Theoretical study of Ga4As4, Al4P4, and Mg4S4 clusters

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Ab initio molecular orbital investigations of the electronic structures, bonding, and stabilities of Ga$_4$As$_4$, Al$_4$P$_4$, and Mg$_4$S$_4$ are reported. The effects of polarization functions and electron correlation are included in these calculations. Our results indicate that the electronegativity difference between the constituents of a mixed cluster plays a very important role in determining its ground state structure. In A_4B_4 mixed clusters, a distorted cubic structure with alternating atomic charges leads to a particularly stable ionic form. This T_d structure consisting of two interpenetrating tetrahedra of the two constituents is the ground state structure for both Al$_4$P$_4$ and Mg$_4$S$_4$. For Ga$_4$As$_4$, there also exists a more covalent Si$_8$-like C_i structure that is 3 kcal/mole more stable than the T_d form. The structures and relative stabilities of these mixed clusters are compared with the results for valence-isoelectronic Si$_8$ and Na$_4$Cl$_4$ clusters.

I. INTRODUCTION

There has been a lot of interest recently in the study of small clusters both experimentally and theoretically.[1–34] Clusters formed from a single element, such as silicon[1–9] or carbon,[10–13] and alkali metal clusters[15] have received the most attention. Among mixed clusters, GaAs clusters[16–30] have been the focus of many investigations due to their importance in the manufacturing of electronic devices. Other clusters such as InP have also been studied, but to a lesser degree.[31,32]

The study of mixed clusters has obvious fundamental importance since the nature of their bonding can show a large variation ranging from ionic to covalent to metallic character. However, theoretical studies of mixed clusters are complicated due to the large number of structural and permutational isomers that have to be considered in order to identify their ground state structures. Nonetheless, several theoretical studies of mixed clusters have been reported in recent years. Balasubramanian performed a series of studies of small mixed clusters (up to four atoms) and their positive and negative ions.[24,25] Meier *et al.* reported calculations for different Ga$_2$As$_2$ isomers,[26] and Lou *et al.* used the local density approximation to study Ga$_n$As$_m$, where $n+m \leqslant 10$.[27] Recently, Graves and Scuseria have used *ab initio* calculations to study the low-energy structures of Ga$_n$As$_n$ clusters ($n=2-4$).[28] In an effort to study the effect of different atomic constituents on the nature of the bonding in a mixed cluster, we recently reported studies of AlP, MgS, and GaAs stoichiometric clusters containing up to six atoms.[29,33,34] The clusters were chosen as prototypes for III–V and II–VI group mixed clusters. We found that the electronegativity difference between the constituents of a mixed cluster plays a major role in structural preferences.

In this work, we continue our investigations by extending the calculations to include Ga$_4$As$_4$, Al$_4$P$_4$, and Mg$_4$S$_4$ stoichiometric mixed clusters. We also further investigate the interplay between ionic and covalent factors in determining the ground state structures. The results of this study, in conjunction with our previous results, can lead to a better understanding of these clusters. We also compare our results to those for Si$_8$ (Ref. 9) and Na$_4$Cl$_4$ (Ref. 14) clusters. This comparison should help us understand the effect of the electronic configurations, atomic sizes, and the electronegativity differences between the constituents on the structures and stabilities of these clusters. In a future publication, we will present our study of the ground and electronic excited states of small InP clusters.[32]

II. THEORETICAL METHODS

Ab initio molecular orbital techniques have been used throughout.[35] All electron calculations were performed for AlP and MgS clusters, while effective core potentials (ECP)[36] were used for GaAs clusters. The ECP was derived by Wadt and Hay from all-electron numerical nonrelativistic Hartree–Fock atomic wave functions, and was fitted to analytical representations for use in molecular calculations.

