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# Fullerene-like III−V Clusters: A Density Functional Theory Prediction

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We present extensive theoretical calculations of the geometric and electronic properties of neutral and ionized III−V (GaP, GaAs, GaN, AlAs, and AlP) fullerene-like clusters of the type $\mathrm{III}_x\mathrm{V}_{x\pm4}$ with a number of atoms up to 52, on the basis of density functional theory. This study predicts the stability of heterofullerenes formed by all of these compounds, with the exception of GaN. We analyze the behavior of the energy gap and of the cohesive energy per atom as a function of the size and composition of the III−V fullerene and in comparison with previous theoretical calculations for BN fullerenes.

## I. Introduction

Large clusters with stable structures for particular numbers of atoms are of great interest for nanotechnology. In this respect, fullerenes stand out as very interesting systems by themselves and as building blocks for nanostructures. Most efforts to identify fullerenes based on other elements than carbon have focused on BN which is the most similar to carbon and exists in nature in the hexagonal (graphite-like) structure.[1−8] However, the observed BN (nested-)cages and wires[1,2] do not clearly show the presence of the characteristic pentagonal rings of carbon fullerenes. Indeed, the presence of pentagonal rings in heterofullerenes implies homopolar bonds in the structure which were considered unfavorable in BN leading most authors to consider the so-called squares-hexagons route.[3−7] However, in a recent theoretical study, Fowler et al.[8] have shown that BN fullerene cages with six pairs of adjacent pentagonal rings (the so-called pentalene unit) minimize the number of homopolar bonds, leading to clusters with stoichiometry $\mathrm{B}_x\mathrm{N}_{x\pm4}$ with six homopolar bonds. Within this class, they observed[9] particularly stable (magic) nuclearities.

Here we suggest that III−V semiconductors with zinc blende bulk structure are also prone to form fullerene-like clusters with pentalene units of the type suggested for BN compounds. Although only experimental observation will establish whether the proposed clusters exist, our extensive numerical calculations strongly support our prediction. We have recently shown[10] by means of ab initio Car−Parrinello molecular dynamics[11] that a small GaP bulk fragment spontaneously organizes in a fullerene-like cage with the stoichiometry $\mathrm{III}_x\mathrm{V}_{x\pm4}$ suggesting a considerable structural stability. Noticeably, this structure falls into the special subclass with six pentalene units. This finding has motivated us to focus on this specific class of fullerenes and extend the analysis of the geometric and electronic properties to various III−V semiconductor materials and to larger nuclearities (up to a total of 52 atoms).

We find that the geometric structure, mostly determined by the bonding angles, is very similar for all compounds of the second and third row of the III−Vs. The interplay between almost tetrahedral bonds on group V and almost planar bonds on group III atoms leads to less spherical clusters than for C fullerenes. A strong indication for their stability is provided by the fact that, especially for clusters with group V atoms in excess of four, the binding energy is only a few percent lower than the corresponding bulk zinc blende structure. The large energy gaps between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and the stability of ionized clusters together with previous results on thermal stability further support our prediction. Conversely, we find GaN clusters to be unstable in our calculations because of the formation of $\mathrm{N}_2$ molecules.

In section II, we describe our theoretical and numerical approach. Section III describes the structural and electronic properties of the studied clusters. All along, we will discuss our results also in relation to the analogous BN clusters. Finally, in section IV, we give a summary and perspectives of this work.

## II. Computational Method and Technical Details

Our results are obtained within a pseudopotential density functional theory (DFT) approach. The density functional is written in a generalized gradient approximation in the form proposed by Becke and Perdew (BP).[12,13] The BP functional has been shown to be quite accurate in reproducing the structure, cohesive energy, and electronic properties of typical bulk semiconductors.[14] We use nonlocal norm-conserving first-principles pseudopotentials[15] and expand the Kohn−Sham single particle wave functions on a plane wave basis set with a cutoff of 12 Rydberg. We have checked that by increasing the energy cutoff from 12 to 16 Ry the bond lengths and electronic states of the $\mathrm{Ga}_{12}\mathrm{As}_8$ cluster vary less than 0.1% and 1%, respectively.

