Spontaneous formation and stability of small GaP fullerenes

V. Tozzini
Istituto Nazionale per la Fisica della Materia and Scuola Normale Superiore, Piazza dei Cavalieri, 7 I-56126 Pisa, Italy

F. Buda
Department of Theoretical Chemistry, Vrije Universiteit, De Boelelaan 1083, NL-1081 HV Amsterdam, The Netherlands

A. Fasolino
Research Institute for Materials, Institute of Theoretical Physics, University of Nijmegen, Toernooiveld, NL-6525ED Nijmegen, The Netherlands

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 GaP clusters suggests the stability of hetero-fullerenes formed by a compound with zincblend bulk structure. We find that GaP fullerenes up to 28 atoms have high symmetry, closed electronic shells, large HOMO-LUMO energy gaps and do not dissociate when ionized. We compare our results for GaP with those obtained by other groups for the corresponding BN clusters.

61.48.+c, 71.15.Pd, 81.05.Tp
The discovery of carbon fullerenes and nanotubes [1,2] has opened a completely new field at the borderline between chemistry and physics leading to many new phenomena and applications.

Up to now, 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 [3–10]. However, the (nested-)cages and wires found for this material [3,4] do not resemble any of the small preferred structures of the carbon fullerene family, particularly due to the absence of the characteristic pentagonal rings. Besides, nanotubes based on other layered materials, such as GaSe [11] and black-phosphorus [12], have been theoretically predicted to be stable. On the basis of density functional calculations it has also been proposed that GaN nanotubes could be synthesised by using carbon nanotubes as a nucleation seed [13].

One intriguing question is whether fullerene cages could be realized in typical semiconductors of the III-V family, like GaAs, InSb or GaP, which do not possess a graphite-like bulk structure. These materials are not considered as good candidates for hollow structures since $\pi$ bonding should be less effective in these larger atoms of higher rows of the periodic table than in the first one [5].

In this letter we show, by means of ab-initio Car-Parrinello Molecular Dynamics [14], 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. We discuss the geometric and electronic structure of GaP cages with either the same or a different number of atoms of the two species. Our results strongly suggest that small GaP fullerenes could be stable, since they have high symmetry, closed electronic shells, large HOMO-LUMO energy gaps and do not dissociate when ionized. We give quantitative estimates of the relative stability of cages formed either by hexagons and pentagons as in carbon fullerenes or by hexagons and squares as proposed for BN [5–9].

Our results are obtained by the Car-Parrinello approach [14] using a Density Functional in the Generalized Gradient Approximation proposed by Becke and Perdew [15,16]. This approximation reproduces the experimental cohesive energy of typical bulk semiconductors within $\approx 5\%$ and underestimates the valence to conduction band excitation energies [17]. We use nonlocal norm-conserving first-principles pseudopotentials [18] 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, so that periodic images are at least 14 Å apart. We have verified that this size is 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 [19,20]. We use throughout an integration time step of 8 a.u. The symmetry of the equilibrium structure is not biased but it is reached spontaneously during the geometry optimization starting from the corresponding regular polyhedron.

The process of formation of the fullerene cage with 28 atoms from a larger bulk-like cluster of 41 atoms (Ga$_{28}$P$_{13}$) is shown in Fig.1, with the help of three snapshots taken during the structural energy minimization which leads to the appearance of the Ga$_{16}$P$_{12}$ fullerene cage [21]. The cage has 12 pentagons and 6 hexagons and $T_d$ symmetry as $C_{28}$. An analysis of the charge distribution shows 108 valence electrons on the bonded cage, exactly the number which corresponds to the neutral Ga$_{16}$P$_{12}$ cluster [22]. Finally in Fig.1d we show
the equilibrium structure of the neutral Ga$_{16}$P$_{12}$ cluster alone.

The observed spontaneous formation of a Ga$_{16}$P$_{12}$ cage with pentagons is surprising since, in the case of BN [5–8], (deformed) squares are found to be energetically much more favorable. For B$_{12}$N$_{12}$, 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$_n$N$_n$ formed by hexagons closed by square rings [5,6,8,9]. Very recently, Fowler et al. [10] have pointed out that, among the cages with pentagons, those with one species in excess of 4 atoms (B$_n$N$_{n+4}$) minimize the number of homopolar bonds. It is remarkable that the cage Ga$_{16}$P$_{12}$ which spontaneously appear in our simulation falls into this class.

