First-principles study of Ga_7As_7 ionic cluster and influence of multi-charge on its structure*

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This paper investigates the structures and stabilities of neutral Ga_7As_7 cluster and its ions in detail by using first-principles density functional theory. Many low energy structures of Ga_7As_7 cluster are found. It confirms that the ground state structure of neutral Ga_7As_7 cluster is a pentagonal prism with four face atoms like a basket structure, as reported by previous works. The ground state structures of positive Ga_7As_7 cluster ions are different from that of the neutral cluster. These investigations suggest that Ga atoms occupy the capping positions more easily than As atoms. Mulliken population analyses also show that Ga atoms can lose or obtain charge more easily than As atoms. It finds that the neutral Ga_7As_7 cluster can become more stable by gaining one or two additional electrons but further more electrons would cause the decrease of binding energy. The ionisation energy increases with the increase of the number of the removed electrons. These calculated results indicate that the net magnetic moment of the neutral Ga_7As_7 cluster is zero because all electrons are paired together in their respective molecular orbits. But for the ionic Ga_7As_7 cluster with odd number of electrons, the net magnetic moment is 1.0 μ_B due to an unpaired electron.

Keywords: cluster ions, ground-state structure, stability

PACC: 7115F, 7125W, 7320

1. Introduction

The semiconductor industry is a highly developing industry, which plays an important role in modern society. Gallium arsenide is one of the most common semiconductor materials. The unique properties of gallium arsenide make it ideal for some applications where silicon is ill–suited. It is necessary to investigate GaAs crystal and clusters theoretically[1,2] and experimentally.[3,4] For the mixed clusters with two elements like Ga and As, the theoretical investigation on them is comparatively difficult because of the computational difficulties associated with the structural and per-mutational variations even though they only contain a few atoms.[5] However, a great effort has been devoted to investigate the properties of the GaAs crystal and clusters because gallium arsenide finds most of its applications due to its superior optical and electrical properties.[6] In the past decades, some development on the study of GaAs clusters had been made both experimentally and theoretically.

Experimentally, the GaAs clusters and their ions were produced by using laser vaporisation followed by supersonic expansion.[7−9] Some theoretical studies on GaAs clusters have also been reported. For neutral Ga_4As_4 cluster, Mohammad *et al.* considered three structures with T_d, C_i, and D_{2d} symmetries using an *ab initio* molecular-orbital method.[10] Song *et al.* examined six structures using *ab initio* method.[11] They found that a rhombic prism structure was the ground-state structure for the Ga_4As_4 cluster.[11] Vasiliev *et al.* studied the absorption spectra of two Ga_4As_4 structures using a time-dependent density functional formalism within the local density approximation.[12] Zhao *et al.* performed calculation on the Ga_4As_4 cluster by using a full-potential linear-muffin-tin-orbital molecular-dynamics method.[13] A new edge-capped pentagonal bi-pyramid structure with the largest binding energy was found. The structure is much more stable than the C_i symmetry structure obtained by Mohammad.[13] For Ga_5As_5 cluster, Lou *et al.* presented two structures using Dmol method. Their binding energies were comparatively low. Its lowest energy structure is a tetra-capped trigonal prism structure.[14] Andreoni considered another three structures,[15] while Yi considered one structure (a cube-based structure) using the cp method.[16] Vasiliev *et al.* also studied the absorption spectra of two Ga_5As_5 structures.[12] Zhao *et al.* also

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studied the Ga_5As_5 cluster using the FP-LMTO-MD method. They presented 27 stable structures for the neutral Ga_5As_5 cluster. A two-capped cube structure was regarded as its most stable structure. They also investigated 9 stable structures for neutral Ga_6As_6 cluster.[17] Recently, Zhao *et al.* investigated Ga_8As_8 cluster.[18] Ten stable structures were obtained including the ring structure presented by Sun *et al.*[4] We have studied Ga_nAs_n (n = 4, 5, 6) cluster ions in detail.[19,20] It was found that gallium atoms were more easily in capped atomic positions than arsenic atoms in the negative Ga_nAs_n clusters. Among those studies, most calculations are confined to the neutral Ga_nAs_n clusters. In fact, charging the neutral clusters can change their structures and properties significantly.

