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Stable structures of neutral and ionic Ge_n ($n=11$–19) clusters

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Abstract

The lowest-energy structures of neutral and ionic Ge_n ($n=11$–19) clusters are obtained by using the full-potential linear-muffin-tin-orbital molecular-dynamics (FP-LMTO-MD) method based on some genetic operations. We find a number of new ground state structures, which are more stable than those reported previously. Most of the lowest energy structures for the neutral and ionic Ge_n ($n=11$–19) clusters are obviously different from those of the corresponding Si_n clusters although the geometrical configurations of the small clusters ($n<10$) are basically the same. Our results also show that all the lowest energy structures of the cationic Ge_n ($n=11$–19) clusters have the similar geometrical configurations to those of the corresponding neutral Ge_n ($n=11$–19) clusters except for $n=11$. However, for the anionic Ge_n ($n=11$–19) clusters, the conclusion is almost the reverse. In addition, for the smaller clusters with $n\leq 13$, the polyhedral structures are more favorable, while the larger clusters from $n=14$ prefer the stacked structures. For the negative ions, their ground state structures transit from stacked structures into compacted structures at $n=18$.

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Keywords: Ionic Ge cluster; Stable structure; Binding energy

1. Introduction

Clusters containing a few to thousands of atoms are of scientific importance. In this regime, their physical and chemical properties change with their size. Therefore, the clusters often demonstrate many unexpected characteristics different from those in the bulk solids. During the past several decades, the cluster science has already obtained huge development. In particular, the semiconductor clusters have been intensively investigated both experimentally and theoretically because of their potential applications in the microelectronics industry. For silicon clusters, many experimental and theoretical reports can be found. However, for germanium clusters, there are only a few reports about their structures and properties [1–9]. So far, the structures of the Ge clusters with only $n\leq 10$ are already well understood, while our knowledge of the Ge clusters with $n>10$ is still quite limited.

Theoretically, Antonio and his co-workers investigated the ground-state structures and finite temperature properties of the Ge clusters ranging from $n=2$ to 14, by using molecular-dynamics simulation along with the method of steepest decent quench [1,2]. The interaction potential adopted was the Stillinger–Weber potential as modified by Ding and Andersen. Ogut et al. studied the electronic structures of the neutral and charged Ge_n clusters ($n=2$–10) using Langevin molecular dynamics coupled to a simulated annealing procedure [3]. Their calculations suggested that the ground-state structures might significantly change in comparison to the neutral case upon charging Ge_n clusters with $n\geq 8$ negatively. In addition, they explained the substantial differences in the photoemission spectra of some anionic Si and Ge clusters. Shvartsburg et al. carried out a systematic ground state geometry search for the Ge_n neutral and cations in the range of $n\leq 16$ using density functional theory-local density approximation and gradient-corrected methods [4]. They found that, like the Si clusters, the Ge clusters consist of the tricapped trigonal prism subunits. However, starting from $n=13$, the structures of the Ge_n and Si_n clusters for certain sizes differ in details. For the larger Ge_n clusters, Wang et al. reported their ground-state structures with up to 25 atoms by using density functional theory (DFT) by use

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of a generalized gradient approximation (GGA) [5]. The Ge_n clusters follow a prolate growth pattern starting from $n=13$. A near-spherical compact cage-like structure appears in the Ge_{19} cluster.

Experimentally, Zhang et al. carried out laser photodissociation studies of the Ge positive cluster ions with up to $n=50$ [7]. At low laser fluences, the larger Ge_n^+ clusters sequentially lose Ge_{10} (and in some cases with lower intensity Ge_7). At high fluences, Ge_n^+ fragments to produce primarily positive ion clusters in the 6–11 size range. Hunter and coworkers examined the mobilities of Ge_n^+ ($n=7$–54) using injecting-ion drift-tube techniques [8]. They observed a prolate growth for the Ge_n^+ cluster ions with $n=10$–35. They also determined the dissociation energies of Ge_n^+ from the analysis of an injection energy threshold for the collision-induced dissociation. By comparison with the results on the dissociation energies, they proposed the structures of the Ge_n clusters with up to 70 atoms as weakly bound assemblies of small stable fragments such Ge_7 and Ge_{10}. Yoshida and Fuke performed photoionization investigation on the Ge_n ($n=2$–57) clusters in the energy region of 5.0–8.8 eV [9]. They found that the ionization potentials of the Ge_n clusters show a major maximum at $n=10$ and a rapid decrease between $n=15$ and 24. The Ge_n ($n>12$) clusters were found to exhibit the large gap in the ionization potentials at around 20 atoms.