We use a periodically repeated cubic simulation box with a side ranging from 15 to 20 Å for different cluster size. This box is large enough to describe isolated clusters. Following Fowler et al.,[8] the initial structure has been derived by decorating

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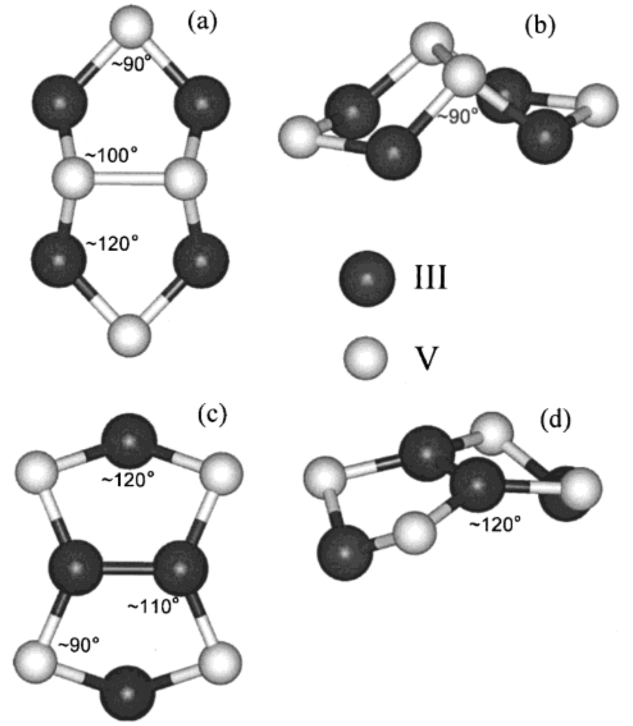

**Figure 1.** Top (a and c) and side views (b and d) of the pentalene units in the $III_xV_{x+4}$ (a and b) and $III_xV_{x-4}$ (c and d) clusters. Typical values of the angles in the optimized structures (see Table 1 and 2) are shown.