For Ga_7As_7 cluster and its ions, many theoretical investigations have been reported. A family of fullerenelike Ga_nAs_n ($6 \leq n \leq 9$) clusters were found by using gradient-corrected density-functional theory and genetic global optimisation approach.[21] Karamanis *et al.* studied equilibrium structures of Ga_nAs_n (n = 6–9) clusters and their relative energy by using the B3LYP/cc-pVTZ-PP method.[22] They also studied the polarisability per atom evolution versus the cluster size for Ga_nAs_n (n = 2–9) by using Hartree–Fock theory and second order Møller–Plesset perturbation theory (MP2). Gutsev *et al.* computed the electronic and geometrical structures of neutral, negatively charged and positively charged Ga_nAs_n (n = 2–15) clusters by using density functional theory with generalised gradient approximation.[23] It was found that the ground-state geometries of $Ga_nAs_n^-$ and/or $Ga_nAs_n^+$ were different from the corresponding neutral one except for n = 7, 9, 12, 14, and 15, where the neutral cluster and its ions have similar structures. They also studied the electronic and geometrical structures of the lowest triplet states of Ga_nAs_n (n = 2–16).[24] In all these papers, the lowest-energy structure of Ga_7As_7 cluster is a basket-like structure.

In this paper, we investigate neutral Ga_7As_7 cluster by using the first-principles density functional theory. Our calculations confirmed that the ground state reported by previous works is the lowest state of Ga_7As_7 neutral cluster.[21−24] Furthermore, we attach importance to the calculation of ionic Ga_7As_7 cluster. We investigated the ground state structure of ionic Ga_7As_7 cluster and the influence of multi-charge on the cluster.

2. Method

We studied the neutral and ionic Ga_7As_7 cluster by using the first-principles density functional theory.[25] Our calculations were performed with the generalised gradient approximation (GGA) by means of the Becke–Perdew functional,[26] which uses Becke's gradient correction to the local expression for the exchange energy and Perdew's gradient correction to the local expression of the correlation energy,[27] as implemented in the Amsterdam density functional (ADF) codes. In the ADF calculations, molecular orbits were expanded by using a large, un-contracted set of Slater-type orbits: TZ2P.[28] The TZ2P basis is an all-electron basis of triple-ζ quality, augmented by two sets of polarisation functions. The frozen-core approximation for the inner-core electrons was used. The orbits up to 2p for silicon and 2p for aluminum were kept frozen. An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular density and to represent the Coulomb and exchange potentials accurately in each self-consistent field (SCF) cycle. The SCF was converged to a value of 10^{-7}. Frequencies were computed using numerical differentiation of gradients computed in slightly displaced geometries.

