

A full-potential linear-muffin-tin-orbital molecular-dynamics study on the distorted cage structures of Si_{60} and Ge_{60} clusters

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1999 J. Phys.: Condens. Matter 11 8517

(<http://iopscience.iop.org/0953-8984/11/43/315>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.220

The article was downloaded on 15/05/2010 at 17:42

Please note that [terms and conditions apply](#).

A full-potential linear-muffin-tin-orbital molecular-dynamics study on the distorted cage structures of Si₆₀ and Ge₆₀ clusters

Bao-xing Li^{†‡}, Ming Jiang[†] and Pei-lin Cao[†]

[†] Department of Physics and State Key Laboratory of Silicon Material, Zhejiang University, Hangzhou, Zhejiang 310027, China

[‡] Department of Physics, Hangzhou Teachers College, Hangzhou, Zhejiang 310012, China

Received 28 April 1999, in final form 4 August 1999

Abstract. Using a full-potential linear-muffin-tin-orbital molecular-dynamics (FP-LMTO-MD) method, we have performed calculations on the structures and the binding energies of Si₆₀ and Ge₆₀ clusters. The results calculated suggest that the stable structures for Si₆₀ and Ge₆₀ clusters are both distorted truncated icosahedra, with T_h symmetry. Their fullerene cage structures remain, but they look like puckered balls. Four distinct Si–Si bond lengths in Si₆₀, three distinct Ge–Ge bond lengths in Ge₆₀, and lower T_h symmetry make the two structures different from that with I_h symmetry and two C–C bond lengths in C₆₀.

1. Introduction

Studies on the structures and electronic and chemical properties of C_n [1–6], Si_n [7–12], and Ge_n [13–17] clusters have produced a wealth of exciting information about their potential applications. Their fullerene structures have attracted considerable attention. The existence of the fullerenes as a family for C and Si clusters has become established; among the various structures, the C₆₀ cage is the most fascinating. The structure of C₆₀ is a truncated icosahedron with I_h symmetry, containing 20 hexagons and 12 pentagons on its almost spherical surface. Silicon and germanium are the heavier homologues in the periodic table. We may expect Si₆₀ and Ge₆₀ also to have cage structures and interesting properties.

Up to now, a few reports [18–25] have involved Si₆₀ structure, but the results are controversial. The authors of references [20–23] have proposed that Si₆₀ still exhibits the same buckminsterfullerene structure (I_h symmetry) as C₆₀, using a double-zeta (DZ) basis set with *ab initio* effective-core potentials (ECP) on silicon atoms or the Austin model 1 method. Their calculated results suggest that the perfect cage structure represents a minimum of the potential energy surface, which is much more favourable than a stacked naphthalene structure or a cylindrical structure. But, using a conventional orthogonal tight-binding molecular dynamics [24], Khan and Broughton have found that the icosahedral cage structure of Si₆₀ is not stable and relaxes into a structure resembling a puckered ball. By the same method, Menon and Subbaswamy found that the perfect icosahedral cage is unstable, distorting to a lower-symmetry C_{2h} structure with no change in the threefold coordination [25]. They proposed that a Si₆₀ network is more stable than a Si₆₀ fullerene with C_{2h} symmetry, but for C₆₀ clusters, the former is less favourable than the latter.

Experimental results are also controversial. A saturation study of Si₆₀ positive ions shows that the average number of ammonia molecules absorbed rapidly is close to 6 [26]. This

may imply the fullerene structure [27]. However, fragmentation analysis of Si_{60} positive ions supports the hypothesis of a stacked naphthalene-like structure [28].

Germanium is contiguous to silicon in the periodic table. A few reports have involved their similarities [14, 15, 29, 30]. Photofragmentation and reactivity results obtained in some of the semiconductor cluster experiments [31, 32] gave evidence that the structures of silicon and germanium clusters may be much the same. For the larger clusters, Si_{60} and Ge_{60} , is there still this similarity between them in structure? Nagase investigated the structure of Ge_{60} [22]. Nagase also proposed that the perfect cage structure is the structure of Ge_{60} . But, the authors of reference [25] concluded that, among the group IV elements, perfect icosahedral symmetry is unique to carbon. In the hope of obtaining more accurate structures and establishing the similarities of and differences between the two clusters, we employ a more sophisticated method to investigate Si_{60} and Ge_{60} . The aim in this paper is to find the structures of Si_{60} and Ge_{60} corresponding to the most important buckminsterfullerene structure (I_h symmetry) of C_{60} , and then to make a comparison between them. Our calculated results reveal that the corresponding structures of Si_{60} and Ge_{60} clusters are both distorted cage structures, with the same symmetry T_h , but Ge_{60} is slightly less distorted than Si_{60} .

