PHYSICAL REVIEW B **79**, 245420 (2009)

Stability of $Ga_xAs_{x\pm4}$ gallium arsenide fullerenes

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(Received 25 February 2009; revised manuscript received 28 May 2009; published 18 June 2009)

We have investigated the atomic structure and stability of $Ga_xAs_{x\pm4}$ gallium arsenide fullerenes by using *ab initio* structure optimization, electronic structure, and molecular dynamics simulations. We found that the hollow gallium arsenide fullerenes are stable when the pentagon edges are shared to reduce the number of homonuclear bonds. We used the energetics, the energy gap in the electronic structure, and the response of the system to thermal excitations as indicators for the stability of the gallium arsenide fullerenes. We found that As-rich fullerenes are more likely to occur and a successful synthesis may involve using high As_2 partial pressure over the GaAs bulk target. The hollow gallium arsenide fullerenes show the signature of structural transformations beyond 500 K through the formation of Ga-Ga homonuclear bonds. Preventing inner Ga atoms to make bonds with each other may be a path for gallium arsenide fullerenes and hollow cages in general.

DOI: 10.1103/PhysRevB.79.245420 PACS number(s): 81.05.Tp, 61.48.−c, 68.65.−k, 73.22.−f

I. INTRODUCTION

The gallium arsenide clusters that were first obtained by laser evaporation of a bulk GaAs target showed odd/even behavior in photoionization experiments,[1] which indicated an extensive surface reconstruction and a large deviation from the tetrahedral bonding. Thus, the gallium arsenide clusters may exhibit different bonding characteristics than their bulk counterparts because of the strong anion-anion bonds.[2] However, the clusters with larger number of atoms adopt the alternating Ga and As atomic arrangements.[3] Therefore, we wonder if reconstructed large clusters may form the Ga-As bonds that may favor a fullerene structure rather than compact clusters with bulklike atomic coordinations. In addition to that of carbon, the cages of III-IV group elements were reported,[4] albeit at low reaction rates.[4] Although the gallium arsenide clusters were discovered in the same apparatus that was used in discovering the fullerenes, the possibility of gallium arsenide fullerene structures was not considered extensively because the surface tension typically prevents hollow clusters.

Hollow cage structures can lead to unique applications that harness the protective chemical environment inside. The metal atom encapsulating semiconducting clusters are suggested for making nanoscale magnetic elements. The encapsulated atoms or molecules are known to stabilize some isomers of carbon fullerenes[5,6] that are otherwise experimentally not viable. In principle, all materials with a near hexagonal structure may form fullerenelike clusters. For example, boron nitride[7,8] and molybdenum disulfide fullerenes[9] are reproducibly synthesized. Similar to boron nitride, cages of other III-IV elements[10] and hollow Ga_nAs_n small clusters[11] were proposed. These and other noncarbon fullerene cage structures are considered as potential building blocks for nanotechnology applications.[12] We speculate gallium arsenide fullerenes as potential building blocks for synthesis of nanostructured semiconducting magnets in a bottom-up approach. However, the stability of gallium arsenide cage structures and optimum synthesis conditions, as well as the basic electronic properties of such hollow gallium arsenide cages, are not known.

