Density functional study Structures, Stabilities and Energetic properties of Ge_n (n= 2-30) clusters

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Abstract

The lowest energy structures of Ge_n (n=2–30) clusters are obtained using the first principles pseudopotential simulated annealing within the generalized gradient approximation (GGA) of density functional implemented in SIESTA method. New low-energy structures are obtained for each cluster size. The optimized clusters reveal that the most stable structures and their corresponding isomers have three dimensional configurations. The relative stabilities in terms of the binding energies, fragmentation energies and second-order difference of energies for all Ge_n (n=2–30) structures have also been investigated and discussed.

Keywords: Ge Clusters, Density functional theory, simulated annealing, Structural properties, SIESTA.

1. Introduction

The study of clusters has attracted much attention for many years [1] because their physical and chemical properties vary greatly with cluster size change [1-2-3], as well as the possibility of using them to form building blocks in groups assembled in nanoparticles or bulk phase and thus used in industry Photovoltaic materials, Catalyst, Nanotechnology and Spintronic [3-4]. All this has made clusters the subject of most imported research over the last four decades [1-4].

Semiconductor clusters, especially germanium and silicon, have been extensively investigated both experimentally and theoretically due to their potential applications in the microelectronics industry [5–6] and are of considerable scientific interest to explore the chemical structure and bonding as well as their thermodynamic stability and photoelectric effect [5–6] . Germanium like silicon is a very important semiconducting materials in periodic table elements [1], But it is a silicon superconductor for being 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[4], in the case of pure germanium clusters with medium or large size and doped germanium clusters , several investigations of their physical properties are previously performed by several authors [1-4] . For example, Ögüt and Chelikowsky. [7] Studied geometries and electronic structures of the neutral and charged Ge_n ($n \leq 10$) clusters using molecular dynamics (MD) and simulated annealing method. Wang and Han. [8] investigated the doping with tungsten and demonstrated that WGe_{12} , WGe_{14}, WGe_{16} structures enhance stabilities over their neighboring clusters while the electron charge transfer always is done from the germanium framework to the W atom. Li et al. [9] was investigated the effect of one atom of Au in anionic germanium clusters $AlGe_n^-$ (n=1-13) and they found that the clusters with n=12 is the most stable one compared to the other size. Shi et al. [10] has been studied the properties of small germanium clusters doped by one aluminum atom and they found that the undoped Ge_{n+1} clusters are more stable than doped $AlGe_n$ clusters. In their study on the properties of Cr atom doped small germanium clusters, Mahtout et al. [1] calculated the electronic and magnetic properties of medium-sized $CrGe_n$ ($15\leq n \leq 29$) clusters. They show that their structures become more compact and switch to near-spherical structure, with one or more core atoms, as the cluster size increases and there is a strong correlation between the geometric structures and the electronic and magnetic properties of $CrGe_n$ clusters. More recently, Siouani et al. [3] calculated the Structure, Stability and Electronic and Magnetic Properties of VGen (N=1-19) Clusters by using first principal DFT investigation, They found that the doping with one V atom contributes to enhance the stability of the germanium clusters and the electron charges always transfer from V atom to the neighboring Ge atoms.

All previous works indicate the great importance of germanium clusters in pure form or in case of dope. So we tried through this work, to study the change in germanium the state of its presence in cluster structures and the study the different properties of the Ge_n clusters that will be compared to previous studies. So, the geometric structures, relative stabilities and energetic properties of small Ge_n (n=2-30) clusters have been systematically investigated by using first principles calculations. The structures of low-lying energy isomers of each cluster size have been optimized and analysed, as well as the binding energy. This paper is organized as followed : we describe in section 2 theoretical methods and computational details used in this work, while results and discussion on the clusters geometries, stabilities and energetic properties of Ge_n clusters, in Section 3. Finally, our main conclusions are given in Section 4.