Structures representing the local minima were obtained by optimizing the geometry for several different starting atomic arrangements at the Hartree–Fock (HF) level of theory. Based on our experience with A_3B_3 clusters where singlet ground state structures were found,[29,33] we have only considered singlet isomers in this study also. Double-zeta plus polarization (DZ+P) basis sets were used to optimize the geometry [the standard 6-31G* basis set[35] for AlP and MgS clusters, and a $(3s3p1d)/[2s2p1d]$ basis set[29] for GaAs clusters]. Local minima were characterized by the presence of all positive vibrational frequencies. Zero-point energies were calculated at the HF/DZ+P level, and scaled by a factor of 0.9 to correct for the systematic overestimation.

These optimized geometries were then used with larger basis sets to perform additional calculations including electron correlation corrections. Second-order Møller–Plesset perturbation (MP2)[37] calculations with a $[6s5p2d]$ basis set[38] were performed for AlP and MgS clusters, and with a $[3s3p2d]$ basis set for GaAs clusters.[39] For the most stable isomer(s) of each cluster, we also performed electron correlation calculations using the quadratic configuration in-
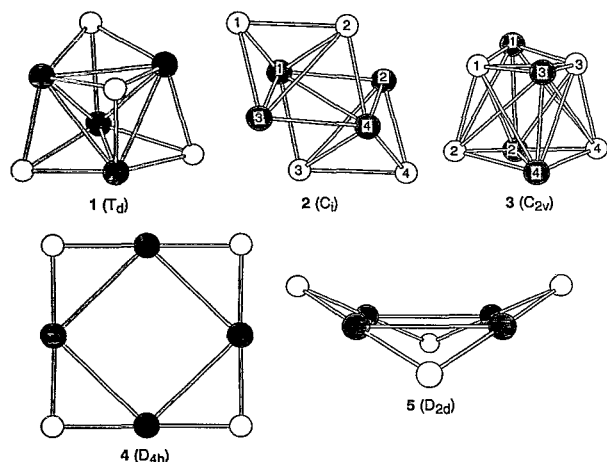
FIG. 1. Low-energy structures for Ga_4As_4, Al_4P_4, and Mg_4S_4 clusters. Atoms are connected if their internuclear distances are within 20% of the bulk values. Dark circles represent Ga, Al, or Mg while open circles represent As, P, or S atoms.

teraction method including the triples corrections, i.e., QCISD(T).[40] This level of theory is known to describe electron correlation effects very accurately even for difficult systems.[41] Finally, the effects of f functions were consid-

ered by performing additional MP2 calculations with $[6s5p2d1f]$ basis set for the ground states of Al_4P_4 and Mg_4S_4 and with a $[3s3p2d1f]$ basis set on the two low-energy isomers of Ga_4As_4.[42]

Atomic charges have been calculated using the natural population analysis.[43,44] This method has proven to be successful in providing a reasonable physical picture of charges in both ionic and covalent systems. It is also relatively insensitive to the basis set size.

III. RESULTS

Figure 1 presents the local minima calculated for Ga_4As_4, Al_4P_4, or Mg_4S_4 clusters. The electropositive atoms (Ga, Al, or Mg) are represented by dark circles and the electronegative atoms (As, P, or S) by open circles. Solid lines have been drawn to represent internuclear distances that are within 20% of the bulk bond lengths. Nevertheless, in our discussion, we refer to the distances between atoms as bond distances only if there is a reasonable bonding electron density between the two atoms as indicated by the natural bonding orbital analysis calculations. Otherwise, we refer to them as internuclear distances.

Table I reports the HF optimized geometries and natural charges of the corresponding clusters in Fig. 1. Table II lists the total (and relative) MP2 energies using the

TABLE I. Optimized molecular geometries (Å and degrees) and atomic charges for the GaAs, AlP, and MgS clusters shown in Fig. 1. A represents Ga, Al, or Mg and B represents As, P, or S atoms.