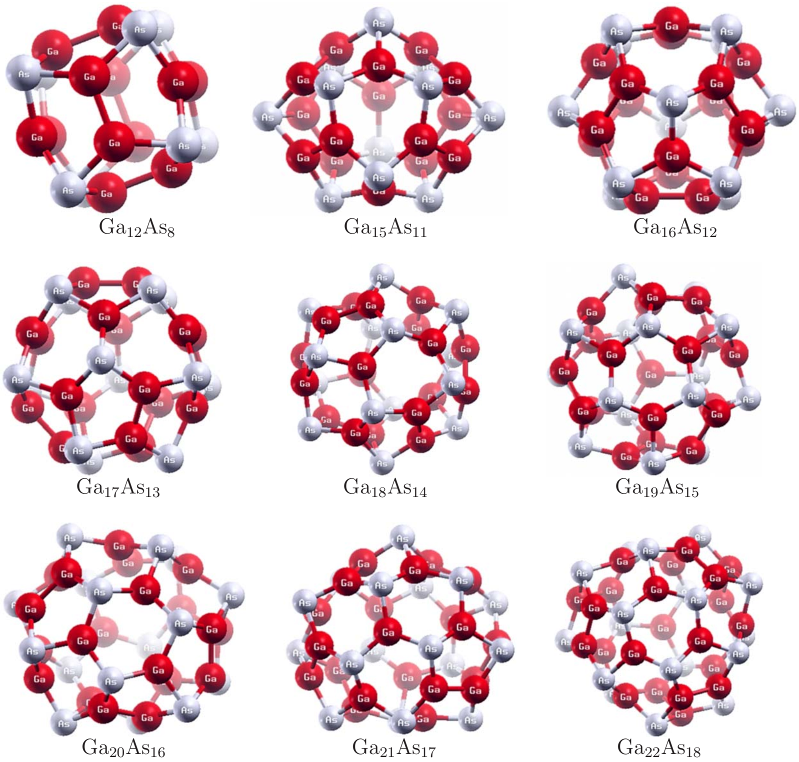
In this work, we investigate the stability and electronic structure of gallium arsenide fullerenes Ga_xAs_y, where $y = x \pm 4$, in order to determine the likelihood of finding hollow gallium arsenide cages. Since an experimental realization of hollow clusters may be hindered by dynamical reasons other than the static properties of these systems, we also performed molecular dynamics (MD) simulations of isolated Ga_xAs_y fullerenes at elevated temperatures in order to assess their thermal stabilities. Since the electronic structure of a cluster could hint on the reactivity and thus on the chemical stability of the system, we provide electronic structure calculations to further determine the possibility of producing air-stable gallium arsenide fullerenes.

A gallium arsenide fullerene cage must contain at least 20 atoms since the smallest fullerene must have 12 pentagons. Thus, a complete search of all possible atomic configurations and the calculation of their energetics are not practical. We therefore make use of the relative stability of boron nitride cage structures[13] as a guide. The fullerenes that obey the isolated pentagon rule (IPR) are most favorable since the shared edge of two pentagons destabilizes the structure. However there exists an additional factor to consider for fullerenes of III-IV group elements since the less stable homonuclear bonds are unavoidable in these systems. But, the number of homonuclear bonds can be minimized by arranging the pentagons adjacent so that some of the homonuclear bonds are shared. We therefore consider only non-IPR fullerenes up to 40 atoms in our calculations, where the stoichiometry is either Ga_xAs_{x+4} or $Ga_{x+4}As_x$.

The organization of this paper is as follows: a brief description of our calculation method and computational details is presented in Sec. II and is followed by our results in Sec. III. The atomic structures and energetics of gallium arsenide fullerenes are discussed in Sec. III A. The electronic structure of the fullerenes is presented in Sec. III B. In Sec. III C, molecular dynamics results are used to determine the thermal stability of the gallium arsenide clusters. Finally, we summarize our findings in Sec. IV.

II. COMPUTATIONAL METHOD

Our geometry optimization and total-energy calculations were based on the density-functional theory within the local-


$Ga_{12}As_8$ $Ga_{15}As_{11}$ $Ga_{16}As_{12}$

$Ga_{17}As_{13}$ $Ga_{18}As_{14}$ $Ga_{19}As_{15}$

$Ga_{20}As_{16}$ $Ga_{21}As_{17}$ $Ga_{22}As_{18}$

FIG. 1. (Color online) The Ga-rich $Ga_{y+4}As_y$ non-IPR fullerenes. The number of Ga atoms is higher than the number of As atoms by 4. The atoms on the shared edges of pentagons are occupied by Ga atoms. The Ga atoms are indicated by red (dark) and As atoms by white (light) colors.

density approximation, as implemented in SIESTA[14] code. We used Perdew-Zunger[15] parametrization for the exchange-correlation functional and a double-ζ basis set augmented by polarization orbitals. The interaction between the core and valence electrons was handled by Troullier-Martins norm-conserving pseudopotentials[16] in their fully separable form.[17] In Ga pseudopotential, also d orbitals are included in the valence configuration. We performed test calculations for zinc blende GaAs bulk and for small gallium arsenide clusters, where either experimental or all-electron computational data are available. Our calculated lattice constant value for bulk GaAs, $a=5.645$ Å, is in very good agreement with experimental lattice constant of $a=5.65$ Å, and bond lengths in small GaAs clusters such as Ga_2As_2 are in good agreement with previous all-electron calculations.[18]