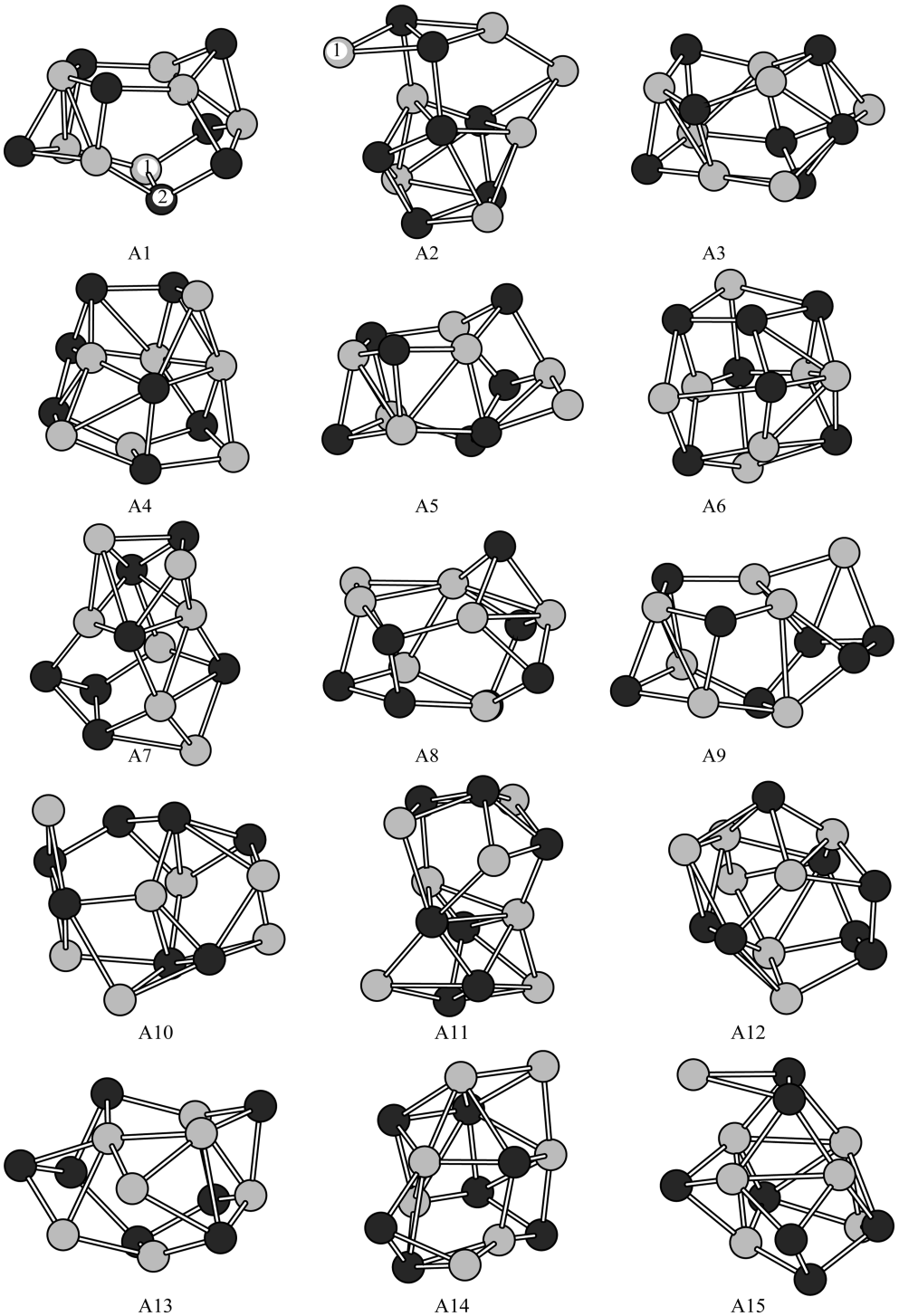
3. Structures and discussion

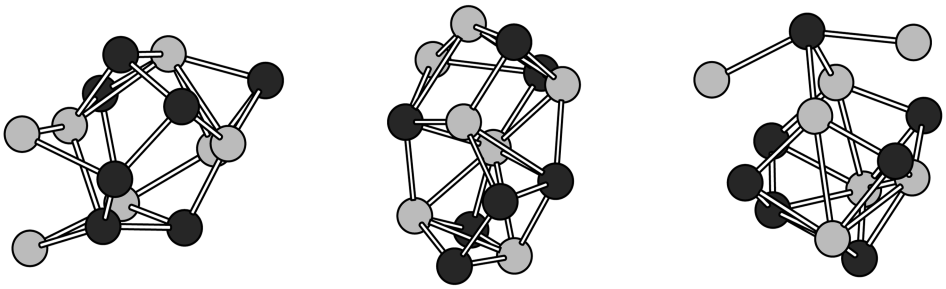
In order to search for the equilibrium structures of Ga_7As_7 cluster systemically, we need many initial geometric configurations as seeds. In the progress of searching the ground state structure for Ga_7As_7 cluster, a huge number of initial atomic configurations are produced automatically within a three-dimensional box, or a cage, or a ball in real space in a random way. The separations of Ga–Ga, Ga–As and As–As atoms are confined within the range from 2.5 to 3.8 Å (1 Å = 0.1 nm). This confinement prevents the initial geometries from being too compressed, or too relaxed. 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 thousands of initial geometrical configurations are relaxed. In some cases, the geometrical optimisation of several different initial configurations gives one same structure. Because we have adopted enough initial geometric configurations including almost all the arrangement of the two kinds of atoms, we have good reason to say that the structure with

