Thermochemical Properties and Growth Mechanism of the Ag-Doped Germanium Clusters, $\text{AgGe}_n^{\lambda}$ with $n = 1–13$ and $\lambda = -1, 0$, and +1

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ABSTRACT: A systematic investigation of the silver-doped germanium clusters $\text{AgGe}_n$ with $n = 1–13$ in the neutral, anionic, and cationic states is performed using the unbiased global search technique combined with a double-density functional scheme. The lowest-energy minima of the clusters are identified based on calculated energies and measured photoelectron spectra (PES). Total atomization energies and thermochemical properties such as electron affinity (EA), ionization potential (IP), binding energy, hardness, and highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) gap are obtained and compared with those of pure germanium clusters. For neutral and anionic clusters, although the most stable structures are inconsistent when $n = 7–10$, their structure patterns have an exohedral structure except for $n = 12$, which is a highly symmetrical endohedral configuration. For the cationic state, the most stable structures are attaching structures (in which an Ag atom is adsorbed on the Ge$_n$ cluster or a Ge atom is adsorbed on the AgGe$_{n-1}$ cluster) at $n = 1–12$, and when $n = 13$, the cage configuration is formed. The analyses of binding energy indicate that doping of an Ag atom into the neutral and charged Ge$_n$ clusters decreases their stability. The theoretical EAs of AgGe$_n$ clusters agree with the experimental values. The IP of neutral Ge$_n$ clusters is decreasing when doped with an Ag atom. The chemical activity of AgGe$_n$ is analyzed through HOMO-LUMO gaps and hardness, and the variant trend of both versus cluster size is slightly different. The accuracy of the theoretical analyses in this paper is demonstrated successfully by the agreement between simulated and experimental results such as PES, IP, EA, and binding energy.

1. INTRODUCTION

With the rapid development of nanotechnology, the research on the geometric configuration and electronic properties of clusters has become more important because clusters play a pivotal role in the transition from the molecule to the condensed phase, especially for semiconductor clusters owing to their interesting chemical structures and bonding motifs, as well as their importance in the microelectronics industry.$^{1–15}$ However, pure semiconductor clusters such as germanium clusters are unstable because they show only $sp^3$ bonding characteristics.$^{16–20}$ Recently, a lot of experimental and theoretical research studies have elucidated that introducing a transition metal atom into germanium clusters can not only heighten their stability, but also deeply affect their electron properties.$^{21–50}$ Studying the structure and growth model of different transition metal (TM)-doped germanium clusters can not only find a stable cage configuration that can be used as a nanomaterial structure, but also lay a foundation for their special physical and chemical properties. To understand how these attractive physical–chemical properties attribute to the doped clusters, it is important to gain the comprehensive knowledge of the ground state and lower-lying electronic and geometric configurations of charged and neutral TM-doped Ge clusters. Therefore, Nakajima and his colleagues have first explored the electronic and geometric configurations of TMGe$_n$ (TM = Sc, Y, Ti, Zr, Hf, V, Nb, Ta, and Lu; $n = 8–20$) clusters by means of dissecting their mass spectra, photoelectron spectra (PES), and reactivities to $H_2O$ adsorption.$^{21}$ Then Zheng and co-workers reported the electron affinities (EAs) and the electronic structures of TM$_x$Ge$_n$ (TM = Ag, Au, Ti, V, Co, Fe, and Cr; $x \leq 2$; $n \leq 14$) through recording and analyzing their PES.$^{22–31}$ Prompted by the experimental observations, some theoretical calculations and simulations of TM-doped germanium clusters have been carried out. For instance, the geometries and electronic
structures of small sized clusters TiGe, VGe, CrGe, NbGe, MnGe, WGe, and ZrGe; X = Ge and Si; TM = Ti, V, Zr, Hf, Cu, and Au; n ≤ 20) using B3LYP or B3PW91 density functional theory (DFT) and presented that the size of the smallest TM-encapsulated into Ge structures was n = 8 for Nb, n = 9 for Zr, Ti, Hf, and Cu, n = 10 for Mo, and n = 11 for Au atoms. 33–35 Kapila et al. investigated the ground-state structures and magnetic moments of CrGe, MnGe, and FeGe using several DFT functionals (PBE0, TPSSh, wB97X, and mPW2PLYP). The results revealed that (i) only the ground-state structure of MnGe (n = 4–9) clusters predicted by the mPW2PLYP functional is consistent with that calculated by the ROCCSD(T) scheme and (ii) the evaluated vertical detachment energy (VDE) by ROCCSD(T) and mPW2PLYP schemes is in good agreement with the experimental data. The mean absolute deviations of VDE from the experiment for ScSi (n = 4–7 and 9) are by 0.08, 0.09, 0.13, 0.19, and 0.21 eV at the ROCCSD(T), mPW2PLYP, B3LYP, TPSSh, and PBE levels, respectively. Further to check the quality of the mPW2PLYP scheme, the bond length and frequency of Ge and AgGe dimers were measured using several DFT functionals (PBE0, TPSSh, B3LYP, and mPW2PLYP) combined with cc-pVTZ-PP basis sets for Ge and Ag atoms and are listed in Table 1. The bond length of Ge and AgGe calculated using the mPW2PLYP scheme is 2.38 and 2.45 Å, which agrees with the experimental values of 2.368 Å and 2.54 Å, respectively. The frequency of Ge evaluated using the mPW2PLYP scheme is 286.3 cm−1, which is in excellent agreement with the experimental value of 287.9 cm−1. The bond distance of 2.34 Å for Au-Ge predicted by the mPW2PLYP scheme is in good agreement with the experimental value of 2.38 Å. Further, the ABCluster’s developers presented many successful examples of ABCluster in a recent article. It is proven to be a successful technique for searching the global minimal structure of atomic and molecular systems of small sizes.

Table 1. Bond Length (Å) and Frequency (cm−1) of Ge2 and AgGe Dimers Calculated by Different Functionals Combined with the cc-pVTZ-PP Basis Set for Ge and Ag Atoms

| Ge2          | AgGe          |
|--------------|---------------|
| Ge2          | AgGe          |
| bond length  | bond length   |
| frequency    | frequency     |
| PBE0         | 2.38          | 2.45          | 203.34         |
| TPSSh        | 2.39          | 2.44          | 210.83         |
| mPW2PLYP     | 2.38          | 2.45          | 201.89         |
| B3LYP        | 2.41          | 2.47          | 196.41         |
| Expt.        | 2.368         | 2.879         | 2.54           |

*ref 15. **ref 66.