2. Theoretical methods and computational details

Structure electronic calculations have been performed by using the density functional theory (DFT) [11] implemented in SIESTA simulation package [12]. This code gives the opportunity to use norm-conserving Troullier-Martins nonlocal pseudopotentials [1-13] and employs a flexible basis set of localized Gaussian-type atomic orbital [1]. The generalized gradient approximation (GGA) of the density functional has been used with the exchange-correlation energy functional parameterized by Perdew and Zunger [14] and Perdew, Burke, and Ermserhof (PBE) [15]. During simulation, volume of the system was kept constant and to avoid interaction between the clusters a big supercell of 40 $\overset{\circ}{A}$ was used. Self-consistent field calculations are carried out with convergence criterion of 10^{-4} a.u. On the total energy and electron density. The K= 0 (Γ) point approximation was used in Brillouin zone sampling. We have used the double ζ (DZ) basis with polarization function for Ge atoms. The used Mesh Cutoff value is 150 Ry and the PAO. Energy shift is taken equal to 50 meV. Conjugate gradient method within Hellmann Feynman forces was used and all the forces are less than 10^{-3} eV/Å. In order to test the method used in geometry optimization with respect to the exchange-correlation functional, to the size and to the cutoff radii of basis sets, we performed calculations on Ge_2 and Ge_3 clusters. Our results in table. 01 is in good agreement with theoretical and experimental results of the literature.

3. Results and discussion

3.1. Structural properties

The geometric structure of clusters is an important feature which affects substantially all of the properties of small atomic system. In cluster physics, these properties may change radically from one structure to another for the same cluster size. According to orbital overlap between neighboring atoms forming the cluster and the atomic positions, For comparison we report in Figure. 01 The lowest-energy structures and their corresponding isomers of germanium clusters. The computational results on structural properties of the lowest-energy of Ge_n clusters are summarized in Table. 02. For each size, data for most stable isomer are reported in bold character. Many of the previous theoretical studies of the literature are in agreement with the obtained best structures, for clusters with n=2, the ground state structures adopt a planar with an average bond length of 2.503 Å. The Ge_3 ground state is a linear and triangular structure with C_{2v} symmetry and average bond length of 2.370 Å is found to be the most stable structure, agreement with previous works[3, 6, 10 and 25] by using different density functional calculations. The most stable isomer of the Ge_4 has D_{2h} symmetry and an average bond length of 2.597 Å which are in good agreement with previous works [3,6, 25 and 26]. For Ge_5 ground state is a triangular bipyramid structure with D_{3h} symmetry and an average bond length of 2.547 Å. This result is consistent with the previous theoretical results [3, 6, 25 and 27]. The most stable isomer for Ge_6 cluster presents a bicapped rectangular structure with C_{2v} symmetry and an average bond length of 2.710 Å, in agreement with previous works [3, 6]. For Ge_7 ground state is a pentagonal bipyramid structure of D_{5h} symmetry and Ge-Ge bond at 2.747 Å which are in good agreement with the results of works [3, 25 and 27]. The lowest-energy Ge_8 cluster displays a capped pentagonal bipyramid structure with C_{2v} symmetry and Ge-Ge bond at 2.776 Å, in agreement with previous works [3, 25 and 27]. In the case of Ge_9, structure with C_{2v} symmetry is found to be the most stable isomer. Its average bond length is calculated to be 2.782 Å. For Ge_{10} ground state is a capped irregular pentagonal prism structure with C_{3v} symmetry and Ge-Ge bond at 2.775 Å. The most stable isomer for Ge_{11} cluster present a caped pentagonal basis structure and with a Cs symmetry and an average bond length of 2.770 Å. The shape of Ge_{12} and Ge_{13} are a compact near spherical structure with C_{2v} symmetry and an average bond length of 2.744 Å and 2.760 Å respectively. The lowest-energy Ge_{14} cluster displays a compact near spherical structure with C_s symmetry and Ge-Ge bond at 2.797 Å, in agreement with previous work [3]. For Ge_{15} and Ge_{16} ground state are a compact near spherical structure with C_{2v} and C_{2h} symmetry and Ge-Ge bond at 2.814 Å and 2.780 Å respectively. In the case of the Ge_{17} cluster, structure has a near spherical shape with Cs symmetry and an average bond length of 2.823 Å. The shape of Ge_{18} is a compact near spherical structure with C_1 symmetry and an average bond length of 2.729 Å. From Ge_{19} to Ge_{28} clusters, a compact near spherical structure with C_1 symmetry is always favored. The average bond lengths are 2.843, 2.735, 2.735, 2.747, 2.766, 2.763, 2.737, 2.761, 2.792 and 2.709 Å for n=19, 20, 21, 22, 23, 24, 25, 26, 27 and 28 respectively. The lowest-energy isomer for Ge_{29} has a compact near spherical shape and an average bond length of 2.702 Å whereas the most stable structure of Ge_{30} adopts a C_1 symmetry with a larger average bond length of 2.739 Å.