Structure	Point group	Parameter	Geometry			Atom	Natural charge		
			GaAs	AlP	MgS		GaAs	AlP	MgS
1	T_d	$r(A-B)$	2.51	2.36	2.44	A	+0.82	+1.12	+1.58
		$r(A-A)$	2.88	2.74	2.98	B	−0.82	−1.12	−1.58
		$r(B-B)$	4.03	3.77	3.81				
2	C_i	$r(A_1-B_1)$	2.38	2.28	2.48	A_1	+0.44	+0.69	+1.29
		$r(A_1-B_2)$	2.63	2.40	2.49	A_2	+0.56	+0.68	+0.44
		$r(A_1-B_3)$	2.45	2.34	2.52	B_1	−0.57	−0.73	−0.87
		$r(A_2-B_3)$	3.23	2.94	3.25	B_2	−0.43	−0.64	−0.86
		$r(A_2-B_4)$	2.63	2.40	2.63				
		$r(A_1-A_2)$	2.89	2.72	2.86				
		$r(A_1-A_3)$	3.32	3.22	4.18				
		$r(A_1-A_4)$	2.93	2.77	3.21				
		$r(B_1-B_2)$	2.52	2.28	2.15				
3	C_{2v}	$r(A_1-B_1)$		2.57		A_1		+0.64	
		$r(A_1-B_2)$		4.02		A_2		+0.71	
		$r(A_2-B_1)$		3.10		B_1		−0.70	
		$r(A_2-B_2)$		2.37		B_2		−0.65	
		$r(A_1-A_2)$		3.26					
		$r(A_2-A_4)$		2.94					
		$r(B_1-B_2)$		2.22					
		$r(B_1-B_3)$		2.36					
4	D_{4h}	$r(A-B)$			2.28	A		+1.61	
		$r(A-A)$			3.61	B		−1.61	
		$r(B-B)$			4.52				
		$\theta(A-B-A)$			104.5°				
5	D_{2d}	$r(A-B)$	2.33	2.20		A	+0.88	+1.14	
		$r(A-A)$	3.15	3.04		B	−0.88	−1.14	
		$r(B-B)$	4.65	4.39					
		$\theta(A-B-A)$	85.1°	87.6°					

TABLE II. Total and relative energies (hartrees and kcal/mol) for GaAs, AlP, and MgS clusters.

| System | Structure | Point group | Total energy (hartrees)[a] | | ZPE[b] (kcal/mol) | Relative energy (kcal/mol) |
			HF	MP2		
Ga₄As₄	1	T_d	−31.899 80	−32.593 05	4.6	+11.4
	2	C_i	−31.885 98	−32.609 70	3.7	0.0
	5	D_{2d}	−31.926 77	−32.586 65	4.2	+15.0
Al₄P₄	1	T_d	−2330.799 09	−2331.546 44	8.4	0.0
	2	C_i	−2330.720 87	−2331.502 90	6.8	+25.7
	3	C_{2v}	−2330.685 99	−2331.483 93	5.9	+36.7
	5	D_{2d}	−2330.783 04	−2331.506 69	7.1	+23.6
Mg₄S₄	1	T_d	−2389.063 08	−2389.765 27	7.1	0.0
	2	C_i	−2388.790 33	−2389.500 92	5.5	+164.3
	4	D_{4h}	−2389.019 66	−2389.702 18	6.1	+38.6

[a]Calculated using $[6s5p2d]$ basis set at the HF/6-31G* optimized geometries for AlP and MgS, and using $[3s3p2d]$ basis set at the HF/$[2s2p1d]$ optimized geometries for GaAs clusters (see text).
[b]Zero-point-energies calculated at the HF/DZ+P level and scaled by 0.9.

$[6s5p2d]$ basis set for AlP and MgS and the $[3s3p2d]$ basis set for GaAs clusters. The listed relative energies include a correction for the scaled zero-point energies calculated at the HF/DZ+P level. Total energies calculated at the QCISD(T) level of theory for the most stable isomer(s) using the HF/DZ+P optimized geometries are listed in Table III.

A. Ga₄As₄

The permutational possibilities of arranging eight atoms to form a mixed cluster are numerous. In this study, we eliminated many of these possibilities by limiting our search to those structural arrangements that are favorable due to electrostatic or covalent bonding considerations. We used structures of Si₈ isomers as well as those from previous studies on Ga₄As₄ as starting points in our geometry optimizations.

