A computational investigation of aluminum-doped germanium clusters by density functional theory study

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ABSTRACT

We report a computational study of the aluminum doped germanium clusters Ge_nAl ($n = 1$–9). The molecular geometries and electronic structures of the Ge_nAl clusters are investigated systematically using quantum calculations at the B3LYP level with the 6-311G(d) basis sets. The growth pattern behaviors, stabilities, electronic properties, and magnetic moments of these clusters are discussed in detail. Obviously different growth patterns appear between small and larger Al-doped germanium clusters, the optimized equilibrium geometries trend to prefer the close-packed configurations for Al-doped germanium clusters up to $n = 9$. The size dependence of cluster average binding energies per atom (E_b/atom), second-order differences of total energies ($\Delta_2 E$), fragmentation energies (E_f) and HOMO–LUMO gaps of Ge_{n+1} and Ge_nAl ($n = 1$–9) clusters are studied. The stability results show that Ge_{n+1} cluster possess relatively higher stability than Ge_nAl cluster. Furthermore, the investigated highest occupied molecular orbital-lowest unoccupied molecular orbital gaps indicate that the Ge_{n+1} and Ge_nAl clusters have different HOMO–LUMO gap. In addition, the calculated vertical ionization potentials and vertical electron affinities confirm the electric properties of Ge_{n+1} and Ge_nAl clusters. Besides, the doping of Al atom also brings the decrease as the cluster sizes increase for atomic magnetic moments (μ_b).

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1. Introduction

The semiconductor clusters with transition metal have attracted great interest for optoelectronic materials, catalyst, and the development of new species in nanoscale applications. Germanium clusters have also widely been studied because they are important for the fine processing of semiconductors and the synthesis of novel materials. The studies have shown that the structure and the bonding of bulk germanium are very similar to that of bulk silicon, and the bulk surfaces show similar reconstruction [1]. However, although small silicon and germanium clusters appear to have similar geometries, the larger ones are fundamentally different [2]. During the past two decades, Ge_n clusters have been intensively studied both experimentally [3–9] and theoretically [10–21] because of their fundamental importance and potential applications in nanoelectronics. The photoionization study has been investigated by Yoshida and Fuke to characterize the electronic structures of germanium cluster, they found a rapid decrease in the ionization potentials (IPs) for Ge_n between $n = 15$

and 26, which was very similar to that for silicon clusters [4]. The low-lying stages of Ge_2 and Ge_2^- have also been probed using negative ion zero electron kinetic energy spectroscopy [7]. Because of the lack of experimental method to characterize the structure of germanium clusters, most of the geometrical data come from theoretical calculations. Geometrical and electronic properties of Ge_n ($n = 5$–10) neutrals, cations, and anions have been investigated using the density functional method of Becke's three-parameter hybrid functional with the Perdew/Wang 91 expression by Li et al. [12]. Yoo and Zeng performed a constrained search for the geometries of low-lying neutral germanium clusters in the size range of $21 \leqslant n \leqslant 29$ [14]. Wang et al. calculated dipole polarizabilities of Ge_n clusters at FF level of density functional theory, which show the dipole moment and polarizabilities of Ge_n clusters are sensitively dependent on the cluster geometries and electronic structures [15]. King et al. reported the effect of electron count on cluster geometry of nine and ten atom germanium clusters using B3LYP level of DFT [20].

The pure germanium clusters are chemically reactive and thus not suitable as a building block of self assembly materials. By an appropriate choice of the metal dopant, it is possible to design metallic as well as semiconducting nanotubes using Ge_n as

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building blocks. Doped germanium clusters have been performed the focus of a few experimental and theoretical studies [22–35], which exhibit many novel properties such as the sizes selectivity, the highest occupied molecular orbital-lowest unoccupied molecular orbital gap, different charge transfer direction and the magnetic property. Tai and Nguyen [22] found the structure and stability of the $Ge_{12}M^x$ clusters with M = Li, Na, Be, Mg, B, Al, and x from −1 to +1, they obtained the high thermodynamic stability of the icosahedra arises from a combination of their closed crystal field shells, spherical aromaticity and electrostatic attraction force. Electronic properties of germanium–fluorine cluster anions ($Ge_nF_m^-$; n = 1–11, m = 1–3) were studied by Negishi et al. using photoelectron spectroscopy with a magnetic-bottle type electron spectrometer, which showed that the doped F atom in Ge_nF^- deprives each Ge_n^- cluster of the excess electron without any serious rearrangement of the Ge_n framework [23]. In addition, the geometries, stability, and electronic properties of TM-doped germanium clusters (TM = Zn, Fe, Mn, Si, Ni, W, Cr, Cu, Au) [25–35] have also been systematically investigated by using different method. The remarkable features of Zn-doped Ge_n clusters are distinctly different from other TM-Ge_n clusters, indication that the growth pattern of the TM-Ge_n clusters depends on the kind of doped TM impurity.