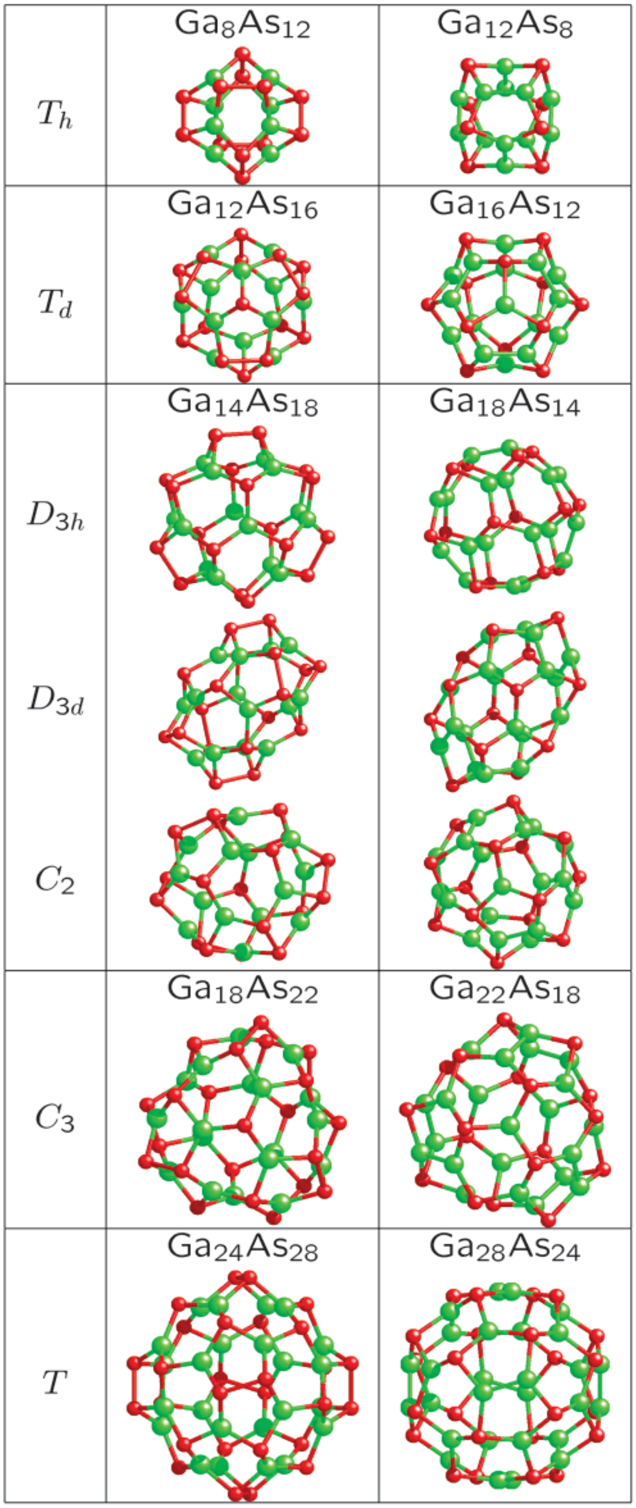

**Figure 2.** Optimized isomers of the $Ga_xAs_{x+4}$ and $Ga_xAs_{x-4}$ series (green = Ga; red = As). The symmetry of the final configurations is indicated.

the polyhedra with six pentalene units as to have all hexagons with III,V alternation and one homopolar bond per pentalene unit. The electronic optimization and structural relaxation have been performed using damped second-order dynamics with electronic mass preconditioning scheme.[11,16] During the structural optimization, the symmetry of the cluster is not constrained.

## III. Results

**III.a. Structural Properties.** The clusters we consider here are characterized by the presence of the pentalene units which we show in Figure 1 for the two cases with homopolar bonds between either group III or group V atoms. The given bonding angles are average values representative for all studied compounds. Interestingly, pentalene units with As−As dimers are also present in the recently resolved $\beta 2(2 \times 4)$ reconstruction of the GaAs (001) surface.[17]

The sideviews clearly show the nonplanarity of the pentalene units, particularly for group V homopolar bonds. As a result, these heterofullerene clusters are less spherical than those formed by carbon. This feature is apparent in Figure 2 where we show the minimum energy structure of all studied clusters formed by Ga and As atoms. We have considered clusters with a stoichiometry of $III_xV_{x\pm 4}$ up to a total of 52 atoms which is the first cluster with isolated pentalene units. Fowler et al.[8] have classified all possible isomers, identifying particularly stable (magic) nuclearities. We have considered all isomers with nuclearity 20, 28, and 32 and only the cluster of $C_3$ symmetry for nuclearity 40 and of $T$ symmetry for nuclearity 52, which are the most stable for BN clusters. For the cases with 28 and 32 atoms, we find that the symmetry of the isomer of minimal energy does not coincide with that found for BN.[8] In particular, we find the 28 atom cluster to have $T_d$ symmetry also when starting from a $C_{3v}$ configuration, which is the most stable for the corresponding BN cluster.[8] For nuclearity 32, we find a reversed order of $D_{3d}$ and $C_2$ isomers, with the former being more stable in our case, although the difference in energy is only ∼50 meV (see also section III.b and Figure 3).

The structural parameters (angles and bond lengths) of all clusters studied with stoichiometry $III_xV_{x+4}$ and $III_xV_{x-4}$ are given in Tables 1 and 2, respectively. For the smallest clusters, we have studied all possible combinations of Ga and Al with P