We have studied the equilibrium structure and electronic states of clusters with 20 and 28 atoms of the type III$_n$V$_{n+4}$, namely Ga$_{12}$P$_8$, Ga$_8$P$_{12}$, Ga$_{16}$P$_{12}$ and Ga$_{12}$P$_{16}$, and compared them to clusters with the same number of III and V atoms, namely Ga$_{10}$P$_{10}$ and Ga$_{12}$P$_{12}$, the latter in the two isomers [3] with hexagons closed either by five- or four-sided faces. The minimum energy structures of Ga$_{16}$P$_{12}$ and Ga$_{12}$P$_{16}$ are found to have T$_d$ symmetry, whereas those of Ga$_{12}$P$_8$ and Ga$_8$P$_{12}$ have T$_h$ symmetry. Among the clusters Ga$_n$P$_n$, the Ga$_{12}$P$_{12}$ with 4-membered rings belongs to T$_h$ whereas those with pentagons present very large distortions around the lower C$_{3v}$ symmetry. The structural parameters of the cages belonging either to T$_h$ or to T$_d$ are given in Table I. Hexagons are found with alternating angles of $88^\circ - 105^\circ$ and $126^\circ - 134^\circ$, pentagons with angles of $85^\circ - 92^\circ$, $114^\circ - 126^\circ$, $\sim 100^\circ$, $\sim 110^\circ$ and deformed squares with angles $75^\circ$ and $98^\circ$. Ga-P distances are in general shorter than in bulk compounds due to predominant sp$^2$ bonding. The radial distance $r$ from the center of the cluster given in Table I indicates a tendency of the anion to occupy positions at larger distances from the center than the cation, as found for ultrasmall cluster [23,24].

As in the case of carbon and BN fullerenes, the GaP clusters would represent metastable states with respect to the bulk equilibrium structure. Therefore only experimental observation can establish with certainty their existence. Nevertheless, there are a few quantities which are used in the literature as indicators of stability. 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 [25]. In Table II we give the calculated HOMO-LUMO energy gap and the cohesive energy for all the clusters studied. Among the cages with pentagons the highest energy gaps are for cluster with P in excess of 4, a composition which has been suggested to be favorable also for BN [10]. However, a very large gap is also found for the Ga$_{12}$P$_{12}$ with squares.

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 II, 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 [6].
We have studied the thermal stability of two clusters with very different energy gaps, namely Ga$_{12}$P$_8$ and Ga$_8$P$_{12}$ (see Table II). 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 $2 \times 10^{15}$K/s, then equilibrated for one ps at the highest temperature, and finally cooled down with the same temperature change rate. For Ga$_8$P$_{12}$ 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.

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$_8$P$_{12}$]$^+$, [Ga$_{12}$P$_{16}$]$^+$ and [Ga$_{16}$P$_{12}$]$^+$. We have included an uniform charge background in order to have an overall neutral system in the supercell calculation. 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$_8$P$_{12}$]$^+$ 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 [26].