2. COMPUTATIONAL METHODS

The initial isomers for AgGe (n = 1–13; λ = −1, 0, and +1) were based on the ABCluster35–37 combined with the Gaussian 09 codes.58 More than 400 isomers for each cluster were first optimized using the PBE0 functional39 with the effective core potential LanL2DZ basis set40 for Ge atoms and the cc-pVQZ-PP basis set51 for Ag atoms. Then, the lower-lying configurations were selected and reoptimized via the PBE0 functional and cc-pVTZ-PP basis set1,52 for Ge and Ag atoms. Harmonic vibrational frequency calculations were carried out at the same level to guarantee that the configurations were true local minimal structures on the potential energy surface. After completing the initial geometrical optimization using the PBE0/cc-pVTZ-PP scheme, once again, we selected the lowest-lying candidates and reoptimized them at the mPW2PLYP/cc-pVTZ-PP level53 without frequency calculations. Finally, single-point energy calculations were carried out using the mPW2PLYP functional in conjunction with the aug-cc-pVTZ-PP basis set61 for Ag atoms and the all-electron aug-cc-pVTZ basis set64 for Ge atoms to further refine the energy. At the mPW2PLYP/aug-cc-pVTZ-PP/mPW2PLYP/cc-pVTZ-PP level, the single-point energy calculations were also performed for comparison.

To check the quality of our used scheme, test calculations were previously performed using the ROCCSD(T) method for ScSi (n = 4–9) clusters and compared with several DFT functionals (PBE, B3LYP, TPSSh, wB97X, and mPW2PLYP).65 The results revealed that (i) only the ground-state structure of ScSi (n = 4–9) clusters predicted by the mPW2PLYP functional is consistent with that calculated by the ROCCSD(T) scheme and (ii) the evaluated vertical detachment energy (VDE) by ROCCSD(T) and mPW2PLYP schemes is in good agreement with the experimental data. The mean absolute deviations of VDE from the experiment for ScSi (n = 4–7 and 9) are by 0.08, 0.09, 0.13, 0.19, and 0.21 eV at the ROCCSD(T), mPW2PLYP, B3LYP, TPSSh, and PBE levels, respectively. Further to check the quality of the mPW2PLYP scheme, the bond length and frequency of Ge2 and AgGe dimers were measured using several DFT functionals (PBE0, TPSSh, B3LYP, and mPW2PLYP) combined with cc-pVTZ-PP basis sets for Ge and Ag atoms and are listed in Table 1. The bond length of Ge2 and AgGe calculated using the mPW2PLYP scheme is 2.38 and 2.45 Å, which agrees with the experimental values of 2.368 Å and 2.54 Å, respectively. The frequency of Ge evaluated using the mPW2PLYP scheme is 286.3 cm−1, which is in excellent agreement with the experimental value of 287.9 cm−1. The bond distance of 2.34 Å for Au-Ge predicted by the mPW2PLYP scheme is in good agreement with the experimental value of 2.38 Å. Further, the ABCluster’s developers presented many successful examples of ABCluster in a recent article. It is proven to be a successful technique for searching the global minimal structure of atomic and molecular systems of small sizes.

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molecular clusters to solve the realistic chemical problems. Therefore, we believe that the results evaluated using the ABCluster global search technique and the mPW2PLYP functional should be reliable.

3. RESULTS AND DISCUSSION

The structures of the optimized geometries of the neutral AgGe\textsubscript{n}, cationic AgGe\textsubscript{n}\textsuperscript{+}, and anionic AgGe\textsubscript{n}\textsuperscript{−} systems, their relative energies, the electronic states, and symmetries are shown in Figures 1−4. For the neutral AgGe\textsubscript{n} (n = 1−13), all the ground states are evaluated to be a doublet; For the cationic state, its lower-lying isomers are calculated to be single except AgGe\textsubscript{2}\textsuperscript{+}, which is simulated to be a triplet; for the anionic state, the ground state is also simulated to be single except AgGe\textsubscript{−} which is simulated to be a triplet.

3.1. Lower-Lying Isomers of AgGe\textsubscript{n} Clusters and Their Growth Mechanism. From Figures 1−4, it can be seen that the lowest structure and some of its isomers for neutral and charged AgGe\textsubscript{n} (n = 1−13) are carefully selected. Isomers are denoted as \textit{nX.Y} in which \textit{n} is the size of Ge\textsubscript{n}, \textit{X} = n, c, and a stand for a neutral, cation, and anion, respectively, and \textit{Y} = 1, 2, 3... is arranged in an ascending energy order of the isomers.

\textit{n} = 1: AgGe, AgGe\textsuperscript{+}, and AgGe\textsuperscript{−}. For AgGe, the ground state 1\textit{n}.1\textit{a} is characterized by the 2\Sigma\textsuperscript{+} electron state with [1σ\textsuperscript{2}2σ\textsuperscript{2}1π\textsuperscript{4}2δ\textsuperscript{2}3σ\textsuperscript{2}2π\textsuperscript{4}] valence electronic configuration in which a bond distance of 2.453 Å is in good agreement with the experimental value of 2.54 Å.\textsuperscript{65} After attaching an electron, the high spin state 3\Sigma\textsuperscript{+} : [1σ\textsuperscript{2}2σ\textsuperscript{2}1π\textsuperscript{4}2δ\textsuperscript{2}3σ\textsuperscript{2}2π\textsuperscript{4}] is calculated to be the ground state of AgGe\textsuperscript{−} (1\textit{a}.1). Following the detachment of one electron, the close shell electronic state 1\Sigma\textsuperscript{+} : [1σ\textsuperscript{2}2σ\textsuperscript{2}1π\textsuperscript{4}2δ\textsuperscript{2}3σ\textsuperscript{2}2π\textsuperscript{4}] becomes the ground state of AgGe\textsuperscript{+} (1\textit{c}.1). The bond lengths of 1\textit{a}.1 and 1\textit{c}.1 are calculated to be 2.465 and 2.452 Å, showing that gaining or losing an electron has little effect on the bond length of AgGe.

\textit{n} = 2: AgGe\textsubscript{2}, AgGe\textsubscript{2}\textsuperscript{+}, and AgGe\textsubscript{2}\textsuperscript{−}. A triangular structure 2\textit{n}.1 with \textit{C}_{2v} symmetry is found for AgGe\textsubscript{2} in which the Ag atom connects with two Ge atoms. For the charged species, the structures of AgGe\textsubscript{2}\textsuperscript{−} and AgGe\textsubscript{2}\textsuperscript{−} are almost unchanged. The anion AgGe\textsubscript{2}\textsuperscript{−} exhibits the \textit{C}_{2v} (\Sigma\textsubscript{1}) structure 2\textit{a}.1 with a closed shell electronic configuration, and cation AgGe\textsubscript{2}\textsuperscript{+} is found to be the 3\Sigma\textsuperscript{1} electron state 2\textit{c}.1 with \textit{C}_{2v} symmetry.
\( n = 3 \): AgGe\(_3\), AgGe\(_3^+\), and AgGe\(_3^-\). For AgGe\(_3\), the \( C_2v \) symmetry planar rhombus of the \( ^2A_1 \) electronic state is predicted to be the ground state (3n.1). The isomer 3n.2 in the \( C_1 \) point group with an \( ^2A' \) electronic state can be viewed as attaching an Ag atom to the face of the most stable Ge\(_3\) structure,\(^2\) which is less stable by 0.28 eV in energy than 3n.1. Following attachment of one electron to form the anionic species, the ground state (3a.1) shape of AgGe\(_3^-\) remains unchanged. In the cationic state, the lowest-energy structure of AgGe\(_3^+\) is a three-dimensional structure 3c.1 (\( C_s \),1A'\)), which corresponds to the neutral structure 3n.2. Isomer 3c.2 (\( C_{2v},1A_1 \)) has a planar shape, which can be viewed as one Ge atom capped in the edge of 2c.1. Interestingly, the 3c.2 in energy is only less stable than the 3c.1 by 0.05 eV, which means that they compete for the ground state of AgGe\(_3^+\).