**TABLE 1: Structural Parameters of the $\mathrm{III}_x\mathrm{V}_{x+4}$ Clusters[a]**

| | | V−V | III−V | III−V−V | III−V−III | V−III−V |
|---|---|---|---|---|---|---|
| $Al_8P_{12}$ | $T_h$ | 2.270 | 2.301 | 100.1 | 84.2 | 119.5 |
| $Ga_8P_{12}$ | $T_h$ | 2.262 | 2.288 | 100.3 | 84.7 | 119.5 |
| $Al_8As_{12}$ | $T_h$ | 2.521 | 2.405 | 97.8 | 82.5 | 119.9 |
| $Ga_8As_{12}$ | $T_h$ | 2.505 | 2.389 | 98.2 | 83.6 | 119.8 |
| $Ga_{12}As_{16}$ | $T_d$ | 2.535 | ~2.37 | 98.4 | 86.6 | 115, 129 |
| $Ga_{14}As_{18}$ | $D_{3h}$ | ~2.5 | ~2.37 | 95,101 | 79−102 | 110, 118, 130 |
| | $D_{3d}$ | 2.497 | ~2.37 | 96−101 | 87−104 | 113−128 |
| | $C_2$ | ~2.503 | ~2.37 | 95−101 | 94−101 | 111−128 |
| $Ga_{18}As_{22}$ | $C_3$ | ~2.497 | ~2.37 | 100−114 | 90, 105 | 112−125 |
| $Ga_{24}As_{28}$ | $T$ | 2.490 | ~2.36 | 99.3, 101.3 | 90.4−102 | 111−125 |

[a] Bond lengths are in Å, and angles are in degrees. For comparison, in bulk zinc blende GaAs, the interatomic distance calculated with the same functional is 2.447 Å.

**TABLE 2: Structural Parameters of the $\mathrm{III}_x\mathrm{V}_{x-4}$[a]**

| | | III−III | III−V | V−III−III | V−III−V | III−V−III |
|---|---|---|---|---|---|---|
| $Al_{12}P_8$ | $T_h$ | 2.510 | 2.306 | 111.0 | 128.9 | 88.8 |
| $Ga_{12}P_8$ | $T_h$ | 2.383 | 2.294 | 112.0 | 126.8 | 88.6 |
| $Al_{12}As_8$ | $T_h$ | 2.522 | 2.409 | 112.3 | 129.2 | 85.0 |
| $Ga_{12}As_8$ | $T_h$ | 2.401 | 2.396 | 113.2 | 127.0 | 85.3 |
| $Ga_{16}As_{12}$ | $T_d$ | 2.366 | ~2.38 | 112.8 | 119.9 | 97.7, 89.5 |
| $Ga_{18}As_{14}$ | $D_{3h}$ | ~2.361 | ~2.37 | 110,114 | 111−131 | 87, 100, 108 |
| | $D_{3d}$ | 2.375 | ~2.37 | 109−116 | 114−131 | 84−105 |
| | $C_2$ | ~2.366 | ~2.39 | 110−114 | 115−131 | 85−107 |
| $Ga_{22}As_{18}$ | $C_3$ | ~2.375 | ~2.38 | 111−113 | 117,121 | 90−103 |
| $Ga_{28}As_{24}$ | $T$ | 2.356 | ~2.35 | 111.9, 112.7 | 118−133 | 91−106 |

[a] Bond lengths are in Å, and angles are in degrees.

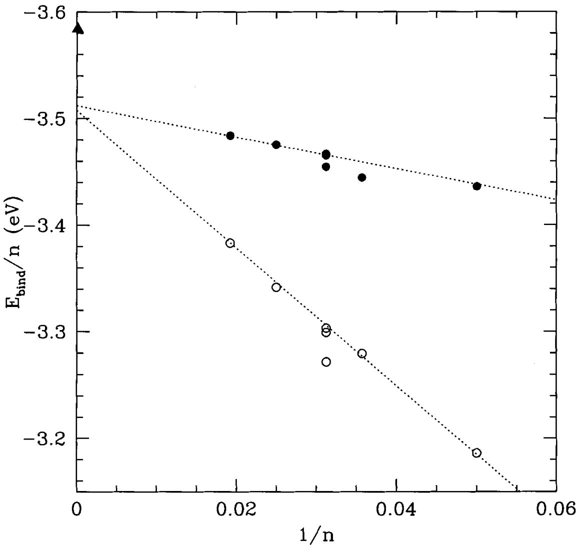

**Figure 3.** Binding energy per atom of the GaAs series as a function of the inverse nuclearity 1/*n*. Filled dots correspond to $Ga_xAs_{x+4}$ structures and empty dots to $Ga_xAs_{x-4}$ structures. The dotted lines are linear fits of the data. The triangle on the vertical axis indicates the zinc blende bulk binding energy.

