Spontaneous Formation and Stability of Small GaP Fullerenes

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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 heterofullerenes formed by a compound with zinc blende bulk structure. We find that GaP fullerenes up to 28 atoms have high symmetry, closed electronic shells, large highest occupied molecular orbital–lowest unoccupied molecular orbital 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.

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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 (graphitelike) 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 synthesized 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, such as GaAs, InSb, or GaP, which do not possess a graphitelike bulk structure. These materials are not considered as good candidates for hollow structures since π 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 highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) energy gaps, and do not dissociate when ionized. We give quantitative estimates of the relative stability of cages formed by either hexagons and pentagons as in carbon fullerenes or 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 by Perdew [15,16]. This approximation reproduces the experimental cohesive energy of typical bulk semiconductors within ≈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 wave functions on a plane wave basis set with a cutoff of 12 Ry. We use a periodically repeated cubic simulation box of a 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 an 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 bulklike 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 $B_{12}N_{12}$ [6], 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 [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 four atoms (B_nN_{n+4}) minimize the number of homopolar bonds. It is remarkable that the cage $Ga_{16}P_{12}$, which spontaneously appears 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 $III_nV_{n\pm4}$, namely, $Ga_{12}P_8$, Ga_8P_{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 [6] 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_8P_{12} have T_h symmetry. Among the clusters Ga_nP_n, the $Ga_{12}P_{12}$ with four-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 $88°-105°$ and $126°-134°$, pentagons with angles of $85°-92°$, $114°-126°$, $\sim100°$, $\sim110°$, and deformed squares with angles 75° and 98°. 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 clusters [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.

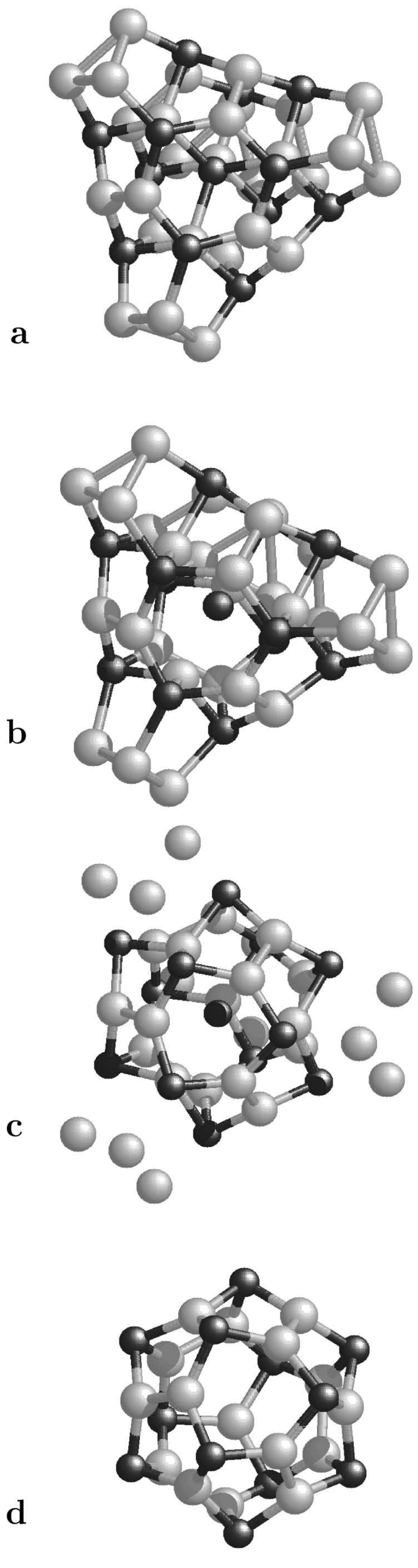

FIG. 1. Ga atoms are represented as large light balls, P atoms as small dark balls. Starting from a truncated bulk structure with tetrahedral symmetry, (a) shows a first step in the evolution towards structural energy minimization. The main rearrangement is the bonding of the peripheral Ga atoms between themselves, 12 atoms in pairs on the edges of the tetrahedron and four triplets on the vertices. In (b) the central P atom breaks its bonds, followed by 12 Ga atoms (c) leading to the formation of a $Ga_{16}P_{12}$ fullerene cage. (d) shows the equilibrium structure of the neutral $Ga_{16}P_{12}$ cluster alone. Notice the nonplanarity of the pentagons. The symmetry of the equilibrium configuration is T_d (see Table I).