\( n = 4 \): AgGe\(_4\), AgGe\(_4^+\), and AgGe\(_4^-\). For AgGe\(_4\), isomer 4n.1 and 4n.2 both have the \( C_s \) symmetry and \( ^2A' \) electronic state. Isomer 4n.1 can be considered as attaching an Ag atom to the face of the most stable Ge\(_4\) structure,\(^2\) and isomer 4n.2 can be considered as attaching a Ge atom to the face of the most stable AgGe\(_3\) structure. Isomer 4n.1 is the lowest-energy isomer, being only 0.03 eV lower than 4n.2, which means both of them compete for the ground state. In the anionic state, the energy of isomer 4a.1 and 4a.2 is also degenerate with an energy gap of 0.03 eV, meaning that the potential energy surface of AgGe\(_4\) is relatively shallow. The analysis of simulated PES (see below) indicates that both can coexist in laboratory. The structures of isomer 4a.1 and 4a.2 are both \( C_s \) symmetry and \( ^1A' \) electronic state. For the cationic state, the \( C_{2v} \) symmetry plane geometry of the \( ^1A_1 \) electronic state is predicted to be the ground state (4c.1) in which an Ag atom attached on the top of the most stable rhombus Ge\(_4\) structure.

\( n = 5 \): AgGe\(_5\), AgGe\(_5^+\), and AgGe\(_5^-\). The AgGe\(_5\) neutral exhibits a \( C_s \) symmetry ground state 5n.1, which can be regarded as an Ag atom capping one face of the most stable Ge\(_5\).\(^2\) After getting one extra electron, the geometry of the corresponding anion has no significant changes. The ground state 5a.1 with \( C_s \) symmetry is more stable in energy than that of isomer 5a.2 and 5a.3 by 0.56 and 0.86 eV, respectively. For the cationic state, the most stable geometry 5c.1 of AgGe\(_5^+\) has

![Figure 2. Shapes, electron states, and relative energies (\( \Delta E, eV \)) of the lower-lying isomers AgGe\(_n\) with \( n = 6−8 \) at (a) neutral, (b) anionic, and (c) cationic states.](image-url)
the $C_{2v}$ symmetry with the $^1B_1$ electronic state, which corresponds to the $5n.1$.

$n = 6$: AgGe$_6$, AgGe$_6^+$, and AgGe$_6^-$. AgGe$_6$ has a $C_s$ ($^2A'$) lowest-energy structure $6n.1$, which can be regarded as attaching an Ag atom to the face of the ground state tetragonal bipyramid Ge$_6$. The lowest stable geometries of the anion AgGe$_6^-$ ($6a.1$) and cation AgGe$_6^+$ ($6c.1$) are almost unchanged as compared to the neutral structure of $6n.1$. Interestingly, the degenerate equilibrium ground states are both found in the anionic and cationic state. Energetically, isomer $6a.2$ is only less stable than $6a.1$ by 0.02 eV for anion AgGe$_6^-$, and isomer $6c.2$ also is only less stable than $6c.1$ by 0.06 eV for cation AgGe$_6^+$. Isomer $6a.2$ and $6c.2$ both can be regarded as attaching an Ag atom to the edge and the top of the most stable Ge$_6$ structure. The analysis of simulated PES (see below) indicates that the $6a.1$ configuration is the ground-state structure.

$n = 7$: AgGe$_7$, AgGe$_7^+$, and AgGe$_7^-$. For AgGe$_7$, the structure of the ground state $7n.1$ ($C_{2v}$, $^2B_1$) and isomer $7n.2$ ($C_{5v}$, $^2A_1$) is 0.22 eV higher in energy as compared to $7n.1$, and both can be considered as an Ag atom capping on the edge and the apex of Ge$_7$ pentagonal bipyramid, respectively. The isomer $7n.4$, which is considered the most stable structure in ref 19, is 0.45 eV higher in energy than $7n.1$. Following attachment of one electron, the $C_{5v}$ symmetry structure $7a.1$, which corresponds to the neutral $7n.2$, acts as the ground state for AgGe$_7^-$. For the cationic state, the geometry of the best isomer for AgGe$_7^+$ is the same as that of the neutral $7n.1$. The $C_{2v}$ symmetry state $7c.1$ ($^1A_1$) is more stable in energy than that of isomer $7c.2$ and $7c.3$ by 0.50 and 0.85 eV, respectively.

$n = 8$: AgGe$_8$, AgGe$_8^+$, and AgGe$_8^-$. The best isomer of neutral AgGe$_8$ ($8n.1$) with $C_s$ symmetry and $^2A''$ electronic state can be seen as attaching an Ag atom to the face of the capped pentagonal bipyramid Ge$_8$. The next isomer $8n.2$ ($C_{5v}$, $^2A'$), being 0.16 eV less stable than $8n.1$, can be viewed as a distorted Ge$_8$ quadrangular prism with a capped Ag atom on one face. Two other isomers $8n.3$ ($C_{1h}$, $^2A$) and $8n.4$ ($C_{2v}$, $^2A'$), which are both formed by adding one Ge atom into the

![](https://pubs.acs.org/doi/figure/10.1021/acsomega.1c00501/19817)

Figure 3. Shapes, electron states, and relative energies ($\Delta E$, eV) of the lower-lying isomers AgGe$_n$ with $n = 9$–11 at (a) neutral, (b) anionic, and (c) cationic states.
pentagonal bipyramid Ge₂, and then attaching one Ag atom, are 0.19 and 0.46 eV less stable, respectively, in energy than 8n₁. For anion AgGe₈⁻, the isomer 8a₁ (C₁,2ₐ), corresponding to neutral 8n₁, is only 0.06 eV lower in energy than 8a₂ (corresponds to the neutral 8n₂). Although isomer 8a₁ has the lowest energy, we consider that 8a₂ is the best candidate for the ground-state structure through the comparison of the calculated and experimental PES (see below). In the cationic state, the Cs symmetry and 1Aₐ'' electronic state 8c₁, which corresponds to neutral 8n₂, is calculated as the lowest-energy structure of AgGe₈⁺. The next isomer 8c₂ (C₁,1ₐ), which is a distorted form of 8n₁, is less stable in energy than the 8c₁ by 0.22 eV.