3.2. Energetic (Relative Stabilities)

3.2.1. Binding energy

We compute the binding energy per atom (E_b) of the Ge_n clusters, In order to predict the relative stabilities of the clusters. The different value of is evaluated for each cluster by using the following formula:

$$E_{b/atom}(Ge_n) = [(n)E(Ge) - E(Ge_n)]/(n),$$

Where $E(Ge)$ is the single atom energy for germanium, and $E(Ge_n)$ are the total energy for pure Ge_n clusters.

The obtained results are reported in tables 02 and the calculated binding energy per atom as a function of cluster size for the best isomers is plotted in Figure. 02. We observe that by increasing the size of the cluster the bonding energy is gradually increasing, indicating that the clusters continue to gain energy during the growth process. In general, the binding energies must increase as the cluster size n increases because the overall stability is expected to increase as the cluster grows larger, and eventually reach the bulk value of binding energy in bulk crystal.

3.2.2. Fragmentation energy

Besides binding energy we find that the fragmentation energy is a good criterion to predict the relative stability of the clusters towards spontaneous fragmentation. we investigate the size dependence of the fragmentation energies (E_f) for Ge_n clusters when we neglecting the effect of free energy changes and dissociation barrier. The obtained values of E_f for different clusters can be evaluated with the following formula:

$$E_f(Ge_n) = E(Ge_{n-1}) + E(Ge) - E(Ge_n),$$

Where E is the total energy of the relevant system. The obtained results and their evolution as a function of size are plotted in Figure 03. We observe that there are oscillating behaviors in the evolution of fragmentation energy for all species. It is known in cluster physics, the clusters with large value of E_f are relatively stronger in thermodynamic stability than neighboring clusters. Consequently, the thermodynamic stabilities of small clusters such as: Ge_4, Ge_9, Ge_{10} and Ge_{27} clusters are relatively strong than neighboring clusters .

3.2.3. Second Order Difference

The second-order difference of total energy (Δ_2E) is a sensitive measurement to reflect the relative stabilities of clusters, in cluster physics. Where the values of Δ_2E are positive this means that the dissociate on of As atom is an unfavorable process and the clusters are particularly stable. The values of Δ_2E are given by the following formula:

$$\Delta_2\mathrm{E}(\mathrm{Ge}_n) = \mathrm{E}(\mathrm{Ge}_{n+1}) + \mathrm{E}(\mathrm{Ge}_{n-1}) - 2\mathrm{E}(\mathrm{Ge}_n),$$

Where E is the total energy of the relevant system. Therefore, the clusters with positive Δ_2E are more stable than those with the negative Δ_2E. The calculated Δ_2E for the lowest energy structures of Ge_n is computed and plotted as a function of clusters size in Figure 04. The particularly prominent maxima of Δ_2E for are found at n= 3, 4, 6, 7, 9, 10, 12, 13, 14, 16, 18, 19, 20, 21, 24, 25, 27 and 29 indicating that these clusters are more stable than their neighboring.