Although many studies have been taken on pure germanium clusters and doped germanium clusters, to our knowledge, surely systematic and theoretical investigated on aluminum-doped germanium clusters have not been reported so far. In this work, an investigation on the structures, stabilities, magnetism, and electronic properties of the Al-doped germanium clusters were calculated using density functional theory by considering a considerable number of structural isomers. In order to reveal the effect of the doped Al atom to the germanium clusters, in this paper, we optimize the geometrical structures of Ge_nAl (n = 1–9) clusters by employing DFT approach to find the structural and stability, and combined with pure germanium clusters for comparison by using identical methods and basis sets.

2. Computational details

The geometry optimizations of the Ge_{n+1} and Ge_nAl (n = 1–9) clusters with spin configurations considered are performed by using density functional theory (DFT) with the B3LYP exchange–correlation potential and 6-311G(d) basis sets. The B3LYP method, it is based on the Becke three-parameter exchange functional and the Lee, Yang and Parr correlation functional [36,37]. In order to test the reliability of our calculations, some test calculations are carried out on Ge_2 and Al_2 using B3LYP, B3P86, PBE1PBE, and B3PW91 method with LANL2DZ, Def2-TZVP, and 6-311G(d) basis sets. The computed spin multiplicities, bond lengths (R_e), vibrational frequencies (ω_e), and dissociation energies (D_e) of dimers (Ge_2, and Al_2) and available experimental and previous theoretical data are summarized in Table 1. Comparing with the experimental data, we can find that the B3LYP method with 6-311G(d) basis sets

Table 1
The computed spin multiplicities, bond lengths (R_e), vibrational frequencies (ω_e), and dissociation energies (D_e) of dimers (Ge_2, and Al_2) and available experimental and previous theoretical data.

Molecule	Method		Spin	R_e (Å)	ω_e (cm^{-1})	D_e (eV)
Ge_2	B3LYP	LanL2DZ	3	2.528	250.1	2.34
		6-311G(d)	3	2.413	276.6	2.87
		Def2-TZVP	3	2.407	279.0	2.93
	B3P86	LanL2DZ	3	2.517	256.4	2.52
		6-311G(d)	3	2.388	288.0	3.02
		Def2-TZVP	3	2.385	290.1	3.08
	PBE1PBE	LanL2DZ	3	2.514	259.4	2.40
		6-311G(d)	3	2.386	292.0	2.89
		Def2-TZVP	3	2.383	294.1	2.97
	B3PW91	LanL2DZ	3	2.520	255.8	2.42
		6-311G(d)	3	2.393	286.5	2.89
		Def2-TZVP	3	2.390	288.4	2.96
	Theory		3[a]	2.548[b]	281[c]	2.34[d]
	Experiment		–	2.44[e]	274[f]	2.65[f]
					286 + 5[g,h]	2.70 ± 0.07[g,h]
Al_2	B3LYP	LanL2DZ	3	2.855	235.1	1.19
		6-311G(d)	3	2.765	252.9	1.29
		Def2-TZVP	3	2.753	259.6	1.36
	B3P86	LanL2DZ	3	2.834	246.4	1.36
		6-311G(d)	3	2.737	266.1	1.47
		Def2-TZVP	3	2.728	271.4	1.53
	PBE1PBE	LanL2DZ	3	2.834	250.7	1.37
		6-311G(d)	3	2.739	268.5	1.48
		Def2-TZVP	3	2.730	274.8	1.54
	B3PW91	LanL2DZ	3	2.839	245.9	1.33
		6-311G(d)	3	2.746	264.0	1.44
		Def2-TZVP	3	2.736	270.0	1.49
	Theory		3[i]	2.7[i]	241.2[i]	1.33[j]
	Experiment		3[k]	2.7[k]	284.2[k]	1.34[l]

[a] Ref. [32].
[b] Ref. [33].
[c] Ref. [34].
[d] Ref. [35].
[e] Ref. [6].
[f] Ref. [7].
[g] Ref. [8].
[h] Ref. [9].
[i] Ref. [39].
[j] Ref. [40].
[k] Ref. [41].
[l] Ref. [42].