and As. It is interesting to notice that the bond angles are almost equal for all compounds, yielding similar aspects to all clusters with the same stoichiometry. The homopolar bond lengths depend marginally on the atomic species of the other component, and the III−V bond lengths are slightly shorter than those in the corresponding bulk zinc blende, which is no surprise in view of the 3-fold coordination. By comparing Tables 1 and 2, one can see that V−III−V and III−V−III angles are comparable for the two types of clusters.

Furthermore, we have considered the $Ga_8N_{12}$ cluster, also in view of a recent paper suggesting the stability of GaN nanotubes.[18] However, in this case, we find that the GaN cluster is not stable against formation of $N_2$ fragments with distances of ~1.12 Å typical of the triple bond of a nitrogen diatomic molecule. Therefore, among the studied compositions, GaN is the only one for which the fullerene structure is unstable.

Because mass spectrometry experiments use the difference in mass-to-charge ratio of ionized atoms or clusters to select them, the stability of the ionized clusters is of importance for their experimental observation. Thus, we have optimized the structure of charged GaAs clusters of several sizes. In our previous work,[10] we observed the stability of positively ionized GaP clusters with nuclearity 20 and 28. Here, we study the stability of positively and negatively ionized $Ga_xAs_{x+4}$ clusters. We have chosen the smallest and the largest clusters, namely $Ga_8As_{12}^+$, $Ga_8As_{12}^-$, $Ga_{24}As_{28}^+$, and $Ga_{24}As_{28}^-$. All of them remain stable, even if small distortions (at most around 3%) with respect to the neutral structure are observed.

**III.b. Energetics and Electronic Properties.** In Figure 3, we present the calculated binding energy per atom of $Ga_xAs_{x\pm4}$ clusters as a function of the inverse nuclearity 1/*n* ($n = 2x \pm 4$). For $n = 32$, we have plotted the three studied isomers of which the $D_{3d}$ is the most stable though very close in energy to the $C_2$. The situation for the analogous BN cluster is reversed.[8] One can see that the clusters with a majority of group V (filled circles) atoms have a higher binding energy and a weaker dependence on the nuclearity than the clusters with a majority of group III atoms (open circles). The dependence is well fitted by a linear slope with a common limiting value for $1/n \rightarrow 0$. The dashed lines represent this best fit. The linear behavior with 1/*n* has been also found for carbon and $B_xN_x$ fullerenes and attributed to strain because of the deviation of the cluster surface from planarity[3]. In the case of heterofullerenes with homopolar bonds, the slope of the 1/*n* dependence of the binding energy per atom $E_b$ is not only due to strain effects but also to the difference in energy of homopolar and heteropolar bonds. In fact, by defining $E_{Ga-As}$, $E_{As-As}$, and $E_{Ga-Ga}$ as the values of the energies of the Ga−As, As−As, and Ga−Ga bonds and by assuming, to a first approximation, them to be independent of

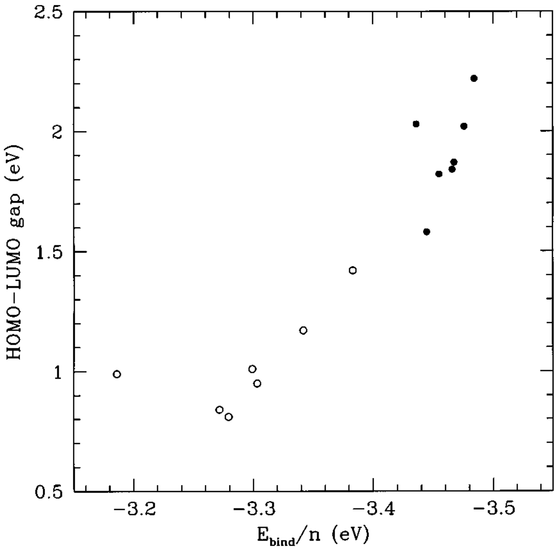

**Figure 4.** HOMO−LUMO energy gap vs the binding energy per atom. Filled dots correspond to $Ga_xAs_{x+4}$structures and empty dots to $Ga_xAs_{x-4}$ structures.

