**Composition Dependence of Structural and Electronic Properties of GaMn Clusters from First Principles**

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I. INTRODUCTION

Due to continued downscaling of electronic devices, it is expected that the building blocks of future electronic devices will be quantum dots and nanoclusters. Intensive studies have been devoted to clusters of various elements. Clusters also exhibit interesting size-dependent properties which mark the transition between molecular and solid-state regimes. With the advancement of experimental techniques, both pure and mixed clusters of different sizes, compositions, and elements can be produced and characterized now. Together with the rapid advancement in spectroscopic methods, theoretical techniques, and computational resources, great interest in the field of cluster science has been generated. In recent years, numerous experimental and theoretical investigations on clusters have been carried out. These studies have shed light on the structures, stabilities, reactivities, and chemical bondings in such clusters. They have helped in building a better understanding on the size evolution of geometric and electronic structures from molecular clusters to the condensed matter.

Clusters are interesting also because of their unique property of high surface to volume ratio. The chemical and physical properties of a solid-state surface is determined by the atomic structure of the surface and certain atomic sites are observed to be more reactive than others. Due to the importance of the surface effect, cluster science plays a very important role in the investigation of the correlation between the reactivity and structure of the local atomic sites. In this respect, clusters consisting of more than one element have richer properties and are more interesting than clusters of pure elements. As a matter of fact, physical properties of heterogeneous clusters can be tuned by composition, in addition to the size, which make them very attractive. Composition-tunable nanocrystals have already found applications in many areas. For example, by increasing the Zn content in ZnCd$_{1-x}$Se and ZnCd$_{1-x}$S nanocrystals, a systematic blueshift in emission wavelength can be produced, resulting in composition-tunable emission across much of the visible spectrum, which found applications in biological detection and imaging.

Among the mixed clusters of semiconductors, GaAs clusters have been the focus of many investigations due to their importance in the manufacturing of microelectronic devices. There have been experimental evidences showing that most of the physical and chemical properties of GaAs clusters converge very rapidly with their size. It becomes possible to employ molecular modeling to study the bulk and surface effects with the evolution of cluster size. This unique feature makes the study of small GaAs clusters particularly interesting in cluster science.

However, progress in theoretical studies on heterogeneous clusters, particularly on composition-dependent properties, has been slow. This is mainly due to computational difficulties arising from the larger number of structural and permutation isomers formed due to the presence of more than one element. On one hand, accurate quantum mechanical calculations are necessary to make reliable predictions on the properties of these clusters. On the other hand, the amount of computational work is enormous in order to find all the stable isomers for a given cluster size and composition. As a result, most of the theoretical studies have focused on clusters of a small number of atoms or limited compositions. Recently, Zhao et al. studied fullerene-like Ga$_m$As$_n$ clusters...
for $6 \geq n \geq 9$. However, until now, the important issue of composition dependence of the physical properties of such clusters largely has not been addressed.

In this paper, we report results of our first-principles studies on the structural and electronic properties of Ga$_n$As$_m$ clusters. We focus on the composition dependence of these properties. Calculations were carried out for clusters formed by even number of atoms and for cluster size up to 16 atoms. Clusters with odd number of atoms were found less stable and are not included in the present study. Even though the physical properties of the clusters depend sensitively on the structural details of the clusters and show large variation with composition, clear trends emerge as the size of the cluster increases. In addition, we compare the performance of pseudopotential–plane-wave method with that of all electron calculations and demonstrate that with sufficient accuracy the more efficient pseudopotential–plane-wave method can be used to make a very reasonable prediction for structural stability and physical properties of such clusters.

II. COMPUTATION METHODS

Among different first-principles approaches, it is generally believed that, with appropriate basis set and exchange-correlation functional, all electron approaches such as the GAUSSIAN program$^{24,25}$ can produce physical properties of molecules or clusters which are often in good agreement with experimental results. GAUSSIAN is based on a linear combination of atomic orbitals. On the other hand, a pseudopotential–plane-wave method, particularly with the ultrasoft pseudopotential,$^{26}$ is more efficient for relatively large clusters. Ideally, it would be desirable to combine the efficiency of the pseudopotential and plane-wave method and accuracy of an all electron calculation. Motivated by this, we used both methods in the present study of the Ga$_n$As$_m$ clusters. Their performance in cluster property prediction is evaluated.

