Research Article

An Investigation of Electronic Structure and Aromaticity in Medium-Sized Nanoclusters of Gold-Doped Germanium

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Received 19 October 2012; Accepted 3 November 2012

Academic Editor: Su Chen

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The electronic property and aromaticity of endohedrally doped AuGe_{10}^- and AuGe_{12}^- clusters are investigated using the density-functional theory (DFT) within the hybrid B3LYP method. The calculated results reveal that the two clusters have high thermodynamic stability reflected by reaction energy. At the same time, it could be hoped that their high stability may arise from the closed-shell spherical aromaticity with eight π -electrons satisfying the $2(N_\pi + 1)^2$ counting rule with $N_\pi = 1$. A popular nucleus-independent chemical shifts (NICSs) calculation on basis of magnetic shieldings is also performed to confirm the aromaticity of the three-dimensional nanoclusters with largely negative NICS values. In addition, the electronic features and chemical bonding of the two clusters are analyzed with the help of the density of states (DOS) and electron localization function (ELF), and the majority of Ge-Ge bonds on the cage show more covalent characters.

1. Introduction

Semiconductor clusters, especially germanium, have been extensively investigated both experimentally and theoretically due to their potential applications in the microelectronics industry [1–6] and are of considerable scientific interest to explore the chemical structure and bonding as well as their thermodynamic stability and photoelectric effect. Unlike silicon, the effective masses of electron and hole in germanium are light; it can generate high carrier mobility and makes germanium attractive for high-performance field-effect logic transistors [7]. However, pure germanium clusters with medium or large size are chemically unstable and quite reactive because of the existence of abundant dangling bonds [5]. Interestingly, the encapsulation of different transition-metal (TM) atoms [8–10] in the medium-sized clusters can saturate the dangling bonds on the germanium cage surface and form sp^3 hybridization, and thereafter stabilize the germanium cages. Consequently, the metal-encapsulated germanium clusters exhibit many fascinating features such as nanostructures, for example, thermodynamic stability [11,

12], magnetic and superconducting behaviors [8, 13, 14], photoelectric effect [15, 16], and reduced energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [9, 17, 18]. Some metal-encapsulated Ge clusters were also proposed as novel cluster-assembled materials due to the small HOMO-LUMO gap within about 2 eV, for example, AuGe_n ($n = 2-13$) [18] and TM@Ge_{12} (TM = Zn, W, and Os) [19, 20]. In an experimental study, the bimetallic CoGe_{10}^- cluster in the mass spectrum was measured using laser vaporization technique [21], and its molecular structure was determined by the density-functional theory (DFT) calculations [22].

To our knowledge, there have been a number of interesting findings on the calculation of metal-encapsulated Ge clusters, for example, NiGe_n ($n = 1-13$) [23], CrGe_n ($n = 1-13$) [24], WGe_n ($n = 1-17$) [25], TMGe_n (TM = Ti, Zr, Hf and Cu; $n = 1-20$) [26, 27], and so on. A few outstanding predictions are medium-sized fullerene-like with 10 or 12 atoms. Kumar et al. [19, 28] reported a series of systematic investigations of TM@X_n (X = Si, Ge, Sn, and Pb; TM = Ni, Pd, Pt, Zn, and Cd; $n = 10$ and 12)

clusters using an *ab initio* ultrasoft pseudopotential method and generalized gradient approximation, and these clusters can be further stabilized by doping of an Ni or Pt atom, leading to some of the smallest metal-encapsulated clusters. King and coworkers [29, 30] explored the possible structures of $M@Ge_{10}^z$ systems ($M = Co$ and Be ; $z = -5$ to $+2$) at the DFT-B3LYP/6-31G(d) level of theory and found that a singlet D_{5h} pentagonal prismatic structure is the global minimum for the trianionic $Co@Ge_{10}^{3-}$ cluster, which is in accordance with the experimental result. Tang et al. [31] investigated the structure, stability, and optical property of $TM@Ge_{12}$ ($TM = Sc-Ni$) using the relativistic all-electron density functional theory. It was found that all the $TM@Ge_{12}$ clusters are perhaps partial metallic, and the ground-state geometry of them is probably pseudoicosahedron. Furthermore, eight π -electron natures make closed-shell spherical systems aromatic according to the $2(N_\pi + 1)^2 [N_\pi = 1]$ rule proposed by Hirsch et al. [32]. In 2005, Chen and coworkers [33] also reported the nucleus-independent chemical shifts (NICSs) approach as an aromaticity criterion based on magnetic properties, which have been applied to characterize the all-metal aromatic/antiaromatic clusters [34].