4. Conclusion

In summary, the lowest energy structures of Ge_n in the size range of 2–30 atoms have been obtained using first-principles simulated annealing GGA density functional calculations implemented in SIESTA method. Our calculations reveal that there is a strong correlation between the geometric structures and the energetic properties of Ge_n clusters. In all cases of this size range, the bond length of Ge_n clusters is longer than the one in bulk germanium. The binding energies generally increase with the increase of clusters size. The fragmentation energy show that the thermodynamic stabilities of small clusters such as: Ge_4 , Ge_9, Ge_{10} and Ge_{27} clusters are relatively strong than neighboring clusters . The second differences of cluster energies show that the lowest energy isomers of n= 3,4,6,7,9,10,12,13,14, 16, 18,19,20,21,24,25,27 and 29 are more stable than neighboring clusters.

5. References

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Figure I.3 *https://journals.aps.org/prb/abstract/10.1103/PhysRevB.55.R4914*

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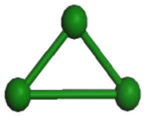
Ge_2 ($D_{\infty h}$)


Ge_3(a)($D_{\infty h}$)


Ge_3(b)(C_{2v})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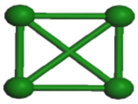
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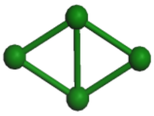
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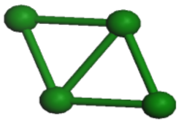
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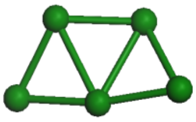
Ge_4(d)(C_{3v})


Ge_4(e)($D_{\infty h}$)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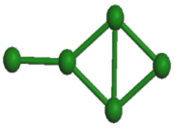
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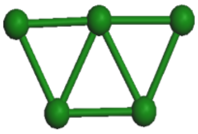
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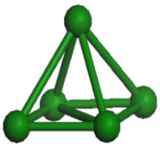
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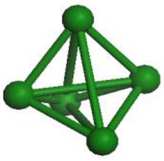
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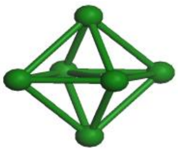
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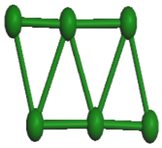
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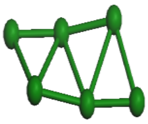
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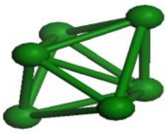
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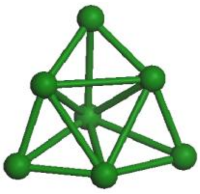
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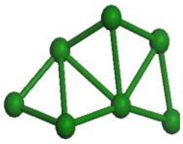
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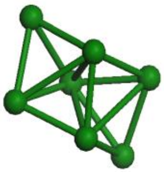
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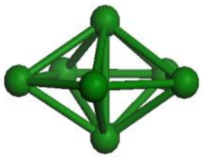
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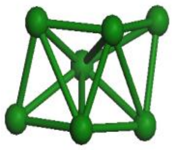
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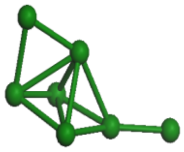
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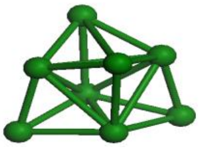
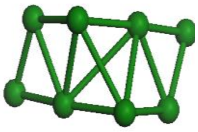