the structure,[10] one can write

$$-E_b = \frac{3}{2}E_{Ga-As} - \frac{6}{n}(E_{Ga-As} - E_{As-As}) - \frac{k}{n}$$

for clusters with As in excess and

$$-E_b = \frac{3}{2}E_{Ga-As} - \frac{6}{n}(E_{Ga-As} - E_{Ga-Ga}) - \frac{k'}{n}$$

for clusters with Ga in excess, where $k$ and $k'$ are coefficients accounting for strain effects due to the curvature. The common limiting value of the two curves is related to the value of the Ga−As bond energy, which can be extrapolated from the fit to be 2.34 eV. The slope of the most stable $Ga_xAs_{x+4}$ clusters (filled circles) is much weaker also due to the fact that $E_{As-As} > E_{Ga-Ga}$, both being less than $E_{Ga-As}$. The slope of the less stable clusters (open circles) is very close to that of BN and C fullerenes as given in Figure 4 of ref 3. Interestingly, because of the much weaker slope of the $Ga_xAs_{x+4}$ clusters, the binding energy of all of them is at most 1% lower than a hypothetical zero curvature structure ($1/n \rightarrow 0$) and a few percent than the zinc blende bulk structure indicated by a filled triangle on the vertical axis. This is a strong support of our prediction of stability of III−V fullerenes with an excess of type V atoms.

A strong correlation between the HOMO−LUMO energy gaps and the relative cluster stabilities has been found experimentally for carbon fullerenes.[19] In Figure 4, we show the energy gap for the GaAs clusters as a function of the binding energy per atom. The clusters with a majority of group V atoms show the largest HOMO−LUMO gaps, which is again a signature of a larger stability of this stoichiometry. A fairly good linear correlation is observed between gap and binding energies in each of the two series, except for the smallest clusters with 20 atoms, possessing only pentagonal faces, which show an anomalously large value of the HOMO−LUMO gap.

An analysis of the molecular orbitals (MOs) has shown that the nature of the bonding in these clusters is not simply described in terms of $s-p$ hybridization as in the corresponding bulk materials. In fact, the MOs composition shows that the $s$ atomic orbitals are mostly contributing to the lowest lying MOs which have almost no $p$ component. On the contrary, the uppermost occupied MOs are characterized by strong $p$ components with very little, if any, $s - p$ mixing.

## IV. Conclusions

In summary, we have considered GaP, GaAs, AlAs, AlP, and GaN heterofullerenes with $III_xV_{x\pm4}$ stoichiometry of nuclearity 20, 28, 32, 40, and 52. Our DFT calculations predict the stability of fullerene-like clusters formed by III−V semiconductor compounds of the second and third row. Conversely, we find GaN fullerenes to be unstable against formation of $N_2$ molecules. In addition to our previous observation of the spontaneous formation of $Ga_{16}P_{12}$ from a bulk fragment,[10] in the present paper, we have shown that all of these structures have high symmetry, large HOMO−LUMO gaps, and closed electronic shells and remain stable also when ionized. These characteristics are more pronounced for the composition with group V atoms in excess of four for which the binding energies are at most 3% less than the zinc blende bulk structure.

As in the case of carbon and BN fullerenes, the III−V clusters would represent metastable states with respect to the bulk equilibrium structure, and only experimental observation can establish with certainty their existence. We hope that this work will stimulate experimental groups to widen their search for heterofullerenes also to III−V semiconductor compounds.

The noticeable stability of these clusters opens the way to the study of superstructures and nanostructures having them as building blocks. Currently work is in progress to study crystals, polymers, and nested structures formed by these clusters.

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