First, we consider a tetracapped tetrahedral structure 1 (T_d symmetry). As represented in Fig. 1, 1 can be viewed as a Ga tetrahedron with all four faces capped by As atoms. This arrangement is somewhat analogous to the Jahn–Teller distorted C_{2v} structure which was found to be a low-lying local minimum for Si₈.[9] However, 1 has no such Jahn–Teller distortion indicating that the electronic configuration is different. Detailed analysis (*vide infra*) shows that 1 is best considered as a distorted cubic structure favorable for ionic bonding. As shown in Fig. 1, each

atom in 1 has the atoms with opposite polarity as nearest neighbors, providing efficient charge alternation.

As shown in Table I, the optimized Ga–As bond distance in 1 is 2.51 Å. The Ga–Ga internuclear distance is 2.88 and the As–As internuclear distance is 4.03 Å. Atomic distances in GaAs clusters are typically longer than the corresponding distances in AlP or MgS clusters due to the larger size of the Ga and As atoms. As given in Table I, the natural atomic charges are ±0.82e. As expected from the electronegativities of the constituents, these charges are smaller in magnitude than those for AlP or MgS clusters. In our previous study of Ga₂As₂ and Ga₃As₃, we obtained natural charges of 0.2–0.6e for structures where covalent bonding is dominant and ≈0.9e for more ionic structures.[29] Thus charges of ±0.82e for 1 clearly show the importance of ionic contributions in this structure. The alternative T_d structure obtained with the As atoms located on the inside tetrahedron was found to be unstable.

The nature of the T_d isomer with the Ga atoms on the inside may appear at first sight to be somewhat surprising since the Ga–Ga bond is significantly weaker than the As–As bond. The explanation is that there is significant contribution of ionic bonding in this isomer as seen by the atomic charges of ±0.82e. Thus, if we start with a cubic (charge alternating) arrangement of atoms which is favor-

TABLE III. Total QCISD(T) energies for the most stable isomer(s) of GaAs, AlP, and MgS clusters.

| System | Structure | Point group | Total energy (hartrees)[a] | | | |
			HF	MP2	MP3	QCISD(T)
Ga₄As₄	1	T_d	−31.896 07	−32.564 44	−32.585 87	−32.643 92
	2	C_i	−31.881 46	−32.577 90	−32.588 35	−32.654 01
Al₄P₄	1	T_d	−2330.633 50	−2331.300 28	−2331.331 20	−2331.388 29
Mg₄S₄	1	T_d	−2388.904 40	−2389.515 81	−2389.559 54	−2389.590 80

[a]Calculated using 6-31G* basis set at the HF/6-31G* optimized geometries for AlP and MgS, and using $[3s3p1d]$ basis set at the HF/$[2s2p1d]$ optimized geometries for GaAs clusters (see text).

able for ionic bonding, and allow for the fact that the ionic radius of Ga^+ is much smaller than the ionic radius of As^-, we can understand the nature of the T_d structure clearly. In fact, in our earlier study[29] on Ga_2As_2 and Ga_3As_3, similar ionic isomers were seen though there were more stable covalently bonded isomers also.

Since a Jahn–Teller distorted bicapped octahedron (C_{2h} symmetry) was found to be the ground state of Si_8,[9] we considered a similar structure for the isoelectronic Ga_4As_4 cluster. As a result of having two atomic types, two different structures of C_{2h} symmetry were considered. These bicapped octahedral structures can be viewed as an overlay of two rhombic structures. In one of them, Ga atoms occupy the short diagonal of each rhombus, while in the other the As atoms are on the short diagonal.

Vibrational frequency analysis of the optimized C_{2h} structure with the Ga atoms on the short diagonals showed that it has an imaginary frequency of $81i(b_g)$. This indicates that the structure is not a local minimum. Relaxing the symmetry of the molecule to C_i led to the local minimum shown as **2** in Fig. 1. Geometry optimization of the other cubic structure (As atoms on the short diagonals of each rhombus) also resulted in **2** after considerable rearrangement. As shown in Table I, the optimized As–As bond length in **2** is 2.52 Å, while the Ga–Ga internuclear distances are 2.89, 2.93, and 3.32 Å. The Ga–As internuclear distances range from 2.38 to 3.23 Å. The atomic charges in **2** (ranging between ± 0.43 and $0.57e$) are smaller than those in the T_d form due to the larger contributions of covalent bonding in **2**, and are similar to the values seen previously for the ground state isomers of Ga_2As_2 and Ga_3As_3.[29]