Ge_8(a)(C_{2v})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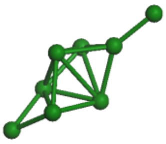
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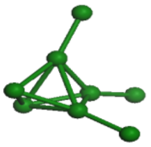
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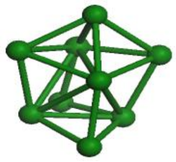
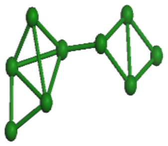
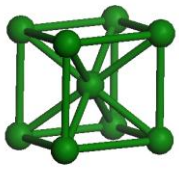
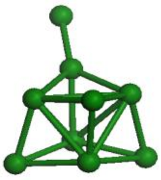
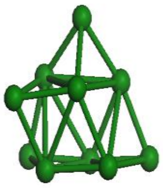

Ge_9 (a)(C_{2v})


Ge_9(b) (C_1)


Ge_9(c)(D_{3d})


Ge_9(d)(C_{3v})


Ge_{10}(a)(C_s)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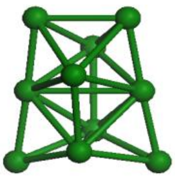
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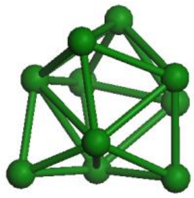
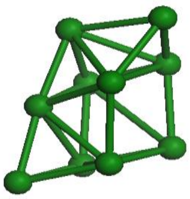

Ge_{10}(d) (C_{3v})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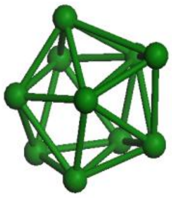
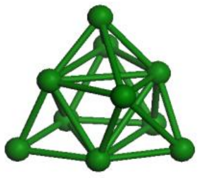

Ge_{10}(f) (C_s)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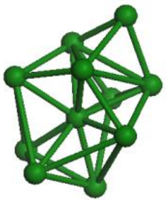
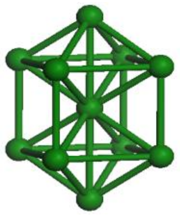

Ge_{11}(a)(C_{3v})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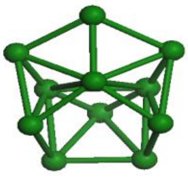
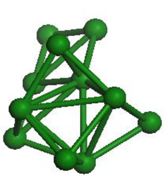
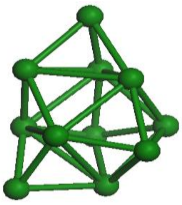

Ge_{11}(c) (C_s)


Ge_{11}(d)(C_s)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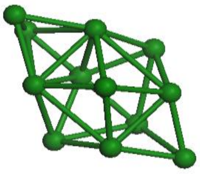
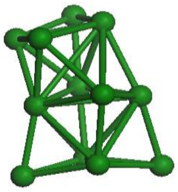
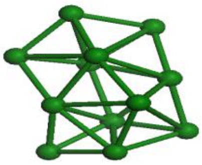
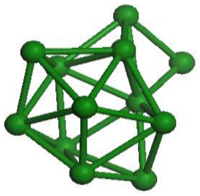
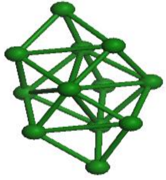

Ge_{12}(a)(C_s)

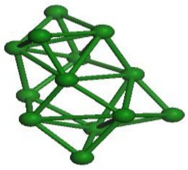

Ge_{12}(b)(C_1)

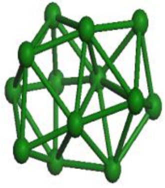

Ge_{12}(c)(C_1)

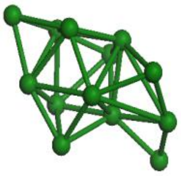

Ge_{12}(d) (C_s)


Ge_{12}(e)(C_{2v})


Ge_{13}(a)(C_{2v})


Ge_{13}(b)(C_2)


Ge_{13} (c)(C_1)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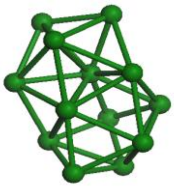
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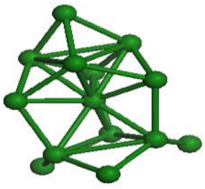
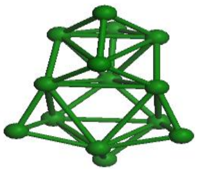