the largest binding energy in this paper is the ground state structure of Ga_7As_7 cluster.

For Ga_7As_7 cluster, its ground-state structure is a pentagonal prism with four face atoms like a basket structure, as reported by the previous works.[21−24] The ground-state structure is shown as A1 in Fig. 1. In addition, we also depicted 17 other stable structures with large binding energies in Fig. 1.

The total binding energies (E_b,) for the stable structures in Fig. 1 and their corresponding gaps (E_g) between the highest-occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are listed in Table 1.





A16 A17 A18

Fig. 1. The stable structures with large binding energies for the Ga_7As_7 cluster. White spheres and black spheres refer to Ga atom and As atom, respectively. The As–As, Ga–As and Ga–Ga bonds are restricted to 3.4, 3.5 and 3.2 Å, respectively.

Table 1. The total binding energies (E_b, in eV) for the stable structures in Fig. 1 and their corresponding gaps (E_g, in eV) between the HOMO and the LUMO.

structure	A1	A2	A3	A4	A5	A6	A7	A8	A9
E_b	45.54	45.08	45.02	45.00	44.97	44.85	44.84	44.84	44.84
E_g	1.11	1.61	1.22	1.40	0.87	0.94	1.10	1.00	0.98
structure	A10	A11	A12	A13	A14	A15	A16	A17	A18
E_b	44.83	44.81	44.80	44.78	44.75	44.74	44.73	44.72	44.72
E_g	1.10	1.15	1.02	1.22	1.01	0.91	1.37	0.87	0.62

The 18 structures of the Ga_7As_7 cluster in Fig. 1 are arranged in the order of stability. Structure A1 is more stable than structure A18. The A1 is the most stable structure among all the structures. It is a pentagonal prism with four face atoms like a basket structure. We can obtain another structure A1' (not shown in Fig. 1) by exchanging atom 1 (gallium atom) and atom 2 (arsenide atom) in structure A1. The A1' has the same stability as A1. The energy difference between A1 and A2 is only 0.46 eV. The A2 seems not to be a very compressed structure. It consists of two subunits of Ga_2As_2 and Ga_5As_5. One is a planar quadrangle; the other is a polyhedron with an edge capping atom. We can see from the picture that the two subunits are connected by three bonds. The two substructures in A2 are both stable because the computation of frequencies on them shows no imaginary frequencies. Structure A3 is like A1 and its energy is 0.52 eV above A1. Structure A4 is regarded as a like-cage structure. Some structures are found to be almost isoenergetic. For example, structures A4 and A5 are nearly energy degenerate within the accuracy of our calculations. Another five structures A6, A7, A8, A9 and A10 are nearly energy degenerate too. In order to confirm the stability of the structures in Fig. 1, we also calculated the frequencies on these structures and found no imaginary frequencies.

We can see that Ga atoms occupy the capping positions more easily than As atoms by observing the structures in Fig. 1. According to their valence bonding characteristics, this property is easily understood. 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 σ bonds, or π bonds with neighbouring atoms. Therefore, in the mixed clusters, the gallium atoms are easily in the capping positions, which need fewer bonds. The result agrees well with the discussions in Refs. [17]–[20]. From Table 1, we can see that A1 has an energy gap E_g of 1.11 eV. All the gaps for the structures are in the neighbourhood of 1.0 eV. All the stable structures with fourteen atoms in Fig. 1 are singlet state because they have even number of valence electrons and furthermore all the electrons are paired together in their respective molecular orbits according to Mulliken population analyses.