Relative energies calculated at the MP2/[3s3p2d] level in Table II indicate that electron correlation corrections are very important in these calculations. While **1** is more stable at the HF level, electron correlation effects favor **2** sufficiently that the relative ordering of the two forms is reversed when correlation energies are included. Since the energy difference between these two structures at this level is relatively small (11 kcal/mol), we performed additional calculations using the QCISD(T)/[3s3p1d] level of theory for both isomers. As shown in Table III, the results indicate that higher order correlation effects favor **1** by $\simeq 2$ kcal/mol so that the energy difference is reduced to $\simeq 9$ kcal/mol. To correct for the limitation of the [3s3p2d] basis set we also performed calculations at the MP2/[3s3p2d1f] level for the two isomers. The f functions also favor the T_d structure by $\simeq 6$ kcal/mol relative to the C_i (results not shown). Thus our large basis set estimate for Ga_4As_4 is that the C_i isomer is more stable than the T_d by about 3 kcal/mol.

Since electron correlation effects reversed the ordering of the two isomers, we performed additional optimizations on both structures at the MP2 level of theory with the polarized double-zeta [2s2p1d] basis set. Many of the bond lengths, particularly the Ga–As distances, changed significantly, generally increasing by 0.03–0.09 Å. Additional QCI/[3s3p1d] calculations at these geometries, however, showed that the change in the relative energies resulting

from these differences is less than 1 kcal/mol. Thus we conclude that the calculated relative energies are reliable though there may be significant geometry changes at correlated levels of theory.

Motivated by the stability of the two-dimensional Ga_3As_3 structure,[29] we optimized the geometry of a planar two-dimensional Ga_4As_4 structure. This D_{4h} structure (**4**) has an imaginary frequency of $31i(b_{1u})$. Relaxing the symmetry to D_{2d} resulted in the local minimum shown as **5** in Fig. 1. Comparison of the geometries of **4** and **5** shows the effect of the symmetry lowering. As shown, two of the As atoms move 16° above the plane of the Ga atoms, while the two other As atoms move below the plane by the same amount. The D_{2d} structure lies 15 kcal/mol above the ground state structure **2** at the MP2/[3s3p2d] level. The Ga–As bonds are 2.33 Å, and the Ga–Ga internuclear distance is 3.15 Å. The Ga–As–Ga angle is 85°. Ionic factors are dominant in this close-to-planar arrangement as indicated from the atomic charges of $\pm 0.88e$. Energetically, this isomer is less stable than the ionic T_d isomer by 4 kcal/mol.

In addition to the above structures, other starting geometries such as square prism and square antiprism with opposite faces of Ga_4 and As_4 were investigated. These were unstable and resulted in high energy isomers.

In summary, our results for Ga_4As_4 clusters indicate that **2** with C_i symmetry is the lowest energy structure. This is in agreement with the HF results (no correlation energy) obtained by Graves and Scuseria[28] and the local density approximation results reported by Lou et al.[27] However, neither of these studies reported the T_d structure as a low energy structure. In fact, Lou et al. reported that such a structure is unstable due to static Jahn–Teller effects. This is in contrast with our results, which clearly indicate that the T_d structure is a local minimum which is very low in energy. In fact, in the next two sections it can be seen that such a T_d structure is the *ground state* for both Al_4P_4 and Mg_4S_4.

B. Al_4P_4

Based on the similarities in the electronic configurations of AlP and GaAs, we expect both clusters to have similar structures. Thus, we started by optimizing Al_4P_4 isomers with similar geometrical arrangements to those in Ga_4As_4.

The tetrahedral arrangement of Al_4P_4 was also found to be a local minimum (**1** in Fig. 1). The interatomic distances in AlP are about 5% smaller than those in GaAs due to the smaller size of the atoms. On the other hand, the atomic charges in AlP are 36% larger than GaAs charges, indicating a higher ionic character. This is consistent with the larger electronegativity difference between Al and P.