2. Method

The FP-LMTO method [35–39] is a self-consistent implementation of the Kohn–Sham equations in the local-density approximation [33]. This method expands the electron wave functions in terms of muffin-tin orbitals [34]. Also, this method uses a completely general form for the potential and density in which space is divided into non-overlapping muffin-tin spheres and the remaining interstitial region (in which the potential is expressed as a linear combination of Hankel functions), instead of the atomic sphere approximation (ASA). The details of how the molecular-dynamics simulation can be performed are given in references [35, 36].

3. Structures and discussion

The perfect truncated icosahedron of C_{60} is a very stable cage structure, in which each atom is bonded to three other atoms and there are two distinct bond lengths: six–six ring fusion and five–six ring fusion. The fullerene cage is the most important structure among all of the isomers of the C_{60} cluster. We wondered whether the heavier homologues Si and Ge would also form the same stable icosahedral cage structures as the C_{60} cluster. Starting with perfect icosahedral configurations in proportion to that of C_{60} , we have performed calculations on Si_{60} and Ge_{60} clusters by using the full-potential linear-muffin-tin-orbital molecular-dynamics (FP-LMTO-MD) method. In the process of optimization, no restrictions are imposed. The process is stopped when the condition of self-consistency is met. We find that the initial perfect icosahedral configurations with I_h symmetry for Si and Ge are both unstable, distorting to a geometry with lower T_h symmetry but the same coordination. We present the three cage structures of the C_{60} , Si_{60} , and Ge_{60} clusters in figure 1, from left to right. Two-dimensional perspective views of two of them (Si_{60} on the left and Ge_{60} on the right) are shown in figure 2, and their point groups, bond lengths, and binding energies are given in table 1. It is obvious that their cage structures have become seriously deformed, like puckered balls, in which three polygons (a pentagon and two hexagons) have been distorted. The included angles between the edges of the polygons have obviously changed. The root mean square deviations $\delta\theta$ of the included angles relative to those of the perfect cage are given in table 2.

The data suggest that Ge_{60} does indeed resemble Si_{60} in structure. However, it is found

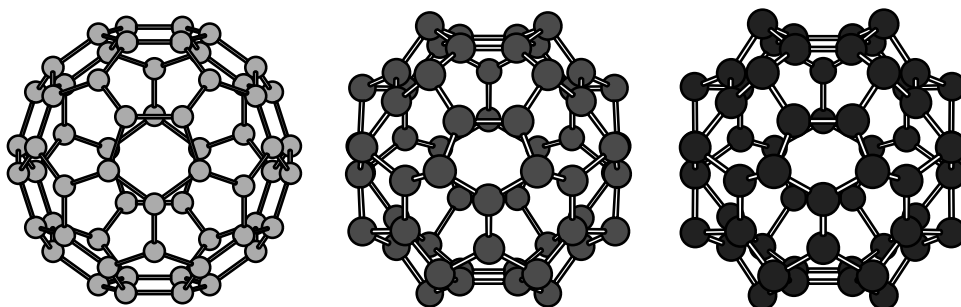


Figure 1. The final configurations of the molecular-dynamics optimization for Si_{60} and Ge_{60} . The distorted structures have T_h symmetry. The structures shown are those of, from left to right, C_{60} , Si_{60} , and Ge_{60} .

