaAs(7B) and its corresponding positive and negative ions. White spheres and black spheres refer to Ga atom and As atom, respectively

TABLE 3: The HOMO-LUMO gaps of the ionic structures corresponding to the structure GaAs(7A)

Structure	GaAs(7A) (2+)	GaAs(7A) (1+)	GaAs(7A) (1-)	GaAs(7A) (2-)
Gap $E_g$	1.28	1.27	0.93	0.98

TABLE 4: The HOMO-LUMO gaps of the ionic structures corresponding to the structure GaAs(7B)

Structure	GaAs(7B) (2+)	GaAs(7B) (1+)	GaAs(7B) (1-)	GaAs(7B) (2-)
Gap $E_g$	1.29	1.10	0.77	1.04

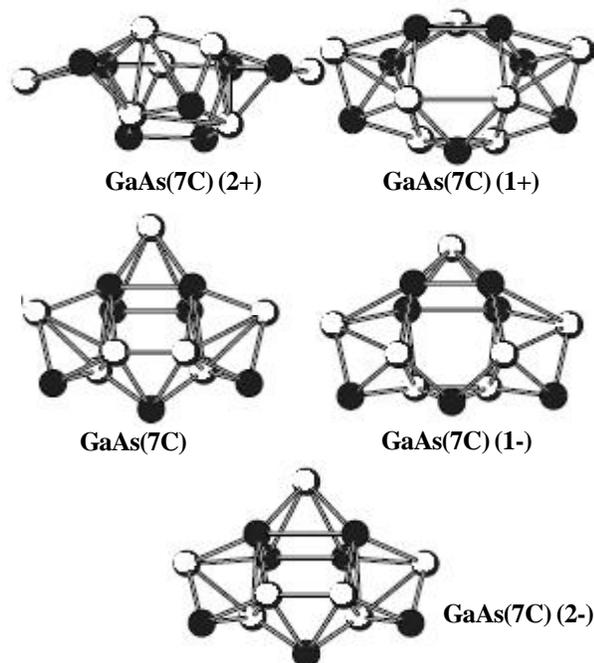
TABLE 2 indicate that most of the structures in figure 1 have a gap of larger than 1 eV. All the stable structures with fourteen atoms are singlet state because they have even number of valence electrons and furthermore all the electrons are paired together in their respective molecular orbitals.

Furthermore, we have also investigated some of the charged cluster structures. Figure 2 shows the stable ionic structures corresponding to neutral GaAs(7A) structure. Structure GaAs(7A) exhibits high stability compared with other structures. It is found from observing figure 1 that charging on the GaAs(7A) structure can change its geometric configuration significantly. In particular, two electrons added to, or removed from

the structure would result in severe structural distortion. Obviously, the structures GaAs(7A)(2-) and GaAs(7A)(2+) are completely different from its neutral structure GaAs(7A). The HOMO-LUMO gaps of the ionic structures are listed in TABLE 3. Because neutral GaAs(7A) is a singlet state structure, the gap of the positive ion GaAs(7A)(1+) is closer to 1.30 eV of its neutral GaAs(7A) structure. But the gap of the corresponding negative ion is only 0.93 eV.

Similarly, for structure GaAs(7B), adding or removing one electron does not change its basic geometrical configuration except for obvious structural distortion. Figure 3 shows its ionic structures. It is found from observing figure 3 that adding or taking away two electrons results in severe structural distortion like the structure GaAs(7A). Their gaps are presented in TABLE 4. Their change characteristic is expected.

For the third most stable structure GaAs(7C), its two negative ions have similar geometrical configurations. But removing electrons affects the geometrical structures more significantly than adding electrons. Structure GaAs(7C)(2+) in figure 4 differs from its corresponding neutral structure GaAs(7C). But two an-



**Figure 4:** The stable structures of neutral GaAs(7C) and its corresponding positive and negative ions. White spheres and black spheres refer to Ga atom and As atom, respectively

**TABLE 5:** The HOMO-LUMO gaps of the ionic structures corresponding to the structure GaAs(7C)

Structure	GaAs(7C) (2+)	GaAs(7C) (1+)	GaAs(7C) (1-)	GaAs(7C) (2-)
Gap $E_g$	1.57	0.69	0.88	0.99

ionic structures are similar to its neutral structure GaAs(7C) except for small local distortion. Furthermore, our calculated results suggest that removing more electrons from the neutral structures makes their stabilities decrease. Some structures would become unstable. But, adding four or five electrons to the neutral stable structures can still keep their stability even though the structural distortion become more and more severe. Obviously, the influence of charge on different structures is different. The ionic structures from the same neutral structure depend on the amount of charge. The gaps for GaAs(7C) and its ions are presented in TABLE 5.

According to the discussions above, it is found that charging the GaAs clusters would change their geometrical structures significantly. In fact, the Ga atom loses electron more easily than the As atom in such a mixed cluster. Therefore, it is expected that there is dipole moment in the neutral GaAs clusters. Removing electrons from, or adding electrons to the structures would

break original electrostatic equilibrium. In the ionic GaAs clusters, it is expected that the electrostatic force between the charged atoms and original dipole moment would change their geometrical structures. On other hand, the mixed clusters have lower symmetry due to different atomic radius and bonding characteristics between two atoms compared with the pure clusters such as  $Si_n$  and  $Ge_n$  clusters. Therefore, similar initial geometrical configurations with different atomic ranking probably change into different stable structures on structural optimization.

One point to mention here is that the values of the HOMO-LUMO gaps in the TABLES are not that large as expected. Most of the density functional theory based calculations probably underestimates the energy gaps<sup>[45]</sup>. But at the same time, it is found that the energy gaps depend their geometrical structures. The property is more obvious in the mixed  $Ga_mAs_n$  ( $m \neq n$ ) clusters. The HOMO-LUMO gaps of  $Ga_nAs_{10-n}$  ( $n=0-10$ ) clusters depend strongly on cluster composition<sup>[46]</sup>. Clusters with even number of Ga atoms generally have larger HOMO-LUMO gaps than those clusters with odd number of Ga atoms. It shows an even/odd alteration with the number of Ga atoms (or As atoms) in the cluster.

## CONCLUSIONS

We have investigated the  $Ga_7As_7$  cluster and the influence of charge on its stable structures using full-potential linear-muffin-tin-orbital molecular-dynamics (FP-LMTO-MD) method. Its lowest energy structure is different from its neighboring clusters. Our calculated results suggest that the gallium atoms in the mixed cluster are usually on capped atom places. On charging the stable structures of the  $Ga_7As_7$  cluster, they undergo severe structural distortion, which depends on the amount of charge and their structures.

## ACKNOWLEDGMENTS

A Foundation for the Author of National Excellent Doctoral Dissertation of PR China under Grant No. 200320, the National Natural Science Foundation under Grant No. 10674039, and the Natural Science Foundation of Zhejiang Province (Grant No. R405097) supported this work.

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