We also optimized a C_{2h} bicapped octahedral structure similar to the ground state of Ga_4As_4. As in the case of Ga_4As_4, this structure has a b_g imaginary frequency of $116i$ cm^{-1}. Again, relaxing the symmetry to C_i led to the local minimum given as **2** in Fig. 1. As shown in Table I, the P–P bond distance is 2.28 Å, and the Al–Al internuclear distances are 2.72, 2.77, and 3.22 Å. The Al–P distances

range from 2.28 to 2.94 Å. As expected, the internuclear distances in this AlP cluster are slightly shorter than the corresponding distances in the analogous GaAs cluster. The atomic charges, on the other hand, are slightly larger. Comparing the atomic charges in **2** (about ±0.7) to the atomic charges in **1** (±1.12) indicate that ionic contributions are less important in **2**. The energy difference between **1** and **2** illustrates the difference between Al$_4$P$_4$ and Ga$_4$As$_4$. While the more covalent **2** is the ground state of Ga$_4$As$_4$, the energy ordering is opposite for Al$_4$P$_4$. In fact, in Al$_4$P$_4$ the T_d form **1** is considerably more stable (by 24 kcal/mol) than **2** at the MP2/[6s5p2d] level of theory. This is clearly attributed to the larger importance of ionic contributions in Al$_4$P$_4$, and is consistent with the larger electronegativity difference between Al and P.

We also optimized the alternative C_{2h} structure composed of P atoms on the short diagonals of the two overlaying rhombic structures. Vibrational frequency analysis indicates that the structure has two b_u imaginary frequencies of 232i and 84i cm^{-1}. Further relaxation eventually led to the C_{2v} structure (via intermediate C_2 symmetry) shown as **3** in Fig. 1. The top rhombus (Al$_1$–P$_1$–Al$_3$–P$_3$) still has the P atoms on the short diagonal, but the lower rhombus (Al$_2$–P$_2$–Al$_4$–P$_4$) now has the Al atoms on the short diagonal. In **3**, the internuclear distance Al$_1$–Al$_3$ is 4.35 Å compared to Al$_2$–Al$_4$ distance of 2.94 Å. On the other hand, P$_1$–P$_3$ is 2.36 Å compared to P$_2$–P$_4$ value of 3.65 Å. The atomic charges in this distorted cubic arrangement (±0.6–0.7e) are also indicative of the covalent nature of the bonding. Although this structure is a local minimum, it is 37 kcal/mol higher in energy than **1**. Among all the structures we investigated, **3** is the only local minimum we found where the electronegative atoms are located on the inside of the atomic arrangement.

The two-dimensional structure (D_{4h}) was also considered as a candidate for the ground state structure of Al$_4$P$_4$. The optimized D_{4h} structure has a small imaginary frequency of 31i(b_{1u}) indicating out of plane distortion. Relaxing the symmetry to D_{2d} resulted in structure **5** in Fig. 1. This structure is almost isoenergetic with the C_i structure above, but it is 24 kcal/mol higher in energy than the T_d structure. The atomic charges of ±1.14e are slightly higher than those in the T_d structure. However, the presence of more neighbors of opposite polarity makes the T_d form more stable. As shown, the Al–P distance is 2.20 Å, and the Al–P–Al angle is 88°. The deviation from the D_{4h} symmetry is small with the P atoms 12° above and below the plane of the Al atoms.

To summarize, the T_d structure is the ground state structure of Al$_4$P$_4$. It is 24 kcal/mol more stable than any other isomer. This is in contrast with Ga$_4$As$_4$ clusters where the energy difference between the isomers is much smaller.

C. Mg$_4$S$_4$

We optimized the geometries of several starting structural arrangements for Mg$_4$S$_4$. Although we expect MgS clusters to behave differently from AlP or GaAs clusters, it

is illustrative to use their atomic arrangements as starting points in the geometry optimizations of Mg$_4$S$_4$ clusters.

