Spontaneous Formation and Stability of GaP Cage Structures: A Theoretical Prediction of a New Fullerene

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ABSTRACT

We report the spontaneous formation of a GaP fullerene cage in ab-initio Molecular Dynamics simulations starting from a bulk fragment. A systematic study of the geometric and electronic properties of neutral and ionized III-V (GaP, GaAs, AlAs, AlP) clusters suggests the stability of hetero-fullerenes formed by compounds with zincblend bulk structure. Our prediction is supported by several indicators: these clusters show closed electronic shells and relatively large energy gaps; the ratio between the cohesive energy per atom in the cluster and in the bulk is very close to the value found for carbon fullerenes of the same size; the clusters are thermally stable up to a temperature range of 1500-2000 K and they do not dissociate when ionized.

INTRODUCTION

The discovery of carbon fullerenes and nanotubes has opened a completely new field at the borderline between chemistry and physics leading to many new phenomena and applications. Most efforts to identify fullerenes based on other elements 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 (nested-)cages and wires[1,2] do not present the characteristic pentagonal rings of carbon fullerenes.

Here we explore the possibility of fullerene cages based on typical semiconductors of the III-V family, like GaAs, GaP, or AlAs, which do not possess a graphite-like bulk structure. We have recently shown[9] by means of ab-initio Car-Parrinello Molecular Dynamics[10], that a small GaP bulk fragment spontaneously organizes in a cage formed by a different number of atoms of the two elements arranged as in carbon fullerenes. Here we extend the analysis of the geometric and electronic structure of cages with the stoichiometry III_x-$V_{x\pm4}$ for various III-V clusters up to a total of 52 atoms.

COMPUTATIONAL DETAILS

Our results are obtained by means of the Car-Parrinello approach[10] using a Density Functional in the Generalized Gradient Approximation proposed by Becke and Perdew[11,12]. This approximation reproduces the experimental cohesive energy

of typical bulk semiconductors within 5 valence to conduction band excitation energies[13]. We use nonlocal norm-conserving first-principles pseudopotentials[14] and expand the single particle wavefunctions on a plane wave basis set with a cut-off of 12 Rydberg. We use a periodically repeated cubic simulation box of 24 Å side, a size found large enough to describe isolated clusters. The electronic optimization and structural relaxation have been performed using damped second order dynamics with electronic mass preconditioning scheme[15]. The symmetry of the equilibrium structure is not biased but it is reached spontaneously during the geometry optimization starting from the corresponding regular polyhedron.

RESULTS

In ref. [9] we have shown that a bulk like cluster with 41 atoms with tetrahedral bulk-like coordinations spontaneously evolves to a $Ga_{16}P_{12}$ bonded cluster with 12 pentagons and 4 hexagons during the simulated energy minimization.

The observed spontaneous formation of a $Ga_{16}P_{12}$ cage with pentagons is surprising since, in the case of BN[3-6], (deformed) squares are found to be energetically much more favorable. For $B_{12}N_{12}$[4], there is an energy difference of 9 eV between the cage with pentagons and the one with squares in favor of the latter which contains only heteropolar bonds and is favored for a material composed by atoms with very different electronegativity as B and N. Therefore, most studies have considered cages B_nN_n formed by hexagons closed by square rings[3,4,6,7].

Very recently, Fowler et al.[8] have pointed out that, among the cages with pentagons, those with one species in excess of 4 atoms (B_nN_{n+4}) minimize the number of homopolar bonds. The cage $Ga_{16}P_{12}$ which spontaneously appear in our simulation falls into this class. Therefore we focus our study on the equilibrium structure and electronic states of $III_nV_{n\pm4}$ clusters, with a total number of atoms ranging from 20 to 52 and for different III-V compounds.