The all electron calculations were carried out using the GAUSSIAN program with the 6-311+G(d) all electron basis set and the B3LYP hybrid exchange-correlation functional.$^{27,28}$ The following convergence criteria were used in our calculations, 0.00045 a.u./bohr (0.023 eV/Å) for the maximum force, 0.0003 a.u./bohr (0.015 eV/Å) for the root-mean-square force, 0.0018 a.u. (0.001 Å) for the maximum displacement, and 0.0012 a.u. (0.0006 Å) for the root-mean-square displacement, respectively.

The pseudopotential–plane-wave calculations were performed using the Vienna $ab$ initio simulation package (VASP),$^{29}$ with the ultrasoft pseudopotential$^{26}$ for electron-ion interactions and the local density approximation$^{30}$ (LDA) for the exchange-correlation functional. Spin-polarized calculations were done for charged clusters.$^{31}$ The cutoff energy for the plane-wave expansion was taken to be 10.6 Ry. All structures, including the charged clusters, were fully optimized using the conjugate gradient method until the Hellmann-Feynman forces were smaller than 0.01 eV/Å. The clusters were placed in a large simple cubic cell of 15 Å size. For charged clusters, a uniform neutralizing background was assumed and the geometries of the clusters were optimized starting with the ground state structures of the corresponding neutral clusters. The background charge introduces an additional shift in the calculated total energy.$^{32,33}$ Since the focus of the present calculations is composition dependence of properties of the Ga$_n$As$_m$ clusters, the calculated total energies of the charged clusters are not corrected.

In the following discussion, AE-B3LYP will be used to denote the all electron calculations with the B3LYP hybrid exchange-correlation functional, and PP-LDA will be used to indicate the pseudopotential calculation with the LDA exchange-correlation functional. Due to the different exchange-correlation functionals used in the calculations, the discrepancy in a property calculated using the two different methods is partly due to the methods and partly due to the exchange-correlation functional. Unless otherwise indicated, we refer to both contributions whenever the PP-LDA results and AE-B3LYP results are compared.

III. RESULTS AND DISCUSSION

A. Stability prediction by different methods

To quantitatively compare the results of AE-B3LYP and PP-LDA, we considered a series of Ga$_3$As$_2$ clusters given in Ref. 34. Each of the nine structures was fully relaxed separately using the two different methods and their energies were calculated. As expected, results obtained with relatively low accuracies in the calculations (smaller basis set and less stringent convergence criteria in GAUSSIAN calculations, and smaller cutoff energy in VASP calculations) were found inconsistent. However, as the accuracies of the calculations improved and when they reached those given in the last section, results obtained using the two different methods showed essentially the same trends. The calculated total

![Graph](https://example.com/graph.png)
binding energies of the various isomers of Ga$_2$As$_2$ cluster are shown in Fig. 1. The only three-dimensional structure, the tetrahedron structure, transformed to the rhombus structure during geometry optimization. It is clear that both AE-B3LYP and PP-LDA predict the same binding energy trend for the Ga$_2$As$_2$ clusters. Even though the binding energies calculated using PP-LDA are consistently larger than the values given by AE-B3LYP, both methods predict the same relative stability of the various isomers. This is encouraging as one can use the more efficient pseudopotential–plane-wave method to optimize the large number of isomers for a given cluster size and composition and determine the most stable structures. Once the ground state geometry is determined, the all electron method can be used to predict its properties. This is the approach we adopted in this work. For each size and composition of the Ga$_m$As$_n$ cluster, we started with a large number of isomers obtained by permutation of atoms based on possible structures. VASP was used to optimize the structures of these isomers. The structure with the lowest total energy was chosen as the ground state structure. GAUSSIAN was used to further relax the structure optimized by VASP and calculate its physical properties. This was done for neutral clusters up to 8 atoms and for charged clusters up to 8 atoms. For larger clusters, the all electron calculation is still very time consuming and they were only studied using the pseudopotential–plane-wave method.