The T_d arrangement for MgS was found to be particularly stable. As listed in Table I, the optimized Mg–S bond distance is 2.44 Å, and the Mg–Mg internuclear distance is 2.98 Å. This structure is highly ionic as indicated from the atomic charges of ±1.58e.

We also optimized a bicapped octahedral structure similar to those studied for GaAs and AlP clusters. Vibrational frequency analysis of the C_{2h} structure with the Mg atoms on the short diagonals of the rhombic structures shows again that it has an imaginary frequency of 27i(b_g). Relaxing the symmetry resulted in structure **2** in Fig. 1. This local minimum (C_i symmetry) is 164 kcal/mole less stable than the T_d structure. Although atomic charges in **2** are somewhat larger than those for the corresponding GaAs or AlP structures, these are still much less than the atomic charges in **1**. It is clear from the energy difference between **1** and **2** that MgS clusters favor ionic arrangements. This is in accordance with the much larger electronegativity difference between Mg and S.

We also optimized a planar arrangement (**4**), where ionic bonding is favored. Unlike the AlP and GaAs clusters where symmetry relaxation to D_{2d} isomers was necessary, the planar D_{4h} structure is a local minimum for Mg$_4$S$_4$. As shown in Table II, **4** is 39 kcal/mol less stable than the tetrahedral structure **1**. The optimized Mg–S bond length is 2.28 Å and the Mg–Mg distance is 3.61 Å. The bonding in this cluster is again dominated by ionic factors as obvious from the high atomic charges (±1.61e). Although ionic factors are dominant in both **1** and **4**, **1** is more stable than **4** due to the higher efficiency of charge alternation in three-dimensions. The principal conclusion from Table II is that ionic structures are much more favorable than covalent structures for MgS clusters.

IV. BONDING

In this section, we discuss the bonding aspects of some of the clusters presented in Fig. 1. As mentioned earlier, atomic connectivities in Fig. 1 are presented to illustrate the structural features and not to identify bonds. For the purpose of identifying bonds, we used the natural bonding orbital method.[43,44] Our results indicate that, for a given structural arrangement, bonding characteristics are very similar in GaAs and AlP clusters. MgS clusters, on the other hand, show the expected differences resulting from the change in the electronic configuration. In this section, we will restrict our discussion to the bonding in the III–V structures **1** and **2** in Fig. 1.

In the T_d structure, each atom is bonded to three neighboring atoms of a different type. Though the distance between the electropositive elements (Al–Al or Ga–Ga) is relatively short, natural bonding analysis indicates that there is no significant bonding between them. The shorter internuclear distance is then a consequence of the smaller ionic radii of the positively charged elements. In this structure each electronegative atom has one lone pair.

For the C_i isomer, our results indicate that each electronegative atom is bonded to two electropositive atoms

TABLE IV. Cohesive energies in eV.

System	Number of Atoms			
	2	4	6	8
Si[a]	1.56	3.17	3.60	3.65
GaAs[b]	0.84	1.88	2.18	2.21
AlP[c]	1.02	2.29	2.63	2.85
MgS[c]	1.07	2.25	2.63	2.91
NaCl[d]		3.38	3.49	3.61

[a]Calculated at the scaled MP4/6-31G* level (see Ref. 9).
[b]Calculated at the QCISD(T)/[3s3p1d] level with corrections for larger basis set effects (see text).
[c]Calculated at the QCISD(T)/6-31G* level with corrections for larger basis set effects (see text).
[d]Obtained using ion–ion potentials (Ref. 14).

and a neighboring electronegative atom, leaving them with a lone pair. Again, the electropositive atoms are not bonded to each other. Although the natural charges on the different electropositive atoms are comparable, the hybridizations are not all similar. In particular, atoms 2 and 3 appear to have a hybridization similar to that of the atom (s^2p^1 like) whereas 1 and 4 are significantly rehybridized (sp^2 like) which facilitates additional bonding. Thus electropositive atoms 1 and 4 are each bonded to three other electronegative atoms, but atoms 2 and 3 each have a lone pair and are bonded to one other atom. Thus there is a trade-off between the promotion energy required to hybridize and the energy gained from the resulting additional bonding in structure 2.