We have also investigated some of the Ge_n clusters [10–13]. Ge_3 has an equilateral triangle (C_{2v}) as its lowest-energy structure of Ge_3. The ground state structure of Ge_4 is a rhombus with D_{2h}. The most stable structures for Ge_{5-7} are trigonal bipyramid (D_{3h}), tetragonal bipyramid (D_{4h}) and pentagonal bipyramid (D_{5h}), respectively. For $n=8$, Ge has a face-capped pentagonal bipyramid as its ground-state structure. The lowest energy structure of Ge_9 has been accepted as a bicapped pentagonal bipyramid with C_{2v}. For $n=10$, the tetracapped octahedron with T_d is the most stable. For the charged Ge_n ($n=2$–10) clusters, some of the ground-state structures are different from those of the neutral clusters [11]. For the larger neutral Ge_n ($n=20$–25) clusters, their ground-state structures are stacked prolate structures [13].

To our knowledge, the reports of the systematic studies on the slightly larger ionic Ge_n clusters are few up to now. In this paper, we have studied the geometrical and electronic structures for the neutral, anionic and cationic Ge_n ($n=11$–19) clusters in detail by full-potential linear-muffin-tin-orbital molecular dynamics (FP-LMTO-MD) methods.

2. Method

The FP-LMTO method [14–17] is a self-consistent implementation of the Kohn–Sham equations in the local-density approximation [18]. This method expands the electron wave functions in terms of muffin-tin orbitals [19]. Also this method uses a completely general form for the potential and density in which space is divided into non-overlapping muffin-tin (MT) spheres and 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 method can be performed are described in Ref. [14–15]. Using the method above, we have performed calculations on a lot of initial atomic configurations set up by random selections of atomic positions in three-dimensional space. The separation of Ge–Ge atoms is confined in some range. Besides, some of the initial structures are built from the smaller germanium clusters by stacking. Optimization runs begin with the initial configurations. The stable structures obtained again construct new geometries by crossover, rotation and reflection operations like in genetic algorithms and single-parent evolution algorithm [20]. In the optimized structures, some structures with larger binding energies are selected. Their subunits or substructures are combined into new initial configurations with the same atomic number by the so-called crossover operation. On the other hand, we can also obtain a new initial geometry by performing rotation and reflection operations on some subunits or substructures of a stable structure through an axis or a plane. The operations are applied to our structural optimization in succession. A number of new isomers are found by mean of the

Table 1
Calculated bond lengths (in angstrom) of Ge_{3-7} clusters obtained by full-potential linear-muffin-tin-orbital molecular-dynamics (FP-LMTO-MD) method, compared to those obtained by Langevin molecular dynamics coupled to a simulated annealing procedure (Langevin MD) [3], B3LYP-DFT and CCSD(T) methods [23]

Cluster	Symmetry	Bond	Bond length (Å)		
			Langevin MD [3]	B3LYP-DFT [23]	FP-LMTO-MD
Ge_3	C_{2v}	d_{1-2}	3.20	2.91	3.12
		d_{1-3}	2.26	2.21	2.33
Ge_4	D_{2h}	d_{1-3}	2.40	2.35	2.48
		d_{3-4}	2.53	2.44	2.62
Ge_5	D_{3h}	d_{4-5}	3.19	3.10	3.15
		d_{1-4}	2.39	2.34	2.47
		d_{1-2}	3.19	3.10	3.29
Ge_6	D_{4h}	d_{1-3}	2.47	2.40	2.55
		d_{3-6}	2.85	2.78	2.94
Ge_7	D_{5h}	d_{6-7}	2.65	2.56	2.77
		d_{1-6}	2.57	2.49	2.65
		d_{2-3}	2.59	2.51	2.66

The label of the atom and bond for Ge_{3-7} are taken from Ref. [10].