We choose three different structures A1, A2, and A4, and investigate the influence of charge on these cluster structures. In Figs. 2–4, we present the stable ionic structures corresponding to neutral structures A1, A2, and A4. We can find by observing Figs. 2–4 that charging the structures can change their geometric configurations significantly. In particular, two or more electrons removed from the structures would

result in severe structural distortion. Different structures have different structural distortion. For example, the effect caused by removal of electrons in structure A2 and A4 is larger than that in other structures. In contrast, adding electrons would have less impact on the structures.

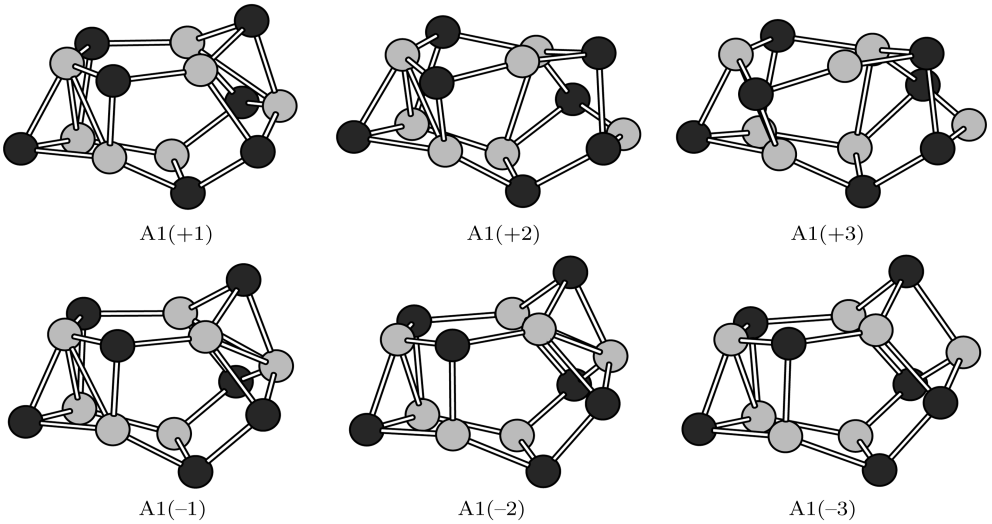


Fig. 2. The stable structures of positive and negative ions corresponding to neutral structure A1. White spheres and black spheres refer to Ga atom and As atom, respectively.