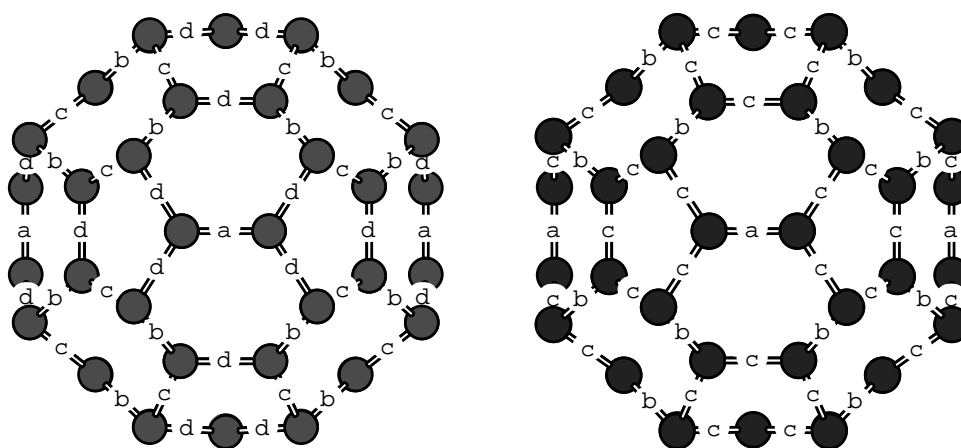


Figure 2. Two-dimensional perspective views of Si_{60} (on the left) and Ge_{60} (on the right). a , b , c , and d represent the four different bond lengths of Si_{60} . There are only three bond lengths, a , b , and c , in the Ge_{60} cluster.

Table 1. The point groups, bond lengths (a , b , c , d (Å)), and binding energies (eV/atom) for Si_{60} and Ge_{60} clusters.

Cluster	Point group	a	b	c	d	Binding energy
Si_{60}	T_h	2.218	2.271	2.280	2.295	4.899
Ge_{60}	T_h	2.364	2.434	2.449	—	3.226

that all three values of $\delta\theta$ for Ge_{60} are less than those of Si_{60} , as given in table 2. In addition, all the five edge lengths of the pentagons in Ge_{60} are equal, but this is not so for Si_{60} . Ge_{60} seems to be slightly less distorted than Si_{60} . Despite their distortion, they both still have high symmetry, T_h . There are four bond lengths, with average 2.279 Å, ranging from 2.218 Å to 2.295 Å for the Si_{60} cluster. But Ge_{60} has only three bond lengths. Its average bond length is 2.439 Å, situated between the minimum 2.364 Å and the maximum 2.449 Å. Obviously, our structures are different from the perfect cage structures reported previously in references [18–23]. Despite

Table 2. Root mean square deviations $\delta\theta$ (deg) of the included angles in the three polygons relative to those of the perfect cage. $\delta\theta_1$ refers to that of the pentagon, $\delta\theta_2$ and $\delta\theta_3$ to those of the two hexagons.

Cluster	$\delta\theta_1$	$\delta\theta_2$	$\delta\theta_3$
Si ₆₀	9.93	8.80	18.62
Ge ₆₀	8.16	8.76	16.43

the structure of Si₆₀ found in this work being similar to that—resembling a puckered ball—reported by Khan, Menon [24, 25], our result is different from theirs. Firstly, the structure obtained by us has a different symmetry from theirs, although these structures have all distorted into lower-symmetry forms. Our structure has T_h symmetry, while Si₆₀ has C_{2h} symmetry in reference [25]. Secondly, there are four distinct bond lengths in our structure, but all of the bonds are approximately of length 2.37 Å in reference [24]. For the Ge₆₀ cluster, to our knowledge, the structure like a puckered ball, with T_h symmetry, is reported for the first time here. Our calculations suggest that the structures of Si₆₀ and Ge₆₀ are about the same. But there are some slight differences between them: four distinct bond lengths in Si₆₀ and three distinct bond lengths in Ge₆₀; and different included-angle changes for the polygons.

4. Summary

Using a full-potential linear-muffin-tin-orbital molecular-dynamics (FP-LMTO-MD) method, we have performed calculations on the structures of the large clusters Si₆₀ and Ge₆₀ corresponding to the fullerene cage structure of the C₆₀ cluster. The calculated results suggest that the corresponding stable structures of the clusters Si₆₀ and Ge₆₀ are both distorted icosahedral cages resembling puckered balls, with T_h symmetry. Ge₆₀ is slightly less distorted than Si₆₀ in structure. There are four different bond lengths in Si₆₀, but only three for the Ge₆₀ cluster.

Acknowledgments

This work was supported by the National Natural Science Foundation of China. We are very grateful to Dr M Qiu and Dr Y J Zhao for fruitful discussions about Si₆₀ and Ge₆₀ clusters.