n = 9: AgGe₉, AgGe₉⁺, and AgGe₉⁻. For the neutral AgGe₉, two degenerate structures, 9n₁ (C₃ᵥ,1ₐ) and 9n₂ (C₃ᵥ,2ₐ), are found within an energy gap of 0.04 eV. Isomer 9n₁ is formed by adding one Ge atom on the face of the most stable structure AgGe₈. Isomer 9n₂ also can be viewed as attaching an Ag atom to the trigonal prism Ge₉⁻. The isomer 9n₃, which is reported as the most stable structure in ref 19, is 0.37 eV higher in energy than 9n₁. For the anion, the geometries of the ground state 9a₁ for AgGe₉⁻ have the same structures corresponding to neutral 9n₂. The best isomer 9a₁ (C₃ᵥ,1ₐ) is 0.30 eV lower in energy than the isomer 9a₄ (corresponding to neutral 9n₁). In the cationic state, the most stable structure 9c₁ (C₃ᵥ,2ₐ), which is formed by adding an Ag atom on the edge of the most stable structure Ge₉⁺, is 0.16 eV more stable in energy than the isomer 9c₄ (corresponding to neutral 9n₁).

n = 10: AgGe₁₀, AgGe₁₀⁺, and AgGe₁₀⁻. The C₃ᵥ symmetry structure of the 2Aₐ electronic state is predicted to be the ground state (10n₁) for AgGe₁₀. It is formed by either adding one Ge atom into the face of structure 9n₂ or adsorbing an Ag atom on the face of the tetracapped trigonal prism Ge₁₀⁻. The isomer 10n₃, which is predicted to be the most stable structure in ref 19, is 0.41 eV higher in energy than 10n₁. In the anionic state, the most stable structure 10a₁ with Cs symmetry and 1A₁ electronic state is formed by adding an Ag atom on the face of bicapped tetragonal antiprism Ge₁₀⁻. The isomer 10a₂ with C₄ᵥ symmetry and 1A₁ electronic state can be formed by attaching an Ag atom on the vertex of the bicapped tetragonal antiprism Ge₁₀⁻. It is only less stable than 10a₁ by 0.06 eV in energy. Simulated PES analysis shows that both isomers can exist (see below). For cationic clusters, the ground-state isomer 10c₁ with Cs symmetry (1A'ₐ) can also be derived by adding an Ag atom on a different face of the tetracapped trigonal prism Ge₁₀⁺.

n = 11: AgGe₁₁, AgGe₁₁⁺, and AgGe₁₁⁻. For AgGe₁₁, the C₁ structure 11n₁, which can be viewed as distorted by a substitution of an Ag atom for a Ge atom of icosahedral-like Ge₁₂₉, is found to be the global minima of the cluster. The isomer 11n₂ with Cs symmetry (2Aₐ) is reported as the most stable structure in ref 19, is 0.19 eV higher in energy than 11n₁. Isomer 11n₃ with Cₛ symmetry (2Aₐ) is an Ag-encapsulated into Ge₁₁ cage, being 0.33 eV higher in energy than 11n₁. Following the attachment of one electron, the most stable structure 11a₁, corresponding to neutral 11n₁, has the Cₛ symmetry and 1A electronic state. The cage
structure 11a.4 (C\textsubscript{2v}1A\textsubscript{1}) is less stable in energy than 11a.1 by 0.79 eV. For the cationic state, the ground state 11c.1 of AgGe\textsubscript{14}\textsuperscript{+} is formed by attaching the additional Ge atom on the face of 10c.1. The structure 11c.2, which is a slightly distorted form of neutral cage structure 11n.3, is less stable in energy than 11c.1 by 0.34 eV.

n = 12: AgGe\textsubscript{12}, AgGe\textsubscript{12}\textsuperscript{+}, and AgGe\textsubscript{12}\textsuperscript{2+}. The ground state 12n.1 of neutral AgGe\textsubscript{12} is an endohedral structure with D\textsubscript{2h} symmetry in which an Ag atom is located inside a Ge\textsubscript{12} cage. The isomer 12n.3 is D\textsubscript{5d} symmetric icosahedron-like in which an Ag atom is located inside a dicapped pentagonal antiprism cage. The isomer 12n.3 is 0.15 eV higher in energy relative to 12n.1. Following attachment of one electron, the ground state 12a.1 of AgGe\textsubscript{13}+, which corresponds to neutral 12n.3, has a high I\textsubscript{h} (\textsuperscript{1}I\textsubscript{h}) symmetric icosahedral structure. This structure is similar to that of the AuGe\textsubscript{13} reported by Zheng in the series of studies on Au-doped Ge\textsubscript{13} clusters.26 For the cationic state, the geometry of the best isomer 12c.1 for AgGe\textsubscript{13}+ is an exohedral structure with C\textsubscript{3v} symmetry and \textsuperscript{A}′ electronic state, which can be viewed as attaching an Ag atom to the face of \textit{hexcapped trigonal prism Ge\textsubscript{12}}. Isomers 12c.2, 12c.3, and 12c.4 are all cage structures, being 0.38, 0.55, and 1.13 eV higher in energy than 12c.1, respectively.

n = 13: AgGe\textsubscript{13}, AgGe\textsubscript{13}\textsuperscript{+}, and AgGe\textsubscript{13}\textsuperscript{2+}. The most stable structure 13n.1 of neutral AgGe\textsubscript{13} is not a cage configuration but an exohedral structure, which can be viewed as replacing a Ge atom of the most stable structure of Ge\textsubscript{13} with an Ag atom. The best isomer 13n.1 with C\textsubscript{3v} symmetry is more stable in energy than the cage structure 13n.2 and 13n.3 by 0.32 and 0.39 eV, respectively. Isomer 13n.4 also is a no-cage structure with C\textsubscript{3v} symmetry, which is reported as the lowest-energy configuration in the literature,15 but here it is 0.54 eV higher than 13n.1. For AgGe\textsubscript{13}+, the ground state 13a.1 (corresponding to the neutral ground state 13n.1) with C\textsubscript{3v} symmetry and \textsuperscript{A}′ electronic state also is an exohedral structure. The isomer 13a.1 is more stable than the endohedral isomer 13a.2, 13a.3, and 13a.4 by 0.68, 0.70, and 0.82 eV, respectively. For AgGe\textsubscript{13}\textsuperscript{+}, the ground state 13c.1 with C\textsubscript{3v} symmetry is calculated to be an endohedral structure, which is a capped fullerene-like cage. The next isomer 13c.2, which can be seen that the Ag-encapsulated into Ge\textsubscript{13} cage of the \textit{dimer-capped pentagonal-hexagonal prism}, is less stable than 13c.1 by 0.06 eV energetically.

3.2. Growth Pattern. Based on the structural features of the determined global minimum structure, the growth mechanism for the clusters AgGe\textsubscript{n} with n = 1–13 emerges as follows: For neutral clusters, the most stable forms of AgGe\textsubscript{n} except the AgGe\textsubscript{12} definitely prefer an exohedral structure, which is formed by attaching an Ag atom to a Ge\textsubscript{n} cluster or a Ge atom to an AgGe\textsubscript{n−1} cluster when n = 1–10, and when n = 13, it is formed by replacing a Ge atom of a Ge\textsubscript{n−1} cluster with an Ag atom. For anionic states, although the lowest-energy structures of AgGe\textsubscript{n−} at n = 7–10 are different from the corresponding neutral clusters, the growth patterns of most stable structures are consistent. For cationic states, the global minimal structures of AgGe\textsubscript{n+} with n ranging from 1 to 12 are formed by attaching an Ag atom to the Ge\textsubscript{n} cluster or a Ge atom to the AgGe\textsubscript{n−1} cluster, and the endohedral structure becomes the ground-state configuration when n = 13. The ground-state configurations of AgGe\textsubscript{n+} are different from the corresponding neutral ground-state structure when n = 3, 4, and 8–13.