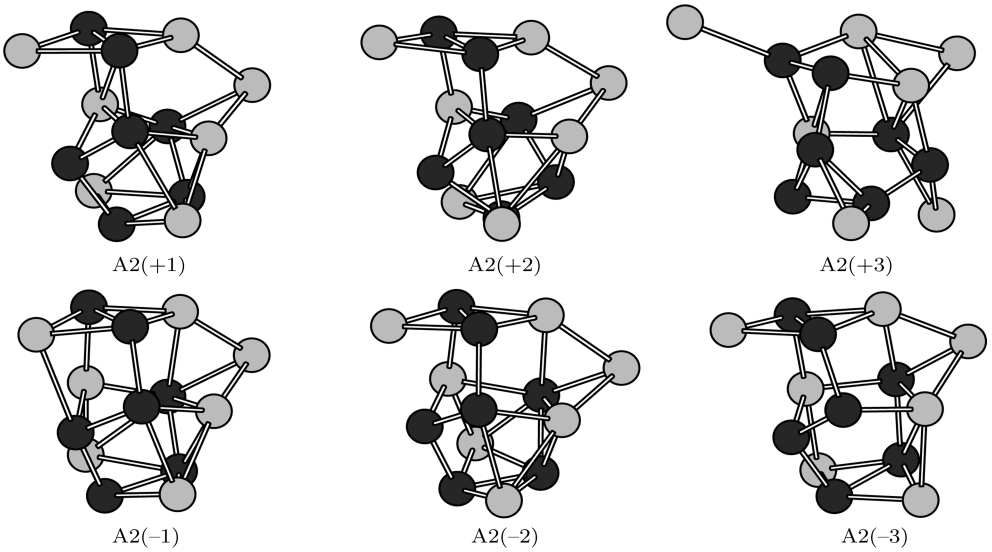
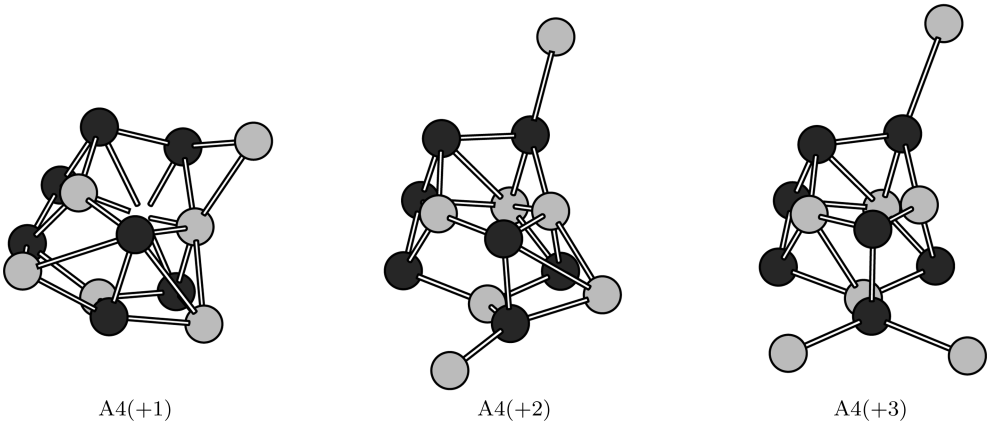
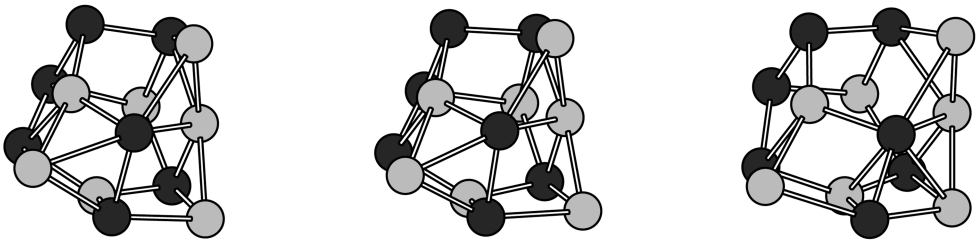


Fig. 3. The stable structures of positive and negative ions corresponding to neutral structure A2. White spheres and black spheres refer to Ga atom and As atom, respectively.





A4(–1) A4(–2) A4(–3)

Fig. 4. The stable structures of positive and negative ions corresponding to neutral structure A4. White spheres and black spheres refer to Ga atom and As atom, respectively.

After analysing the calculated results of the ionic structures, we found the following properties. First, adding or removing one electron does not change the basic geometrical configuration of the Ga_7As_7 cluster but cause some structural distortion. Secondly, the first electronic affinity (EA) for A1 is 2.83 eV (see Table 2), which is largest among the structures. And the first EAs for other structures are also larger than 2.0 eV. The first EA is the amount of energy released when a cluster obtains an electron from its neutral state. Positive first EA suggests that the cluster has a tendency to gain an electron under usual conditions, as it is energetically favourable to do so. When the Ga_7As_7 cluster gain two electrons from their neutral states, the amount of energy released (the second EA) would decrease in comparison with the first electronic affinity. But they are still positive. The second EA for A1 is 2.63 eV. This suggests that the cluster has the ability to gain two electrons. However, it is difficult for the Ga_7As_7 cluster to obtain three electrons or more because the $Ga_7As_7^{-3}$ ions become less stable than their corresponding neutrals. Thirdly, the first ionisation potentials (IPs) of the Ga_7As_7 cluster with larger binding energies are in the range from 6.0 eV to 6.8 eV. The IP of A1 is 6.82 eV (see Table 2). The ionisation energy would increase as more electrons are removed. Fourthly, after the Ga_7As_7 cluster is charged, the energy ordering among different structures would be changed. For example, ionic structures A2(+1), A2(+2) and A2(+3) are more stable than A1(+1), A1(+2) and A1(+3), respectively. The A1(+1), A1(+2) and A1(+3) are not the ground state structures of multi-charged positive ionic Ga_7As_7 cluster. Similarly, A4(+2) is more stable than A2(+2). The ground state structures of $Ga_7As_7^{+1}$, $Ga_7As_7^{+2}$, and $Ga_7As_7^{+3}$ are A2(+1), A4(+2) and A2(+3), respectively. In fact, 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 charged atoms would change their geometrical structures.