References

- [1] Kroto H W, Allaf A W and Balm S P 1991 *Chem. Rev.* **91** 1213
- [2] Phillips J C 1985 *J. Chem. Phys.* **83** 3330
- [3] Elkind J L, Alford J M, Weiss F D, Laaksonen R T and Smalley R E 1987 *J. Chem. Phys.* **87** 2397
- [4] Jarrold M F and Honea E C 1991 *J. Phys. Chem.* **95** 9181
- [5] Diederich F and Whetten R L 1991 *Angew. Chem. Int. Edn Engl.* **30** 678
- [6] Fuke K, Tsukamoto K, Misaizu F and Sanekata M 1993 *J. Chem. Phys.* **99** 7807
- [7] Jarrold M F 1991 *Science* **252** 1085
- [8] Grossman J C and Mitas L 1995 *Phys. Rev. B* **52** 16 735
- [9] Bahel A and Ramakrishna M V 1994 *Phys. Rev. B* **51** 13 849
- [10] Kaxiras E 1989 *Chem. Phys. Lett.* **163** 323
- [11] Ray U and Jarrold M F 1991 *J. Chem. Phys.* **94** 2631
- [12] Raghavachari K 1988 *J. Chem. Phys.* **89** 2219
- [13] Archibong E F and St-Amant A 1998 *J. Chem. Phys.* **109** 962
- [14] Dixon D A and Gole J L 1992 *Chem. Phys. Lett.* **188** 560
- [15] Dai D and Balasubramanian K 1992 *J. Chem. Phys.* **96** 8345
- [16] Dai D, Sumathi K and Balasubramanian K 1992 *Chem. Phys. Lett.* **193** 251

- [17] Dai D and Balasubramanian K 1996 *J. Chem. Phys.* **105** 5901
- [18] Piqueras M C, Crespo R, Orti E and Tomas F 1993 *Synth. Met.* **61** 155
- [19] Crespo R, Piqueras M C and Tomas F 1996 *Synth. Met.* **77** 13
- [20] Piqueras M C, Crespo R, Orti E and Tomas F 1993 *Chem. Phys. Lett.* **213** 509
- [21] Nagase S and Kobayashi K 1991 *Chem. Phys. Lett.* **187** 291
- [22] Nagase S 1993 *Pure Appl. Chem.* **65** 675
- [23] Slanina Z, Lee S L, Kobayashi K and Nagase S 1994 *J. Mol. Struct. (Theochem.)* **312** 175
- [24] Khan F S and Broughton J Q 1991 *Phys. Rev. B* **43** 11 754
- [25] Menon M and Subbaswamy K R 1994 *Chem. Phys. Lett.* **219** 219
- [26] Jarrold M F, Ijiri Y and Ray U 1991 *J. Chem. Phys.* **94** 3607
- [27] Hirsch A, Li Q and Wudl F 1991 *Angew. Chem. Int. Edn Engl.* **30** 1309
- [28] Jelski D A, Wu Z C and George T F 1990 *J. Cluster Sci.* **1** 143
- [29] Pacchioni G and Koutecky J 1986 *J. Chem. Phys.* **84** 3301
- [30] Andzelm J, Russo N and Salahub D R 1987 *J. Chem. Phys.* **87** 6562
- [31] Alford J M, Laaksonen R T and Smalley R E 1991 *J. Chem. Phys.* **94** 2618
- [32] Zhang Q L, Liu Y, Curl R F, Tittel F K and Smalley R E 1988 *J. Chem. Phys.* **88** 1670
- [33] Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
- [34] Andersen O K 1975 *Phys. Rev. B* **12** 3060
- [35] Methfessel M and Schilfgaard M V 1993 *Int. J. Mod. Phys. B* **7** 262
- [36] Methfessel M and Schilfgaard M V 1993 *Phys. Rev. B* **48** 4937
- [37] Methfessel M 1988 *Phys. Rev. B* **38** 1537
- [38] Methfessel M, Rodriguez C O and Andersen O K 1989 *Phys. Rev. B* **40** 2009
- [39] Qiu M, Jiang M, Zhao Y J and Cao P L 1999 *J. Chem. Phys.* **110** 10738