B. Property prediction by different methods

We also compared the properties of the Ga$_m$As$_n$ clusters predicted by AE-B3LYP and PP-LDA methods. Again, results obtained with sufficient accuracy show very good correlation. Figure 2 shows the binding energy per atom [Fig. 2(a)], the gap between the highest occupied molecular orbital (HOMO) energy level and the lowest unoccupied molecular orbital (LUMO) energy level [Fig. 2(b)], the electron affinity [Fig. 2(c)], and the ionization potential [Fig. 2(d)] of the Ga$_m$As$_n$ clusters calculated using both methods. It is clear that for all these physical properties, both methods predict the same trends of the composition dependence of the physical properties. However, there is a systematic difference between the results of AE-B3LYP and PP-LDA.

In the case of the binding energy, the PP-LDA values are larger than those predicted by AE-B3LYP by about 0.87 eV on the average. This difference increases gradually with the ratio of Ga to As atoms in the cluster, from 0.78 eV in the pure As cluster to 0.96 in the pure Ga cluster. The difference is mainly due to the well known problem of LDA which
overestimates the binding energy.\textsuperscript{35} The HOMO-LUMO gaps calculated using the two different methods also show the same trend, even though the results obtained by PP-LDA are consistently smaller than the corresponding values obtained by AE-B3LYP. This is also due to a well known problem of LDA which underestimates the energy gaps. The difference between the results obtained by the two different methods ranges from 0.73 to 1.23 eV.

As seen from Figs. 2(c) and 2(d), the variations in the electron affinity and the ionization energy as functions of Ga to As atom ratio obtained by AE-B3LYP are essentially reproduced by PP-LDA. However, the electron affinity obtained using PP-LDA is larger by 0.77–1.12 eV, while the ionization energy is smaller by 1.12–1.74 eV than the results of AE-B3LYP. This shows that the LDA overbinding is more severe for negatively charged clusters than clusters carrying positive charges. However, we wish to point out that these results were obtained from the uncorrected PP-LDA total energies of charged clusters.

The shortcomings of the LDA can be improved by using alternate exchange-correlation functionals such as the generalized gradient approximation, or certain special treatment.\textsuperscript{35} Such corrections are expected to improve the agreement with the results obtained from the AE-B3LYP method. In the present work, however, we focus on the trends in the composition dependence of the properties of Ga\textsubscript{m}As\textsubscript{n} clusters, rather than on their absolute values. Despite these systematic differences, our results demonstrate that PP-LDA can give a reliable description on the composition dependence of the physical properties of the binary Ga\textsubscript{m}As\textsubscript{n} clusters, provided that the accuracy of the calculation is sufficient.

C. Structures of Ga\textsubscript{m}As\textsubscript{n} clusters

We have investigated the structures and properties of the Ga\textsubscript{m}As\textsubscript{n} clusters for \(m+n=2, 4, 6, \ldots, 16\). For each cluster size and composition, we started with a large number of possible structures which were obtained by gradually adding atoms to smaller clusters and by exchanging some of the Ga and As atoms in a given structure. PP-LDA, with the conjugate gradient algorithm, was used to optimize the structures. Structures of the most stable configuration for each composition and size are shown in Fig. 3. Compared to metal clusters and semiconductor clusters of single element, most of the Ga\textsubscript{m}As\textsubscript{n} clusters have irregular shapes and exhibit low symmetries due to the preference for \(sp^3\) bonding and different electronegativities of Ga and As atoms. In these clusters, the As–As bond length is relatively short (2.57–2.68 Å) and it varies little with composition. The Ga–As bond is also short in As-rich clusters and it increases gradually with Ga to As ratio, varying in the range of 2.50–3.03 Å. In contrast, the Ga–Ga bond is generally longer (2.71–3.17 Å) and it decreases slightly with Ga to As ratio. In most of the clusters, Ga atoms tend to have a higher average coordination number compared to As atoms. In relatively large clusters (12, 14, and 16 atoms), the average coordination number of As atoms remains 3 for most of the As-rich clusters and it increases in Ga-rich clusters, while that of Ga atoms increases with Ga to As ratio and shows more fluctuations. More details of the optimized structures of the Ga\textsubscript{m}As\textsubscript{n} can be found in Ref. 36.