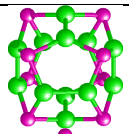
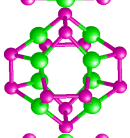
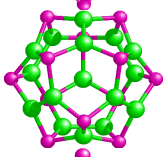
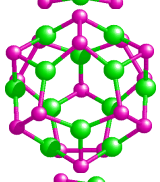
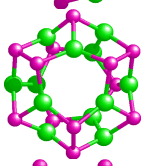
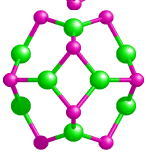
In Tables I and II we show the minimum energy structures of several GaP and GaAs fullerenes with the corresponding symmetry and HOMO-LUMO gap.

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 support our prediction for the stability of the examined GaP clusters by using the following indicators: i) closed electronic shells and large energy gaps; ii) cohesive energy; iii) thermal stability; iv) stability of the ionized clusters.

The first indicator of chemical stability is the energy gap between the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO). In carbon fullerenes a correlation between this energy and the observed fullerenes has been experimentally verified[16].

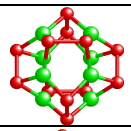
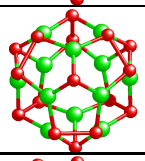
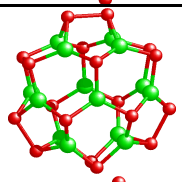
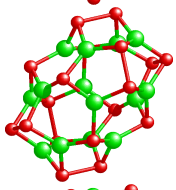
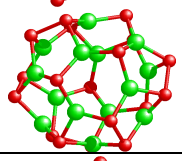
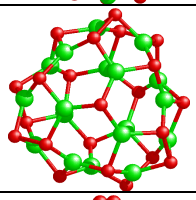
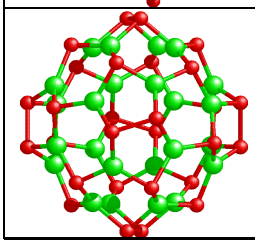
In figure 2 we show the calculated HOMO-LUMO energy gap for all the GaAs clusters studied as a function of the total number of atoms (the nuclearity). The clusters with a majority of atoms of type V show the largest HOMO-LUMO gaps. In general, the gap grows with the cluster size, with a particularly high value for the cluster with 52 atoms as found also for the analogous BN cluster[8].

Table I. Optimised structures, symmetry, HOMO-LUMO energy gaps, cohesive energies and Ga–P binding energies for several GaP clusters. The bulk gap is given for comparison. The annealing temperature is also given for the first two structures.

		HOMO-LUMO gap (eV)	$E_{cohesive}$ (Hartree)	$E_{\mathrm{Ga-P}}$ (eV)	annealing temp. (K)
	$Ga_{12}P_8$ T_h	1.28	-2.5374	$\sim$ 2.59	$\sim$ 1500
	Ga_8P_{12} T_h	2.14	-2.8161	"	$>$ 2000
	$Ga_{16}P_{12}$ T_d	1.09	-3.6876	"	
	$Ga_{12}P_{16}$ T_d	1.55	-3.9452	"	
	$Ga_{10}P_{10}$	1.03	-2.6632	$\sim$2.58	
	$Ga_{12}P_{12}$ (C_{v3})	1.24	-3.2362	"	
	$Ga_{12}P_{12}$ T_h	1.86	-3.3060	$\sim$2.49	
	GaP bulk	1.62			

A comparison of the binding energies per atom between the GaP cages and the zincblend bulk phase of this material is possible only for the clusters with the same number of Ga and P atoms. From the results of Table I, we find that the cohesive energies per atom for $Ga_{12}P_{12}$ with squares, $Ga_{12}P_{12}$ with pentagons, and $Ga_{10}P_{10}$ are about 10% lower than in the bulk. This result is very close to that found for BN and carbon fullerenes of the same size[3].