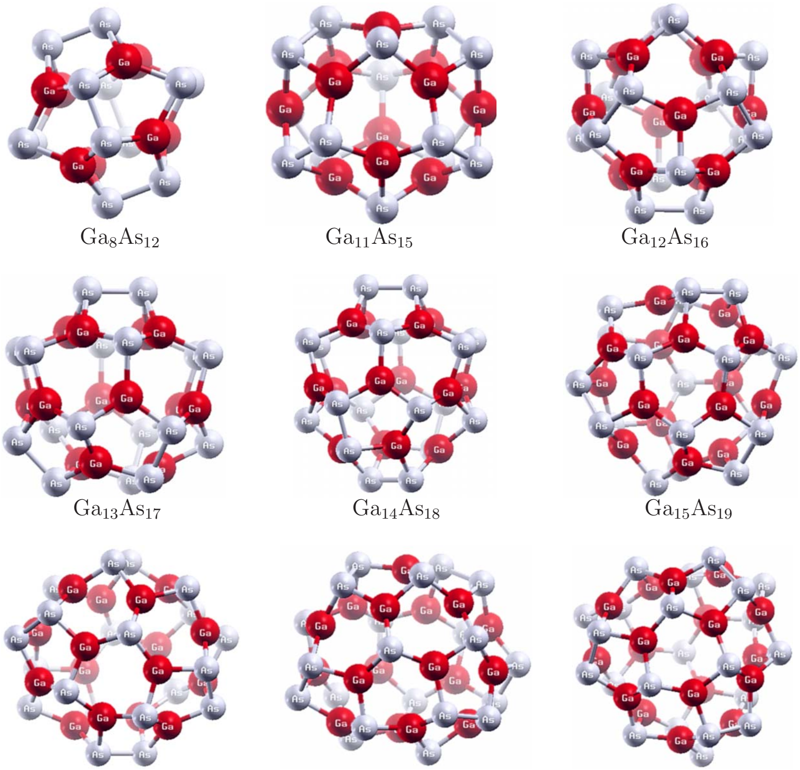
Optimized geometries were obtained without any symmetry constraints and continued until all force components on each atom are less than 0.01 eV/Å using a conjugate-gradient algorithm. We compare total energies of stable fullerenelike clusters to bulk reference GaAs systems to determine the stability of the clusters. The energy gap between the highest-occupied molecular orbital and the lowest-occupied molecular orbital levels is used as an additional guide in determining the stable systems. Thermal stability was determined by using microcanonical molecular dynamics simulations with 1 fs time steps at several elevated average temperature values.

III. RESULTS AND DISCUSSION

In order to determine the stability of gallium arsenide fullerenes we will make use of the cohesive energy, energy change in a model reaction, energy gap in the electronic structure, and thermal stability in molecular dynamics simulations. We first looked at the total energies of optimized gallium arsenide fullerenes. The structures with lower total energies are energetically more likely than the systems with higher values. In a chemical environment, specifically in air, the lower reactivity of the clusters used to decide which systems are chemically more stable. Smaller energy-gap values are used as an indication for lower reactivity and thus increased chemical stability. In addition to these ground-state calculations, we investigated the response of these systems to thermal excitations. The signature of "melting" was searched by molecular dynamics simulations at several temperatures.

A. Structure and energetics of the gallium arsenide clusters

The optimized atomic structures of Ga-rich gallium arsenide fullerenes with the formula of $Ga_{y+4}As_y$ are depicted in Fig. 1 for $8 \leq y \leq 18$, where the dark (red) color denotes the Ga atoms and light (white) color denotes the As atoms. The atoms on the other side are indicated by fading colors. In each structure there are 12 pentagons and six edges are shared by adjacent pentagons. The structures shown in Fig. 1 are the only isomers where alternating Ga and As atoms could be placed to give the minimum number of homonuclear bonds.[13] The common edges of adjacent pentagons consist of Ga-Ga bonds, and there are no other homonuclear bonds. In Ga-rich gallium arsenide fullerenes, Ga-Ga bond length is in the range of 2.41–2.47 Å and Ga-As bond length is in the range of 2.4–2.43 Å. The bond lengths show a negligible cluster size dependence. The Ga-As-Ga bond angles take the values of 90°–104°, while the As-Ga-As bond angles tend to have higher values of 115°–135°. The



Ga_8As_{12} $Ga_{11}As_{15}$ $Ga_{12}As_{16}$

$Ga_{13}As_{17}$ $Ga_{14}As_{18}$ $Ga_{15}As_{19}$

$Ga_{16}As_{20}$ $Ga_{17}As_{21}$ $Ga_{18}As_{22}$

FIG. 2. (Color online) The As-rich Ga_xAs_{x+4} non-IPR fullerenes. The number of Ga atoms is less than the number of As atoms by 4. The shared edges of the pentagons are occupied by As atoms. The Ga atoms are indicated by red (dark) and As atoms by white (light) colors.