In this paper, we report an investigation of electronic structure and aromaticity of the $AuGe_{10}^-$ and $AuGe_{12}^-$ nanoclusters using the hybrid DFT-B3LYP functional in conjunction with LanL2DZ basis set. The choice of endohedral gold atom is due to the fact that the bimetallic gold clusters have some fascinating physical and chemical properties and were experimentally observed using photoelectron spectroscopy [16, 35–37].

2. Theoretical Methods

The molecular structure, electronic property, and spherical aromaticity of $AuGe_{10}^-$ and $AuGe_{12}^-$ clusters were carried out using the hybrid DFT-B3LYP functional [38, 39] implemented in the Gaussian 09 package [40]. The standard double- ξ LanL2DZ basis set [41–43], which provides effective core potentials (ECPs) to consider the relativistic effects of transition metal atoms, was utilized here. Our previous calculations [18] also confirmed the credibility of the theoretical level, and the deviations within 1–6% are acceptable. To search for the most stable structures, a great number of structural isomers were considered for each size, on basis of a global search published previously [18, 44], and the local minima of all the stationary point geometries were determined by vibrational frequency analysis. The density of states (DOS) of the most stable $AuGe_{10}^-$ and $AuGe_{12}^-$ clusters was constructed using GaussSum 2.2 program [45] with the full width at half maximum (FWHM) of 0.3 eV, and the molecular orbitals were plotted with the isodensity surfaces (0.02 e/a.u.^3). In addition, the nucleus-independent chemical shifts (NICS) were calculated by gauge-independent atomic orbital (GIAO) method [46, 47] at the B3LYP/LanL2DZ level of theory. In order to obtain more accurate NICS values, the correlation-consistent cc-pVTZ basis set [48] was also used for Ge atom, whereas the energy-adjusted small-core (19 valence electrons) pseudopotentials (PPs) [49] were used

for Au atom, labeled as cc-pVTZ-PP, and the single-point GIAO calculations at the B3LYP/cc-pVTZ-PP level of theory were performed based on the B3LYP/LanL2DZ-optimized geometries.

3. Results and Discussion

3.1. Geometry and Stability. Using the computation scheme described above, we have extensively explored a number of initial isomers formed from taking the previously reported structures of different $TMGe_{10}$ systems, or doping one Au dopant at all possible positions of the lower-lying Ge_{10} isomers, or replacing one Ge atom of the lower-lying Ge_{11} isomers with an Au atom to form new isomers. As a result, the most stable $AuGe_{10}^-$ cluster is found to be an endohedrally Au-doped pentagonal prism (see Figure 1(a)). It is worth mentioning that, when an electron is added to the lowest-energy neutral $AuGe_{10}$ cluster in C_{2v} symmetry [18], the high D_{5h} -symmetric anionic $AuGe_{10}^-$ cluster with a $^1A_1'$ electronic state forms due to the equal electron distribution for each Ge atom [44], indicating that the neutral $AuGe_{10}$ cluster is an electron-deficient base. The geometry of the lowest-energy $AuGe_{10}^-$ cluster in D_{5h} symmetry is also consistent with the neutral $FeGe_{10}$ cluster [9] as well as the trianionic $Co@Ge_{10}^{3-}$ cluster [29]. In the structure, there are 10 equivalent Ge–Ge bond lengths on two five-numbered germanium rings, and 5 equivalent Ge–Ge bond lengths on side-jointed prism. At the B3LYP/LanL2DZ level of theory, the equilibrium Ge–Ge bond lengths of them are predicted to be 2.722, and 2.858 Å, respectively; and the equilibrium Au–Ge bond lengths in the pentagonal prism are calculated to be 2.721 Å, as shown in Table 1.