Ge_{14}(a)(C_{3v})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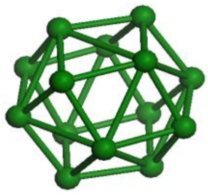
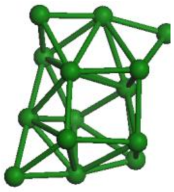
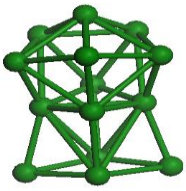

Ge_{14}(c) (O_h)


Ge_{14}(d) (C_1)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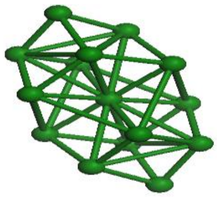
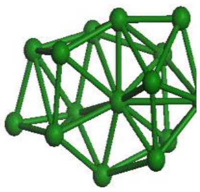
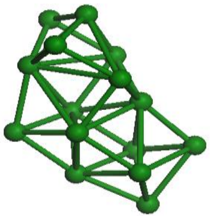
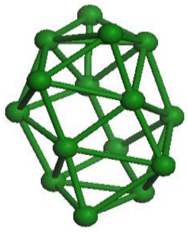
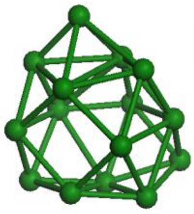
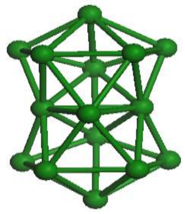

Ge_{15}(a)(D_{3d})

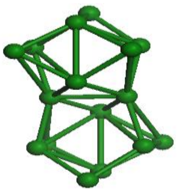

Ge_{15}(b)(C_1)

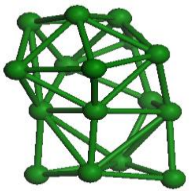

Ge_{15}(c) (C_s)

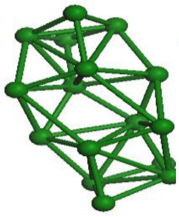

Ge_{15}(d) (C_1)

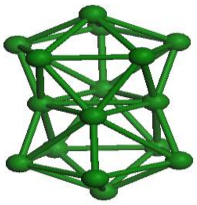

Ge_{15}(e)(C_1)

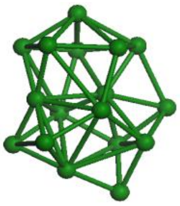

Ge_{15}(f)(C_{2v})

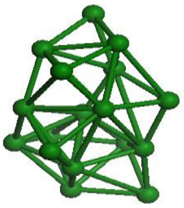

Ge_{16}(a) (C_{2h})

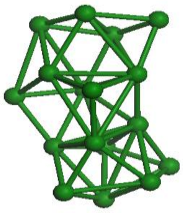

Ge_{16}(b)(C_1)

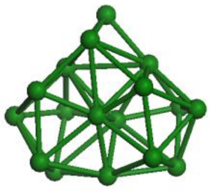

Ge_{16}(c)(C_2)

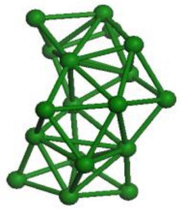

Ge_{16}(d)(C_{2h})

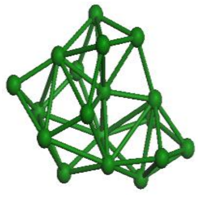

Ge_{17}(a) (C_s)

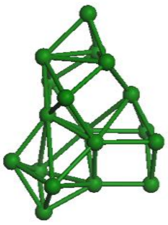

Ge_{17}(b)(C_1)

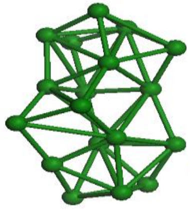

Ge_{17}(c) (C_1)