3.3. Photoelectron Spectra. By comparing the PES obtained by theoretical calculation and experiment, it can not only verify the accuracy of the ground-state structure predicted by the theoretical calculation, but also explain the reliability of the theoretical calculation scheme. In this section, the PES of the ground-state isomers for AgGe\textsubscript{n−} (n = 2–13) are simulated based on the generalized Koopmans’ theorem (denoted as D\textsubscript{0}DFT) combined with Multifrin software68 and compared with experimental data.22 First, the VDE which corresponds to the first peak of PES and the adiabatic electron affinity (AEA) of experiment and simulation are compared and listed in Table 2. Then, the number of other peaks and their relative locations are matched by the simulated PES and experimental one. The simulated PES of the most stable structures and experimental spectra are displayed in Figure 5.

As shown in Figure 5, the simulated PES of the 2a.1 have two different peaks (X and A) within ±4.5 eV located at 2.13 and 3.39 eV, which are in concordance with the experimental data of 2.11 and 3.70 eV.22 From the PES of AgGe\textsubscript{3−}, it can be seen that simulated PES of the 3a.1 have three adjacent peaks (X, A, and B) located at 2.71, 2.94, and 3.19 eV. The first and third peak’s positions can be consistent with the experimental values of 2.74 and 3.13 eV. For AgGe\textsubscript{4−}, the simulated PES of the 4a.1 and 4a.2 have three distinct peaks (X, A, and B) situated at 2.62, 3.62, and 3.98 eV and 2.59, 3.27, and 3.76 eV, respectively. They are in concordance with the experimental data of 2.65, 3.27, and 3.68 eV, respectively. Therefore, we suggest that two energy degenerate isomers 4a.1 and 4a.2 coexist in the experiment. For the simulated PES of 5a.1, there are four peaks (X, A, B, and C) located at 2.98, 3.31, 3.74, and 4.16 eV, which is in good accordance with the experimental data of 3.02, 3.50, 3.85, and 4.22 eV, respectively. For AgGe\textsubscript{5−}, two PES are simulated. The simulated PES of the 6a.1 have three distinct peaks (X, A, and B) situated at 2.71, 3.59, and 4.08 eV, which are in excellent agreement with the experimental values of 2.70, 3.58, and 3.94 eV, respectively. The simulated PES of the 6a.2 have two distinct peaks (X and B) situated at 2.58 and 3.93 eV. Although they are in concordance with the experimental data of 2.70 and 3.94 eV, the number of peaks is obviously insufficient. The simulated PES of the 7a.1 have two different peaks (X and A) within

| n   | VDE | AEA |
|-----|-----|-----|
| 1   | 1.50(1.47) | 1.50(1.47) |
| 2   | 2.13(2.08) | 2.08(2.05) |
| 3   | 2.71(2.65) | 2.55(2.51) |
| 4   | 2.62(2.58) | 2.34(2.30) |
| 5   | 2.98(2.93) | 2.62(2.58) |
| 6   | 2.70(2.63) | 2.73(2.60) |
| 7   | 2.93(2.87) | 2.45(2.37) |
| 8   | 3.24(3.16) | 2.75(2.67) |
| 9   | 3.47(3.40) | 3.07(3.02) |
| 10  | 3.54(3.40) | 2.98(2.94) |
| 11  | 3.32(3.27) | 3.02(2.99) |
| 12  | 3.48(3.41) | 3.19(3.31) |
| 13  | 3.86(3.74) | 3.56(3.48) |

*From ref 22; The values in parentheses are calculated at the mPW2PLYP/aug-cc-pVTZ-pp.
≤4.5 eV located at 2.93 and 3.93 eV, which are in concordance with the experimental data of 2.99 and 3.80 eV.\textsuperscript{22} For AgGe\textsubscript{8}\textsuperscript{−}, there are four different peaks (X, A, B, and C) located at 3.24, 3.64, 4.02, and 4.38 eV in the simulated PES of 8a.2, which well reproduce the experimental values\textsuperscript{22} of 3.27, 3.62, 3.88, and 4.25 eV, respectively. The spectrum of isomer 8a.1 has three distinct peaks (X, A, and B) situated at 2.98, 3.86, and 4.36 eV, which can be ruled out of the most stable structure of AgGe\textsubscript{8}\textsuperscript{−}. For AgGe\textsubscript{6}\textsuperscript{−}, two distinct peaks located at 3.47 and 4.33 eV are obtained in the simulated PES of 9a.1, and they are in reasonable agreement with the experimental values of 3.59 and 4.38 eV.\textsuperscript{22} For AgGe\textsubscript{10}\textsuperscript{−}, two distinct peaks located at 3.54 and 4.02 eV and 3.57 and 4.11 eV are obtained in the simulated PES of 10a.1 and 10a.2, respectively. They agree with the experimental values of 3.64 and 4.03 eV, respectively.\textsuperscript{22} It is to say that these two energy degenerate isomers may coexist in the experiment. Four peaks for simulated PES of 11a.1 are situated at 3.32, 3.79, 4.04, and 4.41 eV, which are in excellent agreement with the experimental data of 3.37, 3.61, 3.90, and 4.15 eV,\textsuperscript{22} respectively. Although Kong\textsuperscript{22} pointed out that the peak shape of experimental PES of AgGe\textsubscript{12}\textsuperscript{−} was wide and it was difficult to observe a clear peak because of the overlap of energy levels, three peaks (X, A, and B) can be roughly assigned to 3.68, 4.11, and 4.50 eV. It is interesting that the simulated PES of 12a.1 have two resolved peaks (X and B) centered at 3.48 and 4.61 eV, which is in good accordance with the experimental data of 3.68 (X) and 4.50 (B) eV,\textsuperscript{22} while the simulated PES of 12a.2 and 12a.3 also have two distinct peaks (X and A) situated at 3.67 and 4.18 eV and 3.54 and 4.30 eV, respectively. They are in concordance with the experimental data of 3.68 (X) and 4.11 (A) eV, respectively. In this case, one
cannot determine which isomer is the ground-state structure. Therefore, we highly suggest that the experimental PES of AgGe$_{12}^-$ should be further examined. The simulated PES of 13a.1 have two major features centered at 3.86 and 4.45 eV, which are in reasonable agreement with the experimental values of 4.04 and 4.38 eV.25

3.4. EAs and IP. From Table 2, it can be concluded that the first theoretical VDEs of AgGe$_n^-$ (n = 2−13) show a good agreement with available experimental values.27 The average absolute deviation of them is 0.07 (0.14) eV (the value in parentheses is calculated at the mPW2PLYP/aug-cc-pVTZ-PF/mPW2PLYP/cc-pVTZ-PF level). The largest deviation is 0.20 eV for AgGe$_{12}$, which is within experimental errors of 0.20 eV. For the AEAs, the quantitative analysis suggests that the mean absolute deviation of simulated of AgGe$_n$ (n = 2−13) from the experimental data is 0.11 (0.12) eV. The largest error is AgGe$_n$ and AgGe$_{10}$ which is off by 0.26 and 0.24 eV, respectively. The reason may be that their experimental PES exhibit a featureless long and very rounded tail, which means that it is difficult to determine the exact AEA value. If AgGe$_7$ and AgGe$_{10}$ are removed, the average absolute deviations are only 0.09 eV. All these show that our theoretical method is reliable and once again confirms that the ground-state configurations in this paper are accurate.