Analogous to the formation of $AuGe_{10}^-$ cluster, all the possible isomers of $AuGe_{12}^-$ cluster are considered. An Au-doped bicapped pentagonal prism is optimized to be the lowest-energy $AuGe_{12}^-$ structure, which displays a 1A_1 electronic state in D_{2d} symmetry (see Figure 1(b)). By comparison, the icosahedral structure of $ZnGe_{12}$ [50] cluster is confirmed to be the global minima in the potential energy surface (PES), but the icosahedral $AuGe_{12}^-$ structure is only a local minimum which is higher in energy than the lowest-energy structure by 0.32 eV [44]. In the bicapped pentagonal prism, the D_{2d} structure has two C_2 axes and two σ_d planes. As a result, four different Ge–Ge bond lengths are predicted to be 2.611, 2.644, 2.647 and 2.855 Å, respectively, whereas the two equilibrium Au–Ge bond lengths are calculated to be 2.814 and 2.942 Å.

As discussed above, the endohedrally doped $AuGe_{10}^-$ and $AuGe_{12}^-$ clusters are the most stable. Obviously, they do not obey the 18-electron counting rule (also known as the octet rule) [51] which may give rise to the high stability of cluster. In 2003, Sen and Mitas [52] also reported the limitation of the 18-electron rule and found that the filling of electron shell according to 18-electron rule is not the only factor in determining the structural stability, and the stability should depend on structural geometry, choice of metal atom, neutral or charged species, and so forth. In addition, one needs to calculate reaction energy to explain

TABLE 1: Optimized bond distances (in Å), NICS values (in ppm) at different positions^a, and electron configurations of the lowest-energy AuGe₁₀[−] (*D*_{5h}) and AuGe₁₂[−] (*D*_{2d}) clusters.

Cluster	$d_{\text{Ge-Ge}}$	$d_{\text{Ge-Au}}$	NICS ^b					Electron configuration
			0.0 Å	0.5 Å	1.0 Å	1.5 Å	2.0 Å	
AuGe ₁₀ [−]	2.722	2.721	−259.6 (−236.1)	−183.7 (−177.4)	−50.7 (−47.3)	−25.2 (−24.4)	−14.1 (−15.7)	(1a ₁ ') ² (1e ₁ ') ⁴ (1a ₂ '') ² (2a ₁ ') ²
	2.858							(2e ₁ ') ⁴ (2a ₂ '') ² (1e ₁ '') ⁴ (1e ₂ ') ⁴ (3a ₁ ') ² (2e ₁ '') ⁴ (2e ₂ ') ⁴ (1e ₂ '') ⁴ (4a ₁ ') ² (5a ₁ ') ² (3e ₂ ') ⁴ (3e ₁ ') ⁴ (3a ₂ '') ² (4e ₁ ') ⁴ (2e ₂ '') ⁴
AuGe ₁₂ [−]	2.611	2.814 2.942	−296.4 (−277.1)	−199.0 (−196.4)	−61.3 (−60.8)	−36.3 (−37.7)	−25.8 (−28.0)	(1a ₁) ² (1b ₂) ² (1e) ⁴ (2a ₁) ²
	2.644							(2b ₂) ² (2e) ⁴ (1b ₁) ² (3e) ⁴
	2.647							(3a ₁) ² (3b ₂) ² (4a ₁) ² (4e) ⁴
	2.855							(1a ₂) ² (2b ₁) ² (4b ₂) ² (5e) ⁴
								(5a ₁) ² (5b ₂) ² (6a ₁) ² (6e) ⁴ (6b ₂) ² (7e) ⁴ (3b ₁) ² (7a ₁) ² (8e) ⁴ (2a ₂) ²

^a NICS values were computed at the GIAO-B3LYP/LanL2DZ//B3LYP/LanL2DZ level, based on the positions located on the radial *L*_{ab} connecting the center site (see Figure 1).^b NICS values in parentheses were obtained from the GIAO-B3LYP/cc-pVTZ-PP//B3LYP/LanL2DZ calculations.