As-Ga-Ga bond angle at the shared pentagon edge is ≈112°, which lies between the above bond angle ranges.

In Fig. 2, the As-rich gallium arsenide fullerenes are shown. In As-rich fullerenes, the shared edges of adjacent pentagons consist of As-As bonds. In both Ga-rich and As-rich fullerenes, arsenic atoms tend to protrude out of the cluster. This behavior is reflected in smaller bond angles of Ga-As-Ga compared to As-Ga-As angles: the Ga-As-Ga bond angle values are between 80° and 100° and the As-Ga-As bond angle values are in the range of $110°-130°$. The As-As bond length varies in the small range of $2.4-2.5$ Å in As-rich fullerenes and the Ga-As bond length is in the range of $2.38-2.42$ Å, which is somewhat smaller compared to the Ga-rich fullerenes. The Ga-As-As bond angle at the shared edge of the pentagons is ≈100°, which is smaller than the bond angle at the shared edge in Ga-rich fullerenes.

The comparison of structural features between Ga-rich and As-rich fullerenes is dominated by the tendency of As to make bonds with 90° bond angle and Ga atoms to make 120° bond angles. As a result, the As atoms stick out of the fullerene surface and more compact fullerenes are formed in the case of As-rich systems, which is best seen by comparing $Ga_{12}As_8$ in Fig. 1 and Ga_8As_{12} in Fig. 2.

Since all the structures shown in Figs. 1 and 2 are relaxed up to a very small residual force values, the gallium arsenide fullerenes correspond to local minima in the energy landscape. This information alone cannot tell which stoichiometry is better for better stability. Therefore, we compare total energies of these fullerenes in order to determine the relative energetic stabilities of different compositions.

The binding energy per atom for gallium arsenide fullerenes with general formula of Ga_xAs_y is shown in Fig. 3(a), where $x+y$ gives the total number of atoms in a fullerene. The binding energy of Ga-rich fullerenes decreases monotonically by the increasing system size and changes by ≈0.15 eV/atom going from Ga_8As_{12} to $Ga_{18}As_{22}$. This behavior indicates that there exists a strain in Ga-rich fullerenes that is released by the enlarged diameter. In contrast, the binding energy of As-rich fullerenes saturates when the system size is beyond 30 atoms. Therefore, the bond angle requirements of the As atoms in the shared edges of adjacent pentagons are satisfied by only a small strain energy investment. The Ga-As bond lengths are not drastically different between the Ga-rich and As-rich fullerenes. Therefore, one of the main reasons for lower total energies in As-rich fullerenes must be the fact that As-As bonds are energetically more favorable than Ga-Ga bonds. This conclusion is in agreement with the findings that As atoms cluster in small gallium arsenide clusters.[2]

Based on the binding energies, the As-rich fullerenes must be more stable than the Ga-rich fullerenes. This was in contrary to our naive expectation based on the atomic structure only. The Ga-rich fullerenes are more round than As-rich fullerenes, and we expected that the Ga-rich fullerenes should be energetically more favorable. However, even for GaAs surface, the ground state structure is the one with As atoms raised above the surface. A similar trend exists also for our gallium arsenide fullerenes.

In order to get an insight on the comparison of the binding energies of the Ga_xAs_y fullerenes with other clusters of gallium and arsenide, we cut a structure of 51 atoms from bulk GaAs crystal. After a full structure optimization, an extensive surface reconstruction is observed. The binding energy for this not-hollow cluster was ≈3.6 eV per atom, which is comparable to our binding energies for the Ga_xAs_y