Vertical ionization potential (VIP) and adiabatic ionization potential (AIP), as important chemical and physical quantities, are discussed in this section. The VIP [defined as the difference of total energies in following manner: VIP = E(optimized neutral geometry) − E(optimized neutral)] and AIP [defined as the difference of total energies in following manner: AIP = E(optimized cation) − E(optimized neutral)] of neutral AgGe$_n$ and pure Ge$_{n+1}$ clusters are calculated and listed in Table 3. No experimental IP of AgGe$_n$ is available for comparison. Therefore, we compared the IP of AgGe$_n$ with that of pure Ge$_n$ clusters as shown in Figure 6. From Figure 6, it can be found that (i) The IP with two different types of VIP and AIP for AgGe$_n$ clusters is lower than that of pure Ge$_{n+1}$ clusters, respectively, meaning that doping an Ag atom in neutral Ge$_n$ will decrease their IP. (ii) For AgGe$_n$ (n = 1−13) clusters, the highest VIP and AIP values are calculated to be 7.71 eV for AgGe$_7$ and 7.10 eV for AgGe$_{10}$, respectively. AgGe$_n$ and AgGe$_{10}$ present the minimum values of VIP and AIP by 5.91 and 5.68 eV, respectively. (iii) For Ge$_{n+1}$ (n = 1−13) clusters, the calculated values of VIP are in good agreement with the experimental data, and their average absolute deviation is only 0.08 (0.09) eV.

3.5. Binding Energy and Relative Stability. The relative stabilities of the most stable structures of AgGe$_n^-$ (λ = −1, 0, +1; n = 1−13) clusters are examined in terms of both binding energy per atom (E$_b$) and second-order difference in energy (Δ$^2$E). E$_b$(AgGe$_n$) and Δ$^2$E(AgGe$_n$) are defined as the following relationships:

$$E_b(AgGe_n) = [nE(Ge) + E(Ag) − E(AgGe_n)]/(n + 1) \quad (1)$$

$$E_b(AgGe_n^+) = [(n − 1)E(Ge) + E(Ge^+) + E(Ag) − E(AgGe_n^+)]/(n + 1) \quad (2)$$

$$E_b(AgGe_n^-) = [(n − 1)E(Ge) + E( Ge^-) + E(Ag) − E(AgGe_n^-)]/(n + 1) \quad (3)$$

$$\Delta^2E(AgGe_n^-) = E(AgGe_{n-1}^-) + E(AgGe_{n+1}^-) - 2E(AgGe_n^-) \quad (4)$$

Where E(Ag), E( Ge), E( Ge$^+$), and E( Ge$^-$) are the total energies of the Ag atom, Ge atom and the charged Ge$^+$ and Ge$^-$, respectively. E(AgGe$_n$), E(AgGe$_n^+$), and E(AgGe$_n^-$) are the total energies of the cluster AgGe$_n$ at neutral, cationic, and anionic states, respectively. To understand how the Ag dopant influences the stability of pure Ge$_n$ clusters, the $E_b$ and $\Delta^2E$ of Ge$_{n+1}^-$ (λ = −1, 0, +1; n = 1−13) are further examined and are defined as follows:

$$E_b(Ge_{n+1}^-) = [nE(Ge) + E( Ge^-) − E(Ge_{n+1}^-)]/(n + 1) \quad (5)$$
\[ \Delta E(Ge_{n+1}^{\lambda}) = E(Ge_n^{\lambda}) + E(Ge_{n+1}^{\lambda}) - 2E(Ge_n^{\lambda}) \]

Where \( E(Ge_n^{\lambda}) \) are the total energies of neutral, cationic, and anionic Ge\(_n\) clusters, respectively. These total energies are calculated through the mPW2PLYP scheme combined with the aug-cc-pVTZ basis set for the most stable structures of neutral and charged Ge\(_n\) clusters reported in previous studies.\(^2\) The \( E_b \) values are listed in Table 4, and the plots are shown in Figures 7 and 8. The plots of \( \Delta E \) are given in Figure 9.

### Table 4. Average Binding Energies (\( E_b \), eV) of AgGe\(_n\)^{\lambda} and Ge\(_n+1\)^{\lambda} (\( \lambda = -1, 0, \text{ and } +1; n = 1-13 \)) Clusters\(^a\)

| \( n \) | \( AgGe_n^- \) | \( AgGe_n^0 \) | \( AgGe_n^+ \) | \( Ge_{n+1}^- \) | \( Ge_{n+1}^0 \) | \( Ge_{n+1}^+ \) |
|------|--------------|--------------|--------------|--------------|--------------|--------------|
| 1    | 1.00         | 0.87         | 1.26         | 1.79         | 1.44         | 1.57         |
| 2    | 2.00         | 1.72         | 1.97         | 2.44         | 2.14         | 2.11         |
| 3    | 2.42         | 2.09         | 2.33         | 2.79         | 2.63         | 2.71         |
| 4    | 2.57         | 2.35         | 2.65         | 3.02         | 2.82         | 2.83         |
| 5    | 2.88         | 2.66         | 2.86         | 3.11         | 3.00         | 3.08         |
| 6    | 2.91         | 2.75         | 2.97         | 3.20         | 3.11         | 3.15         |
| 7    | 2.99         | 2.84         | 3.10         | 3.42         | 3.11         | 3.17         |
| 8    | 3.03         | 2.86         | 3.05         | 3.24         | 3.11         | 3.17         |
| 9    | 3.11         | 2.91         | 3.11         | 3.31         | 3.21         | 3.26         |
| 10   | 3.18         | 3.02         | 3.22         | 3.25         | 3.15         | 3.29         |
| 11   | 3.15         | 3.00         | 3.16         | 3.23         | 3.16         | 3.24         |
| 12   | 3.17         | 3.02         | 3.18         | 3.27         | 3.16         | 3.24         |
| 13   | 3.22         | 3.05         | 3.18         | 3.28         | 3.22         | 3.29         |

\( a \)The values in parentheses are calculated at the mPW2PLYP/aug-cc-pVTZ-pp level.

Figure 7. Average binding energy (\( E_b \), eV) of AgGe\(_n\)^{\lambda} \((\lambda = 0, +1, \text{ and } -1; n = 1-13)\) clusters.