FIGURE 1: Equilibrium structures of the lowest-energy D_{5h} -symmetric AuGe_{10}^- (a) and D_{2d} -symmetric AuGe_{12}^- (b) clusters in [44]. The different NICS sites (purple balls) are indicated.

the thermodynamic stability of the cluster, and the reaction energy (E_r) can be computed according to the following equation:

$$E_r(\text{AuGe}_n^-) = \frac{[E(\text{AuGe}_n^-) - nE(\text{Ge}) - E(\text{Au}^-)]}{(n+1)}, \quad n = 10 \text{ or } 12, \quad (1)$$

where $E(\text{AuGe}_n^-)$, $E(\text{Ge})$, and $E(\text{Au}^-)$ represent the total energies of AuGe_n^- , Ge , and Au^- atoms, respectively. All the total energies include the correction of zero-point vibrational energy (ZPVE). According to our knowledge, the formations of AuGe_{10}^- and AuGe_{12}^- clusters are exothermic with the large negative E_r values, being -2.44 and -2.50 eV. Interestingly, their high thermodynamic stabilities are mainly associated with the geometry and the number of dangling bonds in the two clusters, as mentioned in previous study [18]. Our results also reveal that both of them can appear as stable species, and the two clusters could be synthesized through the exothermic reaction pathway.

3.2. Electronic Structure and Chemical Bonding. In order to explore the electronic features related to the stability of the clusters, we have performed a detailed analysis of the molecular orbitals by examining the partial density of states (PDOS) from the contribution of different orbital components (Au: s , p , d ; Ge: s , p) and the electron density of the HOMO and LUMO states. The plots of PDOS of the AuGe_{10}^- and AuGe_{12}^- clusters are shown in Figures 2(a) and 2(b), respectively.

As for a typical case, each Ge atom is expected to contribute its four valence electrons to the electron shell configuration of the molecular systems. The AuGe_{10}^- cluster with D_{5h} symmetry thus contains 42 valence electrons which are distributed in the following orbital configuration: $(1e_1'')^2 (1e_2')^4 (3a_1'')^2 (2e_1'')^4 (2e_2'')^4 (1e_2'')^4 (4a_1'')^2 (5a_1'')^2 (3e_2'')^4 (3e_1'')^4 (3a_2'')^2 (4e_1'')^4 (2e_2'')^4$, as listed in Table 1. Due to the high D_{5h} symmetry, additionally, the molecular orbitals strongly resemble the spherical features. From the Figure 2(a), we clearly see that the electronic states at high-energy region of around -3.9 eV above come

mainly from p -Ge state; and the contribution from s -Ge state is very little. The difference is that the valence molecular orbitals at around -6.0 eV below mainly ascribe to the contribution of d -Au and s -Ge states; in particular, the E_2' -type valence orbital at -6.77 eV, holding a doubly degenerate state, is composed of d -Au state mixed with s -Ge state. Similar behavior is observed for the D_{2d} -symmetric AuGe_{12}^- cluster which contains 50 valence electrons with an orbital configuration of $[(3e)^4(3a_1)^2(3b_2)^2(4a_1)^2(4e)^4(1a_2)^2(2b_1)^2(4b_2)^2(5e)^4(5a_1)^2(5b_2)^2(6a_1)^2(6e)^4(6b_2)^2(7e)^4(3b_1)^2(7a_1)^2(8e)^4(2a_2)^2]$. The electron density (0.02 e/a.u.³) of HOMO and LUMO states of the two clusters is represented in Figure 2. One can see that both the HOMO and LUMO states are mainly localized around germanium cage, while some electronic distributions around Au atom are also found in the LUMO. It is remarkable that the encapsulation of the Au dopant is responsible for the geometric rearrangement of pure germanium clusters and the reduction of the HOMO-LUMO gaps of pure Ge_{10} and Ge_{12} clusters. Especially for the AuGe_{12}^- cluster the HOMO and LUMO are nondegenerate and are slightly separated from the adjacent occupied and unoccupied orbitals, resulting in its quite small HOMO-LUMO gap of 1.63 eV. Thus, although the germanium is semiconductor element, the AuGe_{10}^- and AuGe_{12}^- clusters may be considered as novel cluster-assembled materials with partially metallic features [19, 44].