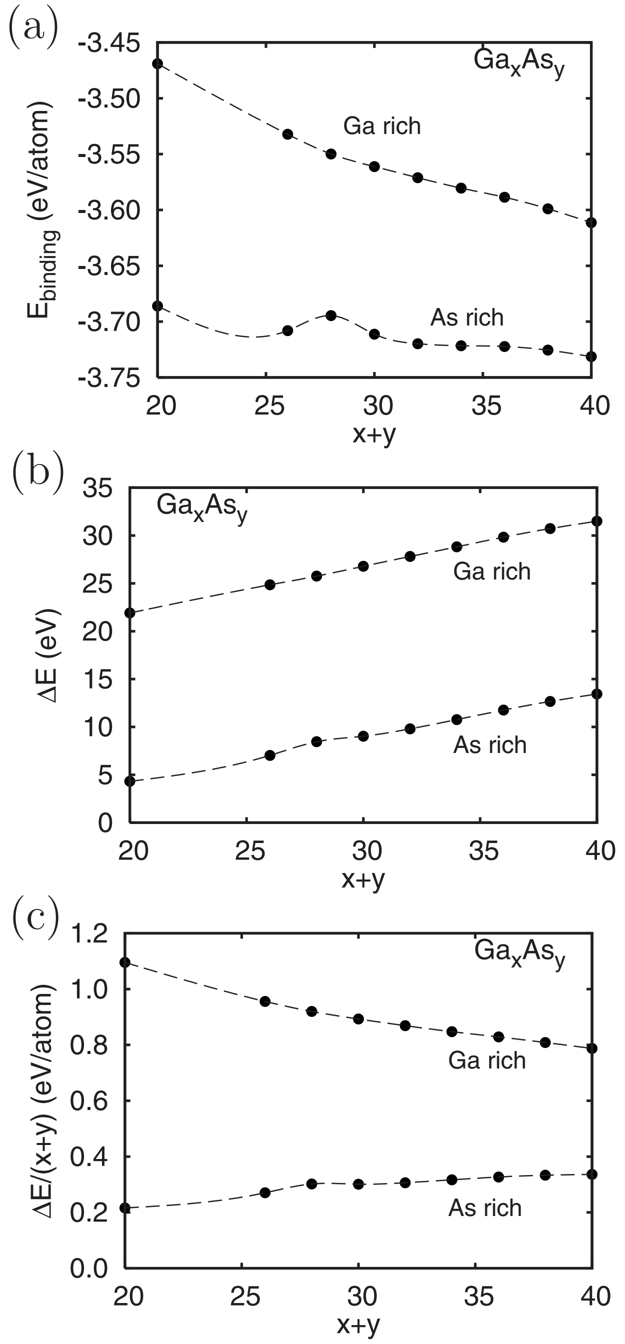


FIG. 3. The energetics of Ga_xAs_y non-IPR fullerenes in Ga-rich fullerenes ($x=y+4$) and in As-rich fullerenes ($y=x+4$). (a) Binding energy of the bulk Ga_xAs_y fullerenes as a function of the total number of atoms ($x+y$). (b) The reaction energy during a synthesis of the fullerenes starting from bulk GaAs and As_2 gas. The reaction energy per atom is shown in (c). Arsenic-rich fullerenes are more stable energetically.

fullerenes. Although the way a cluster is produced from the bulk geometry may be optimized to get better cohesive energy results, the binding energy for our system sizes should be not much different. Therefore, the Ga_xAs_y fullerenes are energetically as stable as their counterparts with filled central regions.

We consider now the energetics of possible reactions using bulk GaAs and As_2 gas as reactants or products, depending on the stoichiometry. The Ga-rich fullerenes are assumed to be obtained by the model reaction $(n+4)\mathrm{GaAs} \rightarrow \mathrm{Ga}_{n+4}\mathrm{As}_n + 2\mathrm{As}_2$ and the As-rich fullerene production is assumed to proceed by consuming the As_2 gas in the $n\mathrm{GaAs}+2\mathrm{As}_2 \rightarrow \mathrm{Ga}_n\mathrm{As}_{n+4}$ reaction. The rate of these reactions can be manipulated by changing the concentration of As_2 over the GaAs bulk sample that is irradiated by the laser. The total-energy change ΔE or the difference between the summation of total energies of the products and that of the reactants is always positive. In other words, we found the above reactions to be endothermic.

The total-energy change ΔE is given in Fig. 3(b) as a function of the total number of atoms $x+y$ in Ga_xAs_y fullerenes and increases by the increasing system size. The energy investment for Ga-rich gallium arsenide fullerenes is higher by ≈ 17 eV per fullerene than for As-rich fullerenes of the same size. In order to obtain Ga-rich fullerenes, the Ga-As bonds must be broken and As-As in As_2 molecule must be formed. Since the As-As bond strength is smaller than that of the Ga-As bond in GaAs solid, we observe large differences between the reaction energies for Ga-rich and for As-rich fullerenes.

The energy change per atom $\Delta E/(x+y)$, which is shown in Fig. 3(c), indicates a larger system size $x+y$ dependence for Ga-rich fullerenes. On the basis of our calculated reaction energy values, the As-rich fullerenes are more probable to occur. The formation energy per atom for As-rich fullerenes is between 0.2 and 0.4 eV. These small energy values should make As-rich fullerenes accessible during laser ablation experiments in a gas environment of high As_2 concentration.