From Figures 7 and 8, it can be seen that: (i) The \( E_b(AgGe_n^-) \) and \( E_b(AgGe_n^+) \) are larger than the corresponding \( E_b(AgGe_n^0) \). This is because AgGe\(_n\) clusters possess an open-shell electronic structure. When an electron is obtained or lost, AgGe\(_n^-\) (except for AgGe\(_2^-\), the most stable state is a triplet) or AgGe\(_n^+\) (except for AgGe\(_1^+\), the most stable state is a triplet) clusters have the closed shell electronic structure, enhancing the stability. It should be noted that the simulated binding energy of AgGe is 0.87 eV, which is perfectly in line with the experimental value of 0.89 eV.\(^6\) (ii) Whether it is neutral or charged AgGe\(_n\) and Ge\(_n+1\), the binding energy is increased with the increase of the cluster sizes. The binding energies of pure Ge\(_n+1\) and its charged clusters are slightly larger than those of Ag-doped germanium corresponding clusters, respectively, which indicates that doping of an Ag atom may decrease the stability of neutral and charged Ge\(_n+1\) clusters. (iii) The maximum values of \( E_b \) are calculated to be 3.02 eV (AgGe\(_4^+\)) and 3.05 eV (AgGe\(_5^+\)) for neutral AgGe\(_n\) clusters and 3.23 eV (Ge\(_{10}^-\)) and 3.22 eV (Ge\(_{14}^-\)) for neutral Ge\(_{n+1}\) clusters, which indicates that they show a good thermodynamic stability. At the anionic state, the value of \( E_b \) is the maximum at \( n = 10 \) (3.18 eV) and \( n = 13 \) (3.22 eV) for AgGe\(_n^-\) clusters and at \( n = 10 \) (3.31 eV) and \( n = 14 \) (3.28 eV) for Ge\(_{n+1}^-\) clusters. At the cationic state, AgGe\(_{10}^+\) presents the highest \( E_b \) value by 3.22 eV for AgGe\(_n^+\) clusters, and Ge\(_{14}^+\) present the
highest binding energy at the same value (3.29 eV) for Ge$_{n}^+$ clusters.

The second-order difference in energy of the nanoalloy cluster is the feature that reflects the relative stability between one cluster and its two directly adjacent clusters. The higher the value of $\Delta^2E_n$, the better the relative stability of the cluster. It can be observed from Figure 9 that the $\Delta^2E$ for AgGe$_{n}^{0/1}$, AgGe$_{10}^{0/1}$, AgGe$_{12}^{0/1}$, Ge$_{1}$, Ge$_{10}^{0/1}$, Ge$_{12}^{0/1}$, and Ge$_{11}^{0/1}$ clusters all have obvious peaks, indicating that their stability is higher than that of the adjacent clusters.

3.6. HOMO-LUMO Gap and Hardness. HOMO-LUMO energy gap ($E_{gap}$) is an electronic property of clusters, which can be used to express the performance of related chemical properties, such as photochemistry and conductivity. The value of $E_{gap}$ means the minimum energy required to transfer an electron from the HOMO to the LUMO. The value of the HOMO-LUMO gap has an inverse response to the external perturbations, which means that a small value corresponds to a large response. Therefore, the $E_{gap}$ of neutral and charged AgGe$_{n}^{\lambda}$ ($\lambda = 0, -1, +1; n = 1-13$) clusters has been computed using the mPW2PLYP scheme and is pictured in Figure 10. It can be found that: (i) For neutral clusters, the values of $E_{gap}$ range from 3.07 to 4.88 eV. The maximum value is calculated at AgGe$_{3}$, and the minimum value is calculated at AgGe$_{7}$. In anionic states, $E_{gap}$ ranges from 3.16 to 4.49 eV. The maximum value is calculated at AgGe$_{12}^{-}$, and the minimum value is calculated at AgGe$_{7}^-$ and AgGe$_{2}^-$. For cationic states, it ranges from 3.63 to 5.74 eV. The minimum value is simulated at AgGe$_{12}^+$, and the maximum value is calculated at AgGe$_{1}^+$. (ii) The $E_{gap}$ of AgGe$_{n}$ clusters are larger than that of AgGe$_{n}^-$ clusters with the exception of $n = 8$ and 12, indicating that an additional electron reduces their chemical stability. Furthermore, after losing an electron, the $E_{gap}$ of AgGe$_{n}^+$ is narrower than that of AgGe$_{n}$ for $n = 3, 5$, and 11–13 and is wider for $n = 1, 2, 4, 6–10$.

Hardness ($\eta$), as another important parameter reflecting the chemical properties, is calculated for AgGe$_{n}^{\lambda}$ ($n = 1-3$), and it can be defined as follows:

$$\eta = \frac{IP - EA}{2}$$

To facilitate comparison, hardness and HOMO-LUMO gap of AgGe$_{n}$ are shown in Figure 11 as a function of cluster sizes. To better understand the relationship of changes between them, the comparison of HOMO with VIP and LUMO with VDE is also given in Figure 11. It can be seen from Figure 11 that the trend of $E_{gap}$ and hardness is slightly different. For example, the hardness analysis of AgGe shows that it has a weak chemical reactivity, but HOMO-LUMO gap analysis indicates that it possesses a strong chemical activity. The reason is that the trend of HOMO and VIP is the same. However, the trend of LUMO and VDE is slightly different.

3.7. Charge Transfer and Partial Density of States (PDOS). In this section, NPAs of the most stable structure for AgGe$_{n}$ ($n = 1-13; \lambda = -1, 0, +1$) clusters were performed using the mPW2PLYP scheme. The results are shown in Table S. From Table S, it can be seen that the valence configurations of the Ag atom in AgGe$_{n}^{\lambda}$ ($n = 1-13; \lambda = -1, 0, +1$) clusters are $S_{p}^{0.36-0.48}$, $4d_{0.77-0.89}$, $S_{p}^{0.01-2.70}$. Regardless of being neutral or charged, the 4$d$ electrons of Ag atoms are almost unchanged, meaning that the 4$d$ electrons of Ag hardly participate in bonding. The calculated charges of Ag atoms in AgGe$_{n}$ ($n = 1-13$) with the exception of $n = 1$ and 12 are 0.02–0.48 a.u., indicating that Ag atoms mainly act as electron donors. The charges of Ag atoms in anionic clusters are the
The charges of Ag atoms in cationic AgGe\(_n^+\) (\(n = 1–12\)) clusters are 0.20–0.69 a.u., which are larger by 0.14–0.47 a.u. as compared with the charges of Ag atoms in neutral clusters. That is to say the germanium clusters provide the majority of lost charges for cationic AgGe\(_n^+\) (\(n = 1–12\)) species. The charges of Ag atoms in the cage-like configuration of AgGe\(_{12}^+\), AgGe\(_{12}^+\), and AgGe\(_{13}^+\) clusters are by −1.8 a.u., indicating that Ag atoms in these clusters act as an electron acceptor.

To better explore the electronic properties and HOMO-LUMO gap changes caused by the doping of Ag atoms, the detailed density of states (DOS) of AgGe\(_7^+\) as an example is provided. The PDOS of pure Ge\(_7^+\) and AgGe\(_7^+\) is shown in Figure 12. It can be seen from Figure 12 that the position of electron donors. The charges of Ag atoms in cationic AgGe\(_n^+\) (\(n = 1–12\)) clusters also act as

Figure 11. Chemical hardness and HOMO-LUMO gap of AgGe\(_n\) clusters.