In 1994, Silvi and Savin [53] reported that the electron localization function (ELF) is currently used to describe the nature of bonding. According to their descriptions, the molecular space is divided into regions or basins of localized electron pairs or attractors. Typically, the existence of a high ELF isovalue (around 0.7 and above) in the bonding region between two atomic basins signifies a localized chemical bond in the region [44, 54]. For the D_{5h} -symmetric AuGe_{10}^- cluster, the ELF basins along Ge-Ge bond upon two five-number germanium rings merge at an isovalue of 0.71 (Figure 3(a)), revealing that these Ge-Ge bonds are covalent in nature, while the five Ge-Ge prismatic bonds have more metallic or less covalent character reflected by the slightly low ELF isovalue at 0.60 (Figure 3(b)). The ELF contour at a low isovalue of 0.32 (Figure 3(c)) shows two polarized basins

FIGURE 2: Density of states (DOS) of the lowest-energy AuGe_{10}^- (a) and AuGe_{12}^- (b) clusters computed at the B3LYP/LanL2DZ level of theory.

FIGURE 3: The ELF isosurfaces of the AuGe_{10}^- and AuGe_{12}^- clusters. Some different isovalues are indicated: (a) 0.71, (b) 0.60, (c) 0.32, (d) 0.72, and (e) 0.29.

between Au and Ge atoms, so all the Au–Ge bonds are far from being covalent in nature but show an ionic character. The most stable AuGe_{12}^- cluster has a high (almost spherical) D_{2d} symmetry. The covalent bonding pattern between germanium atoms becomes more preferable because all atomic basins along the surface bonds in ELF contours almost merge at an isovalue of 0.72 (Figure 3(d)), whereas the Au–Ge bonds display a slightly increased ionic character confirmed by lower ELF isovalue (0.29, Figure 3(e)) and elongated Au–Ge bond lengths (0.093–0.221 Å), as discussed above.

3.3. The $2(N+1)^2$ Rule. Aromaticity is well known as one of the important measures of compounds. Compared to

nonaromatic compounds, analogous aromatic compounds typically give enhanced chemical stability. In general, aromaticity of planar structure can be qualitatively explored using the $4N + 2$ Hückel rule [34]. Another electron counting rule, namely, $2(N + 1)^2$ rule proposed by Hirsch et al. [32], is proven as an effective aromaticity criterion for spherical species (I_h symmetry), as well as the extension of the treatment to inorganic cage molecules [55]. In the latter electron rule, the π -electron system of the species can be approximately considered as a spherical electron gas, which surrounds the surface of a sphere [56]. According to the Pauli principle, if the number of π electrons in a spherical structure satisfies the $2(N + 1)^2$ rule, the structure can show a spherical charge distribution and is therefore expected to be aromatic.

The molecular orbitals (MOs) of the AuGe_{10}^- and AuGe_{12}^- clusters are depicted in Figures 2(a) and 2(b), respectively. We see that the valence electron orbitals of them are divided into two different subsets occupied by σ or π electrons. In Figure 2(a), the D_{5h} -symmetric AuGe_{10}^- cluster contains eight valence π -electrons in four MOs, for example, $-5.52(\text{A}_1', 1)$, $-2.98(\text{E}_1', 2)$, and $-2.60(\text{A}_2'', 1)$, and these π -electrons satisfy the $2(N_\pi + 1)^2 [N_\pi = 1]$ counting rule. Similarly, eight valence π -electrons are also found for the D_{2d} -symmetric AuGe_{12}^- cluster (Figure 2(b)) and occupy the $-5.89(\text{A}_1, 1)$, $-3.31(\text{B}_2, 1)$, and $-2.92(\text{E}, 2)$ orbitals. As a consequence, the two π -electron systems make the AuGe_{10}^- and AuGe_{12}^- clusters spherically aromatic. This aromatic feature can be regarded as one of the main reasons in the structural stabilization of endohedrally doped AuGe_{10}^- and AuGe_{12}^- clusters. However, it is noteworthy that the $2(N + 1)^2$ electron counting rule cannot be solely used to explain the aromaticity of compounds. For instance, the bianionic Si_{12}^{2-} cluster contains eight π electrons, but gives

an antiaromatic character [57]. Therefore, the aromaticity of both the AuGe_{10}^- and AuGe_{12}^- clusters needs to be further confirmed by NICS values given in next section.