B. Electronic structure of the gallium arsenide fullerenes

We use the energy gap E_g, which is the difference between lowest-unoccupied energy level and highest-occupied energy level, as an indicator for the chemical stability of the fullerenes. The clusters with small energy gaps are often not air stable and are absent in isotope mixtures. Our results for E_g are summarized in Fig. 4, where solid circles are used for As-rich fullerenes and open circles are used for Ga-rich systems. The As-rich fullerenes has E_g of 1.5–1.7 eV, while the E_g of Ga-rich fullerenes are below 1.0 eV. The values shown in Fig. 4 point out a stark difference between the reactivity of Ga-rich and As-rich fullerenes: the As-rich fullerenes are expected to be more resilient in air than the Ga-rich fullerenes. This conclusion is inline with our above findings, which were based on the energetics of the optimized gallium arsenide fullerenes.

In order to get a hint about the bonding character in the Ga_xAs_y clusters, we have performed Mulliken population analysis. We regarded the population numbers as indicators for the direction of the charge transfer between the atoms. Note that the absolute value of the population numbers contains uncertainty since these numbers do depend on the basis set chosen. Our analysis indicates a charge transfer in the fullerenes similar to the bulk GaAs, albeit at smaller values. Therefore, the bonding between Ga and As atoms are partially ionic in the Ga_xAs_y fullerenes.

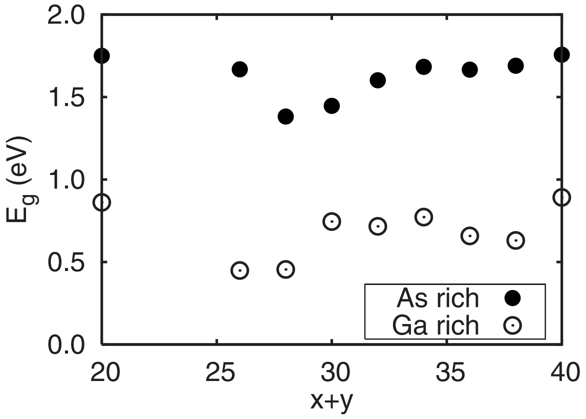


FIG. 4. The energy gap in the electronic structure of $\mathrm{Ga}_x\mathrm{As}_y$ non-IPR fullerenes. Open circles denote the gallium-rich fullerenes ($x=y+4$) and solid circles denote arsenic-rich fullerenes ($y=x+4$). The arsenic-rich fullerenes are expected to be more stable.

C. Thermal stability of the gallium arsenide fullerenes

We started our microcanonical MD simulations with optimized coordinates and with the initial temperature of T_0. Since the total energy is constant during the simulation, the average temperature after the system reaches equilibrium should be $T_0/2$ if the system stays in the harmonic limit. In the case of exploring the unharmonic regime, the average equilibrium temperature would stay below $T_0/2$. Such a deviation from the value that was based on the equipartition theorem indicates an onset of a phase transition or a so-called melting although the transitions are not sharp in small systems.

The average temperature $\langle T\rangle$ in our microcanonical MD simulations with the initial temperature values of T_0 is presented in Fig. 5(a) for all gallium arsenide fullerene structures that are shown in Figs. 1 and 2. For each MD run, the system was equilibrated for 0.5 ps before the time average of the temperature over 2 ps was calculated. In Fig. 5, the open circles are used for Ga-rich fullerenes and solid circles are used for As-rich fullerenes. The dotted line denotes the expected place of the data points if the system stayed in the harmonic limit. Above $\langle T\rangle \approx 500$ K, the molecular dynamics simulations show an onset of a phase transition. Although the atomic structure is not disintegrated within our MD time scale of a few picoseconds, we do not expect these fullerene structures to be stable beyond 500 K.

The difference in the stabilities of Ga-rich and As-rich fullerenes is apparent also in Fig. 5(a): the average temperature values $\langle T\rangle$ for Ga-rich fullerenes are systematically lower than that for As-rich fullerenes. Therefore, a higher amount of energy is invested as the potential energy in Ga-rich clusters than in As-rich clusters. This energy investment is in the potential energy toward imminent structural changes.