Table II. Optimised geometries, HOMO-LUMO gaps and bond lengths for some of the clusters of the Ga_xAs_{x+4} serie.

	gap (eV)	As–As (Å)	Ga–As (Å)
 Ga_8As_{12} T_h	2.03	2.505	2.389
 $Ga_{12}As_{16}$ T_d	1.57	2.535	~ 2.4
 $Ga_{14}As_{18}$ D_{3h}	1.82	~ 2.5	~ 2.37
 D_{3d}	1.87	2.497	~ 2.37
 C_2	1.84	~ 2.503	~ 2.37
 $Ga_{18}As_{22}$ C_3	1.99	~ 2.497	~ 2.37
 $Ga_{24}As_{28}$ T	2.22	2.485	~ 2.0

We have also studied the thermal stability of two clusters with very different energy gaps, namely $Ga_{12}P_8$ and Ga_8P_{12} (see Table I). For both clusters, we have performed two annealing cycles of about 3 ps, up to 1500 K and up to 2000 K. The system is heated with a rate of 2×10^{15}K/s, then equilibrated for one ps at the highest temperature, and finally cooled down with the same temperature change rate. For Ga_8P_{12} no bond breaking or structural rearrangements occur in both cycles

and the structure comes back to the same minimum energy configuration when the temperature is lowered. This is also the case for $Ga_{12}P_8$ in the annealing up to 1500 K, whereas at 2000 K some structural rearrangement takes place leading to a distorted structure with higher energy when cooled down. These results indicate that the thermal stability is correlated with the width of the energy gap.

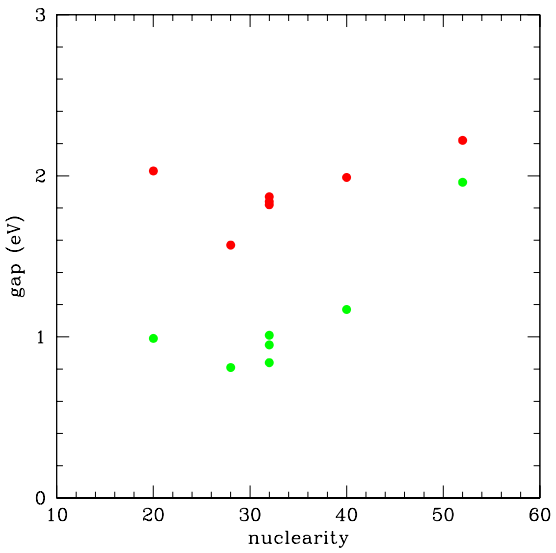


Figure 2. HOMO-LUMO gap of the GaAs clusters as a function of the number of atoms in the cluster. Dark (red) dots correspond to Ga_xAs_{x+4} clusters, light (green) dots to $Ga_{x+4}As_x$ clusters. The "magic" clusters, that is, the more stable of the serie, have been chosen.

Mass spectrometry experiments use the difference in mass-to-charge ratio of ionized atoms or clusters to select them. Therefore one basic requirement for the possible detection of such clusters is that they remain stable also when ionized. We have investigated the stability of some positively ionized clusters, $[Ga_8P_{12}]^+$, $[Ga_{12}P_{16}]^+$ and $[Ga_{16}P_{12}]^+$. The electronic structure remains almost unaffected and degeneracies are broken by negligible amounts in the order of hundredths of eV. Only minor structural distortions occur upon ionization. In particular, the six equivalent P-P (Ga-Ga) bond lengths split into three different classes. Remarkably, during a molecular dynamics run for $[Ga_8P_{12}]^+$ we observe a dynamical exchange between these three classes of bond lengths with each other. This effect produces features in the low frequency vibrational spectrum in the range $30-120$ cm^{-1} which might be detected by infrared multiphoton ionization spectra[17].

CONCLUSIONS

In summary, our MD results strongly suggest that small fullerenes formed with III-V semiconductor compounds could be stable, since they have high symmetry, closed electronic shells, and large HOMO-LUMO energy gaps. These clusters are thermally stable also when ionized.

The cages with the stoichiometry III_x-V_{x+4}, which minimizes the number of homopolar bonds, are particularly stable and show the largest HOMO-LUMO gaps.

We hope that this work will stimulate experimental groups to widen their search for hetero-fullerenes also to III-V semiconductor compounds.

ACKNOWLEDGMENTS

FB acknowledges financial support from the PPM (Prioriteitsprogramma Materialenonderzoek) project number 96PPM001.

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