3.4. NICS Values of Clusters. The aromaticity of a chemical compound can be usually discussed in terms of various criteria, but the criteria used to validate the aromaticity are sometimes controversial, likely Si_{12}^{2-} cluster. Herein, we performed a calculation of NICS proposed by Chen and coworkers [33], based on magnetic shieldings. Aromaticity is expected to be evaluated by a negative NICS value, and antiaromaticity by a positive NICS value. In general, a ghost atom is placed at the center of a spherical geometry to obtain NICS value. In order to get a reasonable value, however, we considered many different sites along central axis inside or outside the cage to test the variation of NICS value, as depicted in Figure 1. A radius (L_{ab}) from the center site of the cage to each ghost atom is also defined with $0 \leq L_{\text{ab}} \leq 3.0$.

Using the GIAO-B3LYP/LanL2DZ level of theory, we have calculated the NICS values of the AuGe_{10}^- and AuGe_{12}^- clusters. In order to give a proper description of magnetic and electronic properties, a large basis set (cc-pVTZ-PP) in our NICS calculations is also necessary with the same method. The NICS values of the two clusters are given in Table 1. We see that the NICS value at the center site is the largest one among all considered sites, being -259.6 and -296.4 ppm for AuGe_{10}^- and AuGe_{12}^- clusters, respectively. From Figure 4 we see that the NICS values of the AuGe_{10}^- cluster rapidly decreases to $L_{\text{ab}} = 1.5$ (-25.2 ppm) and then slowly decreases to $L_{\text{ab}} = 3.0$ (-8.5 ppm). Obviously, the NICS values close to the outer surface are relatively smaller than those inside the cage. Similar behavior is found for the AuGe_{12}^- cluster, and it gives a slightly larger NICS value than AuGe_{10}^- cluster. We also find that the NICS values with LanL2DZ basis set are in good agreement with the results with cc-pVTZ-PP basis set, except for the value at the center site that is relatively large with the deviation of about 20.0 ppm. Thus, the aromaticity of both the AuGe_{10}^- and AuGe_{12}^- clusters, characterized by the $2(N_{\pi} + 1)^2 [N_{\pi} = 1]$ electron counting rule, is confirmed by largely negative NICS values. Moreover, the two clusters have very strong aromatic character at the center site, and the aromaticity will weaken outside the cage and vanish beyond.

4. Conclusions

Using the hybrid DFT-B3LYP functional, we have studied a large number of structural isomers for medium-sized AuGe_{10}^- and AuGe_{12}^- clusters. The endohedrally Au-doped pentagonal prism and bicapped pentagonal prism are found to be the most stable AuGe_{10}^- (D_{5h}) and AuGe_{12}^- (D_{2d}) structures, respectively. Analysis of reaction energy indicates that the endohedrally doped AuGe_{10}^- and AuGe_{12}^- clusters have the high thermodynamic stability. We see that the high-energy regions of molecular occupied orbitals of the two compounds come mainly from the contribution of p -Ge state by means of the partial density of states (PDOS). The electron localization functions (ELFs) are also considered

FIGURE 4: Comparison of NICS values of anionic AuGe_{10}^- and AuGe_{12}^- clusters using two different LanL2DZ and cc-pVTZ-PP basis sets with the same B3LYP functional, based on the B3LYP/LanL2DZ geometries.

to explore the chemical bonding of the two clusters, and in some regions more metallic (or less covalent) character between germanium atoms becomes more preferable, for example, pentagonal prismatic bonds. In the AuGe_{10}^- and AuGe_{12}^- structures, eight valence π -electrons satisfy the $2(N_{\pi} + 1)^2 [N_{\pi} = 1]$ counting rule and make the AuGe_{10}^- and AuGe_{12}^- clusters spherically aromatic. An NICS calculation on basis of magnetic shieldings is carried out to confirm the aromaticity of the three-dimensional clusters reflected by largely negative NICS values. Additionally, NICS is also relatively insensitive to the level of theory used in the study, for example, basis set.

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