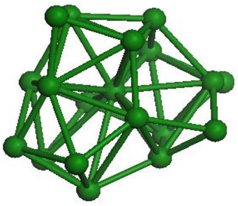

Ge_{17}(d)(C_s)

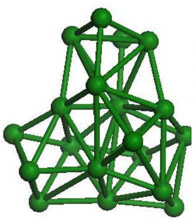

Ge_{18}(a)(C_2)

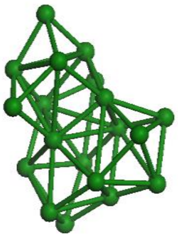

Ge_{18}(b)(C_s)

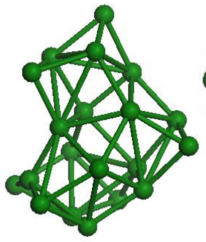

Ge_{18}(c) (C_s)

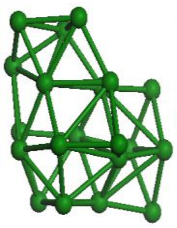

Ge_{18}(d) (C_1)

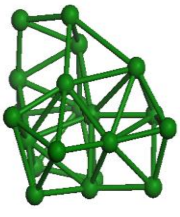

Ge_{19}(a) (C_1)

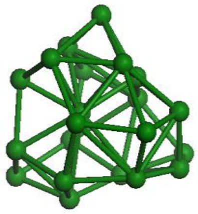