Another quantity to disclose the onset of a structural transition is the time-averaged potential energy $\langle U\rangle$. The time average of the potential-energy difference from the $T=0$ value of the potential energy $\langle \Delta U\rangle$ is shown in Fig. 5(b), where the x axis is time average of the temperature. The classical behavior with $3/2kT$ slope is indicated by the dashed line in Fig. 5(b), which must be followed if the system stays in the harmonic limit. Note that the average potential energy values for Ga-rich fullerenes have the largest deviations. Therefore, the Ga-rich fullerenes should go through a structural transition at earlier temperatures than their As-rich counterparts.

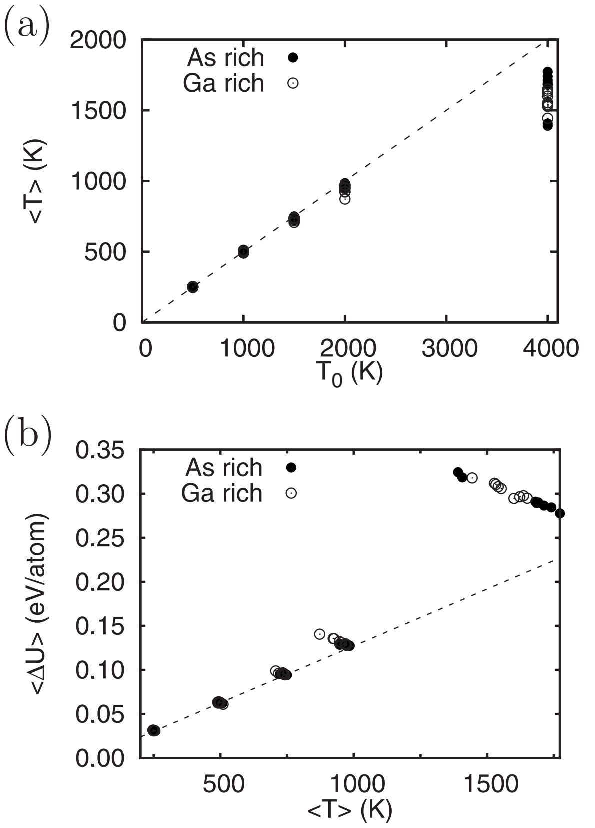


FIG. 5. MD simulations of $\mathrm{Ga}_x\mathrm{As}_y$ fullerenes. (a) The average temperature $\langle T\rangle$ during microcanonical classical MD simulations, which were started with the initial temperature of T_0. (b) The time-averaged potential energies of the clusters versus the time-averaged temperature $\langle T\rangle$ of the system during microcanonical MD simulations. The dashed lines represent the behavior of a system within the harmonic limit. The deviation from the linear line is an indicator of the onset of a structural transition.

Our molecular dynamics results suggest that gallium arsenide fullerenes are stable under moderate thermal excitations and start melting above ≈ 500 K. The As-rich fullerenes are more resilient to thermal excitations. Our results suggest that gallium arsenide fullerenes are stable with comparable binding energies to bulk GaAs and have an energy gap in the electronic structure on the order of the band gap of the bulk GaAs. Among the gallium arsenide fullerenes, we found that As-rich fullerenes with general formula of $\mathrm{Ga}_x\mathrm{As}_{x+4}$ are more likely to occur. The As-rich fullerenes have higher energy gaps in their electronic structure. Thus, they are expected to be stable in air and in other chemically active environments. Molecular dynamics simulations corroborate with the ground-state data and indicate that these structures are stable under moderate thermal excitations. We suggest that these stable As-rich fullerenes may

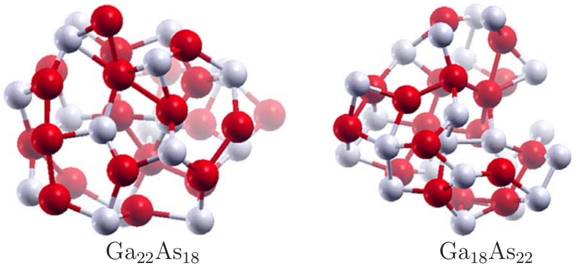


FIG. 6. (Color online) The atomic structure of thermally decaying (a) $Ga_{22}As_{18}$ and (b) $Ga_{18}As_{22}$ fullerenes, where the Ga atoms are indicated by red (dark) and As atoms by white (light) colors.

be produced in a high-As_2-concentration atmosphere.