Ga\textsubscript{m}, As\textsubscript{n}, and Ga\textsubscript{m}As\textsubscript{n} clusters as well as the limited non-stoichiometric GaAs clusters (Ga\textsubscript{m}As\textsubscript{n}, \(n \neq m\)) were studied by a number of authors.\textsuperscript{14,37–46} Some of the optimized structures obtained in the present work are similar to those of the earlier studies. For example, the distorted prism structure of Ga\textsubscript{m} and the structure of Ga\textsubscript{8} are the same as those obtained by Gong and Tosatti.\textsuperscript{37} The prism angle of 76.9° for Ga\textsubscript{8} and the nearest neighbor and the next nearest neighbor distances of 2.44 and 2.62 Å in the structure of Ga\textsubscript{8} are also in good agreement with those of the earlier study. Structures of Ga\textsubscript{3}As\textsubscript{4} (square bipyramid), Ga\textsubscript{5}As\textsubscript{3} (face-capped trigonal bipyramid), and Ga\textsubscript{3}As\textsubscript{5} (edge-capped trigonal bipyramid) are also similar to those obtained by Lou \textit{et al.}\textsuperscript{38} Al-Laham and Raghavachari\textsuperscript{39} also obtained the same Ga-capped trigonal bipyramid structure for Ga\textsubscript{3}As\textsubscript{3}. Another stable structure, the edge-capped trigonal bipyramid, was reported in a number of studies.\textsuperscript{14,41,42} However, according to Song \textit{et al.}, this structure is less stable than the face-capped trigonal bipyramid structure.\textsuperscript{43} The optimized structure of Ga\textsubscript{4}As\textsubscript{4}, a distorted cubic structure, is in good agreement with that obtained in a more recent study\textsuperscript{44} which, however, is different from that obtained in earlier studies.\textsuperscript{38,40,42,44} As the size of the cluster increases, the structures become very complicated and there is less agreement between structures obtained in different studies.\textsuperscript{14,21,38,42}

D. Composition-dependent properties of Ga\textsubscript{m}As\textsubscript{n} clusters

For property prediction, the PP-LDA optimized structure was further optimized using AE-B3LYP for small clusters (\(m+n=2, 4, 6, \text{ and } 8\)). As illustrated in Sec. III A, further structural optimization does not change the relative stability of the isomers, but it is necessary in order to make a meaningful property prediction by AE-B3LYP. Further structural optimization by GAUSSIAN generally resulted in very little changes in the structures of the clusters. For relatively larger clusters (\(m+n=14 \text{ and } 16\)), PP-LDA was directly used to calculate the properties of the clusters. For clusters of 10 and 12 atoms, only the neutral clusters were further optimized using GAUSSIAN. Therefore, the binding energy and HOMO–LUMO gap were calculated using AE-B3LYP on GAUSSIAN optimized structures, and the electron affinity and ionization energy were calculated using PP-LDA for these clusters.

The calculated binding energies for all the clusters studied here are shown in Fig. 4(a). As mentioned above, the binding energies of smaller clusters (for \(m+n=12\)) were obtained using AE-B3LYP, while those of larger sizes were calculated using PP-LDA. The PP-LDA results are overestimated due to reasons mentioned above. The binding energy decreases with the Ga to As ratio, or composition, \(x=m/n(m+n)\), indicating that for clusters of the same size, As-rich clusters are more stable than Ga-rich clusters. The higher binding energy of As-rich clusters could be attributed to shorter and stronger As–As bonds. It is noted that the binding energy of the As dimer is 3.6 eV while that of a Ga dimer is less than 0.5 eV. The As dimer bond (2.1 Å) is also shorter than the Ga dimer bond (2.68 Å).

We can also see that the binding energy increases with the size of the cluster. However, the binding energies of the sto-
ichiometric Ga\textsubscript{n}As\textsubscript{m} clusters are still much smaller than that of bulk GaAs. The binding energies of Ga\textsubscript{7}As\textsubscript{7} and Ga\textsubscript{8}As\textsubscript{8} are 4.07 and 4.10 eV/atom, respectively, while the binding energy of bulk GaAs obtained using a similar calculation is 4.84 eV/atom.