Table 2. The binding energies for the positive and negative ionic structures corresponding to neutral structures A1, A2 and A4.

charge / structure	+3e	+2e	+1e	0	−1e	−2e	−3e
A1	15.38	28.92	38.72	45.54	48.37	48.17	44.47
A2	18.31	29.80	38.81	45.08	47.34	46.84	43.00
A4	17.62	29.83	38.69	45.00	47.30	46.78	43.08

According to Mulliken population analyses, it is found that Ga atoms lose or obtain charge more easily than As atoms in Ga_7As_7 cluster. We take the structure A2 as an example. The Ga atom labeled with Arabic numeral 1 in the neutral structure A2 has a charge of 0.20 e, while it possesses charge of 0.75 e and –0.23 e in the ionic structures A2(+3) and A2(-3), respectively. The charge difference is around 1.0 e. The total charge difference between A2(+3) and A2(-3) with 14 atoms is 6.0 e. The Ga atom labeled with Arabic numeral 1 accounts for one-sixth of the charge difference. Similarly, other Ga atoms can also lose or obtain charge easily. Therefore, it is easy to understand why some edge atoms or atop atoms are usually

Ga atoms in the positive multiply charged GaAs clusters like A4(+2) and A4(+3). In fact, in the neutral structure A2, most of Ga atoms lose charge which is transferred to As atoms. Of course, the Ga atoms in different positions have different charge. Because of charge transfer and lower symmetry, the Ga_7As_7 isomers become polarised molecules. Therefore, there are either large or small dipole moments in the Ga_7As_7 isomers. The dipole moments for neutral structures A1, A2 and A3 in Fig. 1 are 0.96 1.01, and 3.57 Debye, respectively.

When carrying out structural optimisation, we have also investigated the possible magnetism of the Ga_7As_7 cluster. For the neutral isomers, all the calculated total magnetic moment is zero. This suggests that the neutral Ga_7As_7 cluster is not magnetic because all the electrons are paired together in their respective molecular orbits. But, for the ionic Ga_7As_7 cluster with odd number of electrons, their total magnetic moment is 1.0 μ_B. Here we define the magnetic moment as the difference between the electronic occupation numbers of spin-up and spin-down (in Bohr magnetron unit μ_B). One unpaired electron results in net magnetic moment of 1.0 μ_B.

4. Conclusions

We investigated the Ga_7As_7 ionic cluster and the influence of charge on its stable structures by using the first-principles density functional theory. The ionic structures are different from the neutral structures. Our results suggest that gallium atoms in the mixed cluster occupy the capped atom positions more easily. Charging the stable structures of the Ga_7As_7 cluster can cause structural distortion depending on the amount of charge and their structures. One or two additional electrons could enhance the stability of the Ga_7As_7 cluster, but furthermore electrons would reduce its binding energy. On the other hand, removal of more electrons always needs more energy. Our results also show that the net magnetic moment of the neutral Ga_7As_7 cluster is zero because of a closed shell electronic structure with a doubly occupied orbital. However, the ionic Ga_7As_7 cluster with an odd number of electrons has a net magnetic moment of 1.0 μ_B due to one unpaired electron.

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