We depict a Ga-rich fullerene in Fig. 6(a) and a As-rich fullerene in Fig. 6(b), which are collapsed in our molecular dynamics simulations at elevated temperatures, that is, reaching 1500 K. The final structure is not necessarily the ground-state atomic structure for these clusters and subsequent reconstruction may occur after the collapse of the cage. However, it is apparent that a hollow cage is unstable at high temperatures of 1500 K. We observe new Ga-Ga bonds appearing in Fig. 6(a) during the collapse, which is not surprising since the structure has excess Ga. However, the collapsing As-rich fullerene in Fig. 6(b) has also a noticeable tendency to form Ga-Ga bonds during the collapse. Therefore, we conclude that the collapse of the fullerenes is initiated by Ga-Ga bond formations. There is also an indication that As atoms prefer to stay on the surface while the system goes through the structural changes. We expect the system to evolve further. In principle, the collapse of the fullerene may be avoided if the Ga atoms are prevented from making Ga-Ga homonuclear bonds. We expect this could be achieved by inclusion of a transition metal atom inside, which will be the subject of our future study on this system.

IV. SUMMARY AND CONCLUSION

In summary, we have investigated the atomic structure and stability of $Ga_xAs_{x\pm4}$ gallium arsenide fullerenes by using *ab initio* structure optimization, electronic structure, and molecular dynamics simulations. We found that the hollow gallium arsenide fullerenes are stable when the pentagon edges are shared to reduce the number of homonuclear bonds. We used the energetics, the energy gap in the electronic structure, and the response of the system to thermal excitations as indicators for the stability of the gallium arsenide fullerenes. We found that As-rich fullerenes are more likely to occur and a successful synthesis may involve using high As_2 partial pressure over the GaAs bulk target. The hollow gallium arsenide fullerenes show the signature of structural transformations beyond 500 K through the formation of Ga-Ga homonuclear bonds. Thermal stability is the biggest obstacle for obtaining the gallium arsenide fullerenes in experiments. Preventing inner Ga atoms to make bonds with each other may be a path for gallium arsenide fullerenes and hollow cages in general.

ACKNOWLEDGMENTS

S.B. acknowledges financial support from the Nanoscale Science and Engineering Center for High-Rate Nanomanufacturing (NSF NSEC under Grant No. 425826). Calculations were performed at the High Performance Computing Center at Michigan State University.

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[1] S. C. O'Brien, Y. Liu, Q. Zhang, J. R. Heath, F. K. Tittel, R. F. Curl, and R. E. Smalley, J. Chem. Phys. **84**, 4074 (1986).
[2] W. Andreoni, Phys. Rev. B **45**, 4203 (1992).
[3] L. Wang, L. P. F. Chibante, F. K. Tittel, R. F. Curl, and R. E. Smalley, Chem. Phys. Lett. **172**, 335 (1990).
[4] Y.-C. Zhu, Y. Bando, L.-W. Yin, and D. Golberg, Chem.-Eur. J. **10**, 3667 (2004).
[5] M. Takata, B. Umeda, E. Nishibori, N. Sakata, Y. Saito, M. Ohno, and H. Shinohara, Nature (London) **377**, 46 (1995).
[6] E. Nishibori, K. Iwata, M. Sakata, M. Takata, H. Tanaka, H. Kato, and H. Shinohara, Phys. Rev. B **69**, 113412 (2004).
[7] D. Golberg, Y. Bando, O. Stéphan, and K. Kurashima, Appl. Phys. Lett. **73**, 2441 (1998).
[8] E. Bengu and L. D. Marks, Phys. Rev. Lett. **86**, 2385 (2001).
[9] A. Zak, Y. Feldman, V. Alperovich, R. Rosentsveig, and R. Tenne, J. Am. Chem. Soc. **122**, 11108 (2000).
[10] V. Tozzini, F. Buda, and A. Fasolino, Phys. Rev. Lett. **85**, 4554 (2000).
[11] J. Zhao, R.-H. Xie, X. Zhou, X. Chen, and W. Lu, Phys. Rev. B **74**, 035319 (2006).
[12] J. Zhao, L. Ma, D. Tian, and R. Xie, J. Comput. Theor. Nanosci. **5**, 7 (2008).
[13] P. W. Fowler, K. M. Rogers, G. Seifert, M. Terrones, and H. Terrones, Chem. Phys. Lett. **299**, 359 (1999).
[14] J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, J. Phys.: Condens. Matter **14**, 2745 (2002).
[15] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[16] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
[17] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).
[18] G. L. Gutsev, M. D. Mochena, and C. W. Bauschlicher, Jr., Chem. Phys. Lett. **439**, 95 (2007).