TABLE I. Point symmetry and atomic positions of the clusters with symmetry T_d and T_h. Values of the parameters and of the radial distance r from the center of the cluster are in angstroms. The positions of the minimum energy structure vary less than 0.01 Å from the given values.

$Ga_{16}P_{12}(T_d)$					$Ga_{12}P_{16}(T_d)$				
4 Ga	$3m$	xxx	$x = -1.96$	$r = 3.39$	4 P	$3m$	xxx	$x = -2.37$	$r = 4.11$
12 Ga	m	xxz	$x = 0.83$ $z = 3.30$	$r = 3.50$	12 P	m	xxz	$x = 0.81$ $z = 3.75$	$r = 3.92$
12 P	m	xxz	$x = 2.87$ $z = -0.03$	$r = 4.06$	12 Ga	m	xxz	$x = 2.33$ $z = -0.12$	$r = 3.30$

$Ga_{12}P_8(T_h)$					$Ga_8P_{12}(T_h)$					$Ga_{12}P_{12}$ square (T_h)				
8 P	3	xxx	$x = 2.05$	$r = 3.55$	8 Ga	3	xxx	$x = 1.54$	$r = 2.67$	12 P	i	$0yz$	$y = 3.36$ $z = 1.74$	$r = 3.78$
12 Ga	i	$0yz$	$y = 2.61$ $z = 1.19$	$r = 2.87$	12 P	i	$0yz$	$y = 3.18$ $z = 1.13$	$r = 3.37$	12 Ga	i	$0yz$	$y = 2.81$ $z = 1.39$	$r = 3.13$

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, and (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. 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 the 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 zinc blende 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 [5].

We have studied the thermal stability of two clusters with very different energy gaps, namely, $Ga_{12}P_8$ and Ga_8P_{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 2×10^{15} K/s, then equilibrated for 1 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.

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 $[Ga_{16}P_{12}]^+$. We have included a 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 $[Ga_8P_{12}]^+$ 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}

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 $E_{\text{Ga-P}} = -2.593$ eV, $E_{\text{Ga-Ga}} = -1.133$ eV, and $E_{\text{P-P}} = -2.349$ eV (see text).

Cluster	HOMO-LUMO gap (eV)	E_{cohesive} (Hartree)	E_{fit} (Hartree)	Error (%)
$Ga_{12}P_8$	1.28	−2.5374	−2.5370	−0.01
Ga_8P_{12}	2.14	−2.8161	−2.8052	−0.39
$Ga_{16}P_{12}$	1.09	−3.6876	−3.6806	−0.19
$Ga_{12}P_{16}$	1.55	−3.9452	−3.9488	0.09
$Ga_{10}P_{10}$	1.03	−2.6632	−2.6711	0.30
$Ga_{12}P_{12}$ (pentagon)	1.24	−3.2362	−3.2429	0.21
$Ga_{12}P_{12}$ (square)	1.86	−3.3060	−3.4308	3.78

which might be detected by infrared multiphoton ionization spectra [26].

It is interesting to compare cages closed either by four- or five-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 an equal number of atoms $\mathrm{III}_n\mathrm{V}_n$ with square rings to the more favorable structures with pentagons of the type $\mathrm{III}_n\mathrm{V}_{n+4}$. 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: $E_{\text{Ga-P}} = -2.593$ eV, $E_{\text{Ga-Ga}} = -1.133$ eV, and $E_{\text{P-P}} = -2.349$ 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 clusters with pentagons, whereas they 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 $E_{\text{Ga-P}} = -2.499$ eV, a smaller value than in the clusters with pentagons. However, as 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-atom cage with the same symmetry of C_{28} support the possible existence of GaP fullerenes. We hope that our work will stimulate experimental groups to widen their search for heterofullerenes also to III-V compound semiconductors.

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