It is interesting to compare cages closed either by 4- or 5-membered rings. As already mentioned, such a comparison has been done for B$_{12}$N$_{12}$ in Ref. [6]. However there are no results comparing clusters with equal number of atoms III$_n$V$_n$ with square rings to the more favorable structures with pentagons of the type III$_n$V$_{n+4}$. The authors who have proposed the latter stoichiometry [10], in fact, do not give a comparison to cages with square rings. Although it is impossible to compare directly the cohesive energy of structures with a different number of atoms of each species, we are in a position to give an estimate of the bond energy for the two types of cages. Given the number of each type of bond in all the structures with pentagons studied so far and the values of the total cohesive energy, we estimate by a best fit the following energies per bond: $E_{Ga-P} = -2.593$ eV, $E_{Ga-Ga} = -1.133$ eV, $E_{P-P} = -2.349$ eV [27]. As shown in Table II, these values yield the correct cohesive energy with a relative error of 0.4% at most for all cluster with pentagons, whereas overestimate the cohesive energy of the cluster Ga$_{12}$P$_{12}$ with squares. In this cluster, in fact, there are only Ga-P bonds yielding directly $E_{Ga-P} = -2.499$ eV a smaller value than in the clusters with pentagons. However, as it can be seen in Table II, it is the isomer with squares which has the lowest energy among the two Ga$_{12}$P$_{12}$. The 1.9 eV energy difference between them is much less than the 9 eV found for B$_{12}$N$_{12}$ [6]. This is most probably due to the less ionic character of the GaP bonds. The difference in electronegativity of Ga and P is in fact $\sim 0.4$ against $\sim 1$ for BN. The observed spontaneous formation in our simulations of a cage with the same topology of C$_{28}$ shows a possible evolution pattern from ionized bulk fragments to classical fullerene cages formed by pentagons and hexagons.

In summary, we have shown, by means of ab-initio Car-Parrinello Molecular Dynamics, that small GaP fullerenes have highly symmetric structures, closed electronic shells and large
HOMO-LUMO gaps and cohesive energy. These clusters are thermally stable and remain in the same structure also when ionized. These findings together with the observed spontaneous formation in our simulations of a 28 atoms cage with the same symmetry of C\textsubscript{28} support the possible existence of GaP fullerenes. We hope that our work will stimulate experimental groups to widen their search for hetero-fullerenes also to III-V compound semiconductors.

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REFERENCES

[21] In Ref. [20] we have noted that also III-V clusters included in sodalite show the tendency to organize in hollow shells of cations and anions.
[22] The neutral Ga_{28}P_{13} cluster with 149 electrons has one unpaired electron in the uppermost occupied state. Just below this state, the electronic structure presents one 3–fold and one 1–fold degenerate state. Interestingly, the 28 atom cage forms spontaneously whenever we have completely filled states, namely for 148, 142 and 140 electrons, which would describe an ionized bulk-like fragment.
[27] The values of \( E_{Ga-Ga} \) and \( E_{P-P} \) are close to the experimental bond energies, 1.17 eV and 2.08 eV for Ga and P, respectively, given in J. Emsley, *The elements*, Oxford University Press, New York, 1989.
TABLES

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**TABLE I.** Point symmetry and atomic positions of the clusters with symmetry T\textsubscript{d} and T\textsubscript{h}. Values of the parameters and of the radial distance r from the center of the cluster are in Angstrom. The positions of the minimum energy structure vary less than 0.01 Å from the given values.
TABLE II. HOMO-LUMO gap and cohesive energy of the clusters studied. For reference, the indirect energy gap of bulk GaP within the Local Density Approximation is 1.62 eV. The cohesive energy is obtained as the difference of the total energy minus the energy of the isolated pseudoatoms. Within the same approximations these values are -2.15045 Hartree and -6.46295 Hartree for Ga and P, respectively. The cohesive energy per GaP pair in the bulk is found to be 0.2976 Hartree. In the last two columns we give the values and the relative error of the cohesive energy estimated from the calculated bond energies $E_{Ga-P} = -2.593$ eV, $E_{Ga-Ga} = -1.133$ eV, $E_{P-P} = -2.349$ eV (see text).
FIG. 1. Ga atoms are represented as large light balls, P atoms as small dark balls. Starting from a truncated bulk structure with tetrahedral symmetry, Fig.1a shows a first step in the evolution towards structural energy minimization. The main rearrangement is the bonding of the peripheral Ga atoms between themselves, 12 atoms in pairs on the edges of the tetrahedron and four triplets on the vertices. In Fig.1b the central P atom breaks its bonds, followed by 12 Ga atoms (Fig.1c) leading to the formation of a Ga$_{16}$P$_{12}$ fullerene cage. Fig.1d shows the equilibrium structure of the neutral Ga$_{16}$P$_{12}$ cluster alone. Notice the non-planarity of the pentagons. The symmetry of the equilibrium configuration is Td (see Table I).
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