V. COHESIVE ENERGIES

The QCISD(T) total energies (Table III) in conjunction with zero-point energies and a correction for the effect of larger basis sets (not shown) have been used to calculate the binding and cohesive energies of A_nB_n clusters. These results are also compared to the results for the smaller clusters studied earlier,[29,33,34] and to the analogous silicon[9] and NaCl (Ref. 14) clusters. The larger basis set correction is defined to be the energy difference between MP2/[6s5p2d1f] and MP2/6-31G* for both AlP and MgS clusters, and between MP2/[3s3p2d1f] and MP2/[3s3p1d] energies for GaAs clusters.

The cohesive energies (binding energy per atom) of Si, GaAs, AlP, MgS, and NaCl small clusters are given in Table IV. Generally, cohesive energies for these clusters show a monotonic increase with the size of the cluster. In addition, Mg_4S_4 and Al_4P_4 show a much larger increase in cohesive energy on going from six- to eight-atom cluster than Ga_4As_4. This can be mainly attributed to the particular stability of the ionic structure 1 for these clusters. As shown in Table IV, dimers have much smaller cohesive energies than larger clusters. Thus there is a clear tendency for these dimers to form larger clusters.

Our calculated cohesive energy for Ga_2As_2 (1.88 eV) is in good agreement with Balasubramanian's best estimate (1.75–1.88 eV).[25] It is also in excellent agreement with Graves and Scuseria's CCSD(T) all electron calculations (1.70 eV).[28] Graves and Scuseria also reported the cohe-

sive energies of Ga_3As_3 and Ga_4As_4 at the HF level of theory. Comparison with our results shows that the HF calculated cohesive energies for Ga_3As_3 and Ga_4As_4 (0.93 and 1.02 eV, respectively) are underestimated by 1.0–1.2 eV due to the contributions of electron correlation effects.

We also used the QCISD(T) total energies to calculate the binding energies of the Ga_2As_2, Ga_3As_3 and Ga_4As_4 clusters with respect to GaAs($^3\Sigma^-$) dimer. Our calculated values are 2.09, 2.68, and 2.75 eV for Ga_2As_2, Ga_3As_3, and Ga_4As_4, respectively. These are in good agreement with the results of the local density approximation.[27]

VI. COMPARISON WITH OTHER CLUSTERS

In the highly covalent Si_8 clusters, the energy difference between the distorted bicapped octahedral ground state structure (analogous to 2) and the tetracapped tetrahedral structure (analogous to 1) is 9 kcal/mol.[9] For Ga_4As_4, the covalent ground state structure 2 is only 3 kcal/mol more stable than the ionic structure 1. In Al_4P_4 clusters, where the electronegativity difference between the constituents is relatively larger, we find that the ionic form 1 is more stable than the covalent form 2 by 26 kcal/mol. This energy difference between the ionic and covalent isomers become very high (164 kcal/mol) in the highly ionic Mg_4S_4 clusters.

In mixed clusters, where both ionic and covalent factors are important, the interplay between these factors determine the relative energies of the local minima. The relative contributions of these factors can change from one size cluster to another due to the formation of particularly stable ionic structures in some cases. In our study of mixed A_nB_n clusters ($n=1$–4), we found that when n is even, there exist specially stable structures resulting from maximum charge alternation. In addition, stable covalent structural arrangements can occur when the electronegative atoms of these clusters are at close proximity.

VII. CONCLUSIONS

The calculated structures and atomic charges for the different isomers show the importance of the difference in electronegativity between the constituent atoms in determining ground state structures. As expected, ionic forms are favored when the electronegativity difference between the constituents of a mixed cluster is large. In eight-atom clusters, a distorted cubic form with alternating atomic charges gives the best charge alternation. It is more stable than the highly ionic close-to-planar atomic arrangement due to the enhanced charge alternation achieved in three-dimensions. On the other hand, covalent isomers favor three-dimensional structures that facilitate better overlap of the bonding orbitals.

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