It is interesting to note that for relatively larger clusters, the binding energy versus composition curve shows a downward bending around the composition of 50\% Ga atoms. This indicates that the mixed binary clusters are energetically favored compared to two pure metal clusters formed by the same numbers of atoms, particularly for equal numbers of Ga and As atoms. That is, considering \( n \) Ga atoms and \( n \) As atoms, the binary cluster Ga\textsubscript{n}As\textsubscript{n} is energetically favored compared to two metal clusters, Ga\textsubscript{n} and As\textsubscript{n}, because the total binding energy of the binary cluster, \( E_{Ga_nAs_n} = 2nE_b(x = 0.5) \), where \( E_b(x) \) is the normalized (per atom) composition-dependent binding energy given in Fig. 4(a), is larger than the sum of the total binding energies of the two metal clusters, \( E_{Ga_n} + E_{As_n} = n[E_b(x = 0) + E_b(x = 1)] \), as suggested by the results shown in Fig. 4(a). This difference is 3.27 eV for the 16-atom cluster based on the binding energy curve for the 16-atom cluster or 5.72 eV if the actual binding
energies of the eight-atom pure metal clusters are used. The calculated energy gap between the HOMO and the LUMO, electron affinity, and ionization energy for various clusters considered are shown in Figs. 4. As these properties are more sensitive to the detailed structures of the cluster, they show larger variations in their composition dependence, particularly for small clusters.

Apart from clusters of a few atoms, the HOMO-LUMO gap shows a general decreasing trend as a function of the composition, with As-rich clusters having large energy gaps compared to Ga-rich clusters of the same size. The overall large HOMO-LUMO energy gap relative to bulk GaAs is due to quantum confinement and implies higher resistance against charge excitation from the HOMO to the LUMO energy level.

The electron affinity and ionization energy were calculated by adding and removing an electron from the cluster and then taking the difference in total energies of the charged system and the neutral cluster. The structures of the charged clusters were fully relaxed before their total energies were calculated. The calculated electron affinity and ionization energy also show larger fluctuations, particularly for clusters of small sizes. However, we can still see a slowly increasing trend in electron affinity as a function of Ga concentration in the clusters. This trend becomes more obvious as the size of the clusters increases. On the other hand, the variation in the ionization energy is very small across the whole Ga concentration. It only decreases by a very small amount which mainly occurs in the very As-rich and Ga-rich clusters. For clusters containing 20%–80% of...
Ga atoms, the ionization energy is almost a constant.

In general, all clusters are energetically in favor of the negatively charged state, as the process of capturing an electron is exothermic. All clusters but As$_4$ have large electron affinity (>1 eV or more). As$_4$ is a strongly bonded cluster and it is magic, similar to Sb$_4$. Therefore, its electron affinity is low. Among the clusters of the same size, the Ga-rich clusters are slightly more favorable for capturing an electron and becoming anionic. On the other hand, the large ionization energy indicates that it is relatively difficult to remove an electron from a neutral cluster to make it positively charged, and this becomes very difficult in small As-rich clusters. These trends are consistent with the trend in the relative stability of the clusters.

**IV. CONCLUSION**

We have studied the structural and electronic properties of Ga$_m$As$_n$ clusters for $n + m$ up to 16 using both all electron calculations with the B3LYP exchange-correlation functional and pseudopotential–plane-wave method with LDA. By carefully comparing results obtained using both methods for small clusters, we have demonstrated that with sufficient accuracy, PP-LDA can predict the structural stability and properties of the clusters as well as AE-B3LYP, apart from the systematic overestimation in binding energy and underestimation of the HOMO-LUMO gap. The stability of the Ga$_m$As$_n$ clusters were found to decrease with increasing Ga concentration for clusters of the same size. The mixed clusters (Ga$_m$As$_n$) were predicted to be energetically more favorable compared to separate pure metal clusters (Ga$_m$ and As$_n$). The HOMO-LUMO gap of the Ga$_m$As$_n$ clusters was found generally to decrease with Ga to As ratio, while the electron affinity and ionization energy are only weakly dependent on the composition, with the electron affinity increasing and ionization potential decreasing as the Ga concentration increases. However, there are large fluctuations in the predicted properties, particularly those of small clusters.

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