Figure 12. PDOSs for Ge\(_7^+\) and AgGe\(_7^+\) show a significant change in the PDOS at the Fermi level because of doping of Ag.

| species charge | electron configuration | species charge | electron configuration | species charge | electron configuration |
|----------------|-----------------------|----------------|-----------------------|----------------|-----------------------|
| AgGe           | −0.05                 | [core]5s\(^{-1}\)4d\(^{0}\)5p\(^{0}\)6s\(^{2}\) | AgGe\(^−\)      | −0.05                 | [core]5s\(^{−2}\)4d\(^{2}\)5p\(^{1}\)7s\(^{1}\) |
| AgGe\(_2^1\)   | 0.20                  | [core]5s\(^{−1}\)4d\(^{0}\)5p\(^{0}\)6s\(^{2}\) | AgGe\(^−\)      | 0.20                  | [core]5s\(^{−2}\)4d\(^{2}\)5p\(^{2}\)7s\(^{1}\) |
| AgGe\(_3^1\)   | 0.28                  | [core]5s\(^{−1}\)4d\(^{0}\)5p\(^{0}\)6s\(^{2}\) | AgGe\(^−\)      | 0.28                  | [core]5s\(^{−2}\)4d\(^{2}\)5p\(^{3}\)7s\(^{1}\) |
| AgGe\(_4^1\)   | 0.32                  | [core]5s\(^{−1}\)4d\(^{0}\)5p\(^{0}\)6s\(^{2}\) | AgGe\(^−\)      | 0.32                  | [core]5s\(^{−2}\)4d\(^{2}\)5p\(^{4}\)7s\(^{1}\) |
| AgGe\(_5^1\)   | 0.28                  | [core]5s\(^{−1}\)4d\(^{0}\)5p\(^{0}\)6s\(^{2}\) | AgGe\(^−\)      | 0.28                  | [core]5s\(^{−2}\)4d\(^{2}\)5p\(^{5}\)7s\(^{1}\) |
| AgGe\(_6^1\)   | 0.30                  | [core]5s\(^{−1}\)4d\(^{0}\)5p\(^{0}\)6s\(^{2}\) | AgGe\(^−\)      | 0.30                  | [core]5s\(^{−2}\)4d\(^{2}\)5p\(^{6}\)7s\(^{1}\) |
| AgGe\(_7^1\)   | 0.48                  | [core]5s\(^{−1}\)4d\(^{0}\)5p\(^{0}\)6s\(^{2}\) | AgGe\(^−\)      | 0.48                  | [core]5s\(^{−2}\)4d\(^{2}\)5p\(^{7}\)7s\(^{1}\) |
| AgGe\(_8^1\)   | 0.16                  | [core]5s\(^{−1}\)4d\(^{0}\)5p\(^{0}\)6s\(^{2}\) | AgGe\(^−\)      | 0.16                  | [core]5s\(^{−2}\)4d\(^{2}\)5p\(^{8}\)7s\(^{1}\) |
| AgGe\(_9^1\)   | 0.19                  | [core]5s\(^{−1}\)4d\(^{0}\)5p\(^{0}\)6s\(^{2}\) | AgGe\(^−\)      | 0.19                  | [core]5s\(^{−2}\)4d\(^{2}\)5p\(^{9}\)7s\(^{1}\) |
| AgGe\(_10^1\)  | 0.32                  | [core]5s\(^{−1}\)4d\(^{0}\)5p\(^{0}\)6s\(^{2}\) | AgGe\(^−\)      | 0.32                  | [core]5s\(^{−2}\)4d\(^{2}\)5p\(^{10}\)7s\(^{1}\) |
| AgGe\(_11^1\)  | 0.02                  | [core]5s\(^{−1}\)4d\(^{0}\)5p\(^{0}\)6s\(^{2}\) | AgGe\(^−\)      | 0.02                  | [core]5s\(^{−2}\)4d\(^{2}\)5p\(^{11}\)7s\(^{1}\) |
| AgGe\(_12^1\)  | −1.80                 | [core]5s\(^{−1}\)4d\(^{0}\)5p\(^{0}\)6s\(^{2}\) | AgGe\(^−\)      | −1.80                 | [core]5s\(^{−2}\)4d\(^{2}\)5p\(^{12}\)7s\(^{1}\) |
| AgGe\(_13^1\)  | 0.23                  | [core]5s\(^{−1}\)4d\(^{0}\)5p\(^{0}\)6s\(^{2}\) | AgGe\(^−\)      | 0.23                  | [core]5s\(^{−2}\)4d\(^{2}\)5p\(^{13}\)7s\(^{1}\) |
occupied spin up and spin down states is identical for DOS of pure Ge. However, after the doping of Ag atoms, a new occupied spin up state in DOS is created, which causes a significant change in the HOMO-LUMO gap (from 4.86 to 3.29 eV). The electronic states of the HOMO mainly come from the 5s orbital of Ag atoms and 4s and 4p orbitals of the Ge cluster because the 0.48 a.u. charge transfer from the 5s orbital of Ag atoms to the 4s4p orbital of the Ge cluster as can be seen from Table S.

4. CONCLUSIONS

A systematic investigation of the silver-doped germanium clusters AgGe with \( n = 1−13 \) in the neutral, anionic, and cationic states is performed using the unbiased global search technique combined with the double-density functional scheme. The lowest-energy minima of the clusters are identified based on calculated energies and the measured PES. Total atomization energies and thermochemical properties such as EA, IP, binding energy, hardness, and HOMO-LUMO gap are obtained and compared with those of pure germanium clusters. The structural evolution for AgGe\(_{n}\) (\( n = 1−13; \lambda = −1, 0, \) and +1) emerges as follows: For neutral and anionic clusters, although the most stable structures are inconsistent when \( n = 7−10 \), the structure patterns both are exohedral structures except for \( n = 12 \), and a highly symmetrical endohedral configuration is formed when \( n = 12 \). For the cationic state, the most stable structures are attaching structures (in which an Ag atom is adsorbed on the Ge\(_n\) cluster or a Ge atom is adsorbed on the AgGe\(_{n−1}\) cluster) at \( n = 1−12 \), and when \( n = 13 \), the cage configuration is formed. The analyses of binding energy indicate that doping of an Ag atom into the neutral and charged Ge\(_n\) clusters may decrease their stability. The EAs of AgGe\(_n\) clusters including AEAs and VDEs are presented and are in perfect agreement with the experimental values. The IP including VIP and AIP of neutral Ge\(_n\) clusters is decreased when doped with an Ag atom. The HOMO-LUMO gaps of neutral AgGe\(_n\) (\( n = 1−13 \)) excluded \( n = 8 \) and 12 are larger than that of anionic clusters. For cationic states, the HOMO-LUMO gaps of AgGe\(_n\) are wider than that of AgGe\(_n\) for \( n = 1, 2, 4, \) and 6–10 and are narrower for \( n = 3, 5, \) and 11–13. The variant trend of the HOMO-LUMO gap and hardness versus cluster size is slightly different. The accuracy of the theoretical analyses in this paper is demonstrated successfully by the agreement between simulated and experimental results such as PES, IP, EA, and binding energy.

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