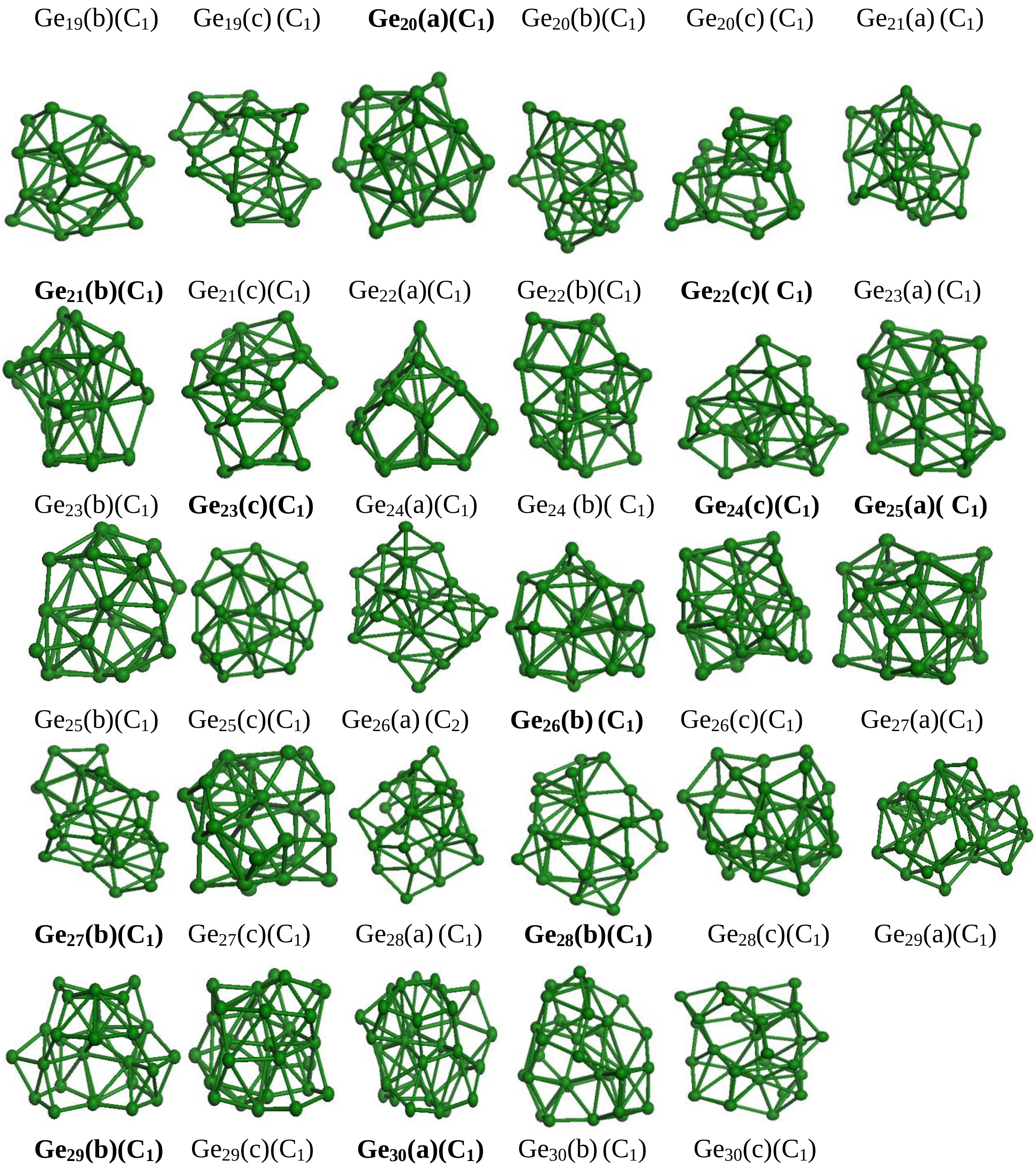


Figure 01. Ground state structures and their corresponding isomers for Ge$_n$ (n = 2-30) clusters.

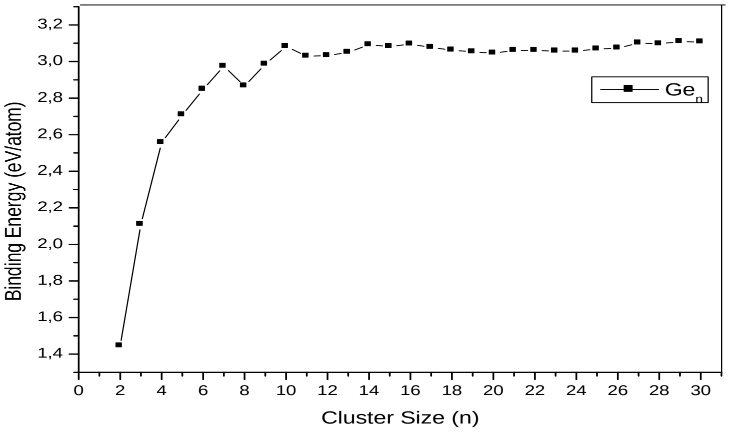


Figure. 02: Size dependence of the binding energy of Ge$_n$ (n = 2-30) clusters.

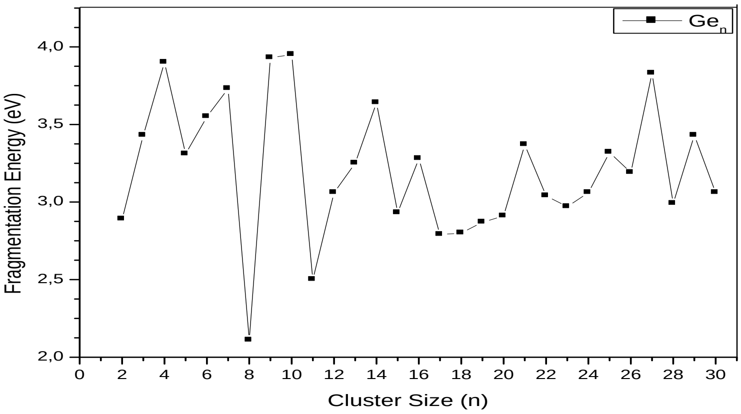


Figure. 03: Size dependence of the Fragmentation energies of Ge$_n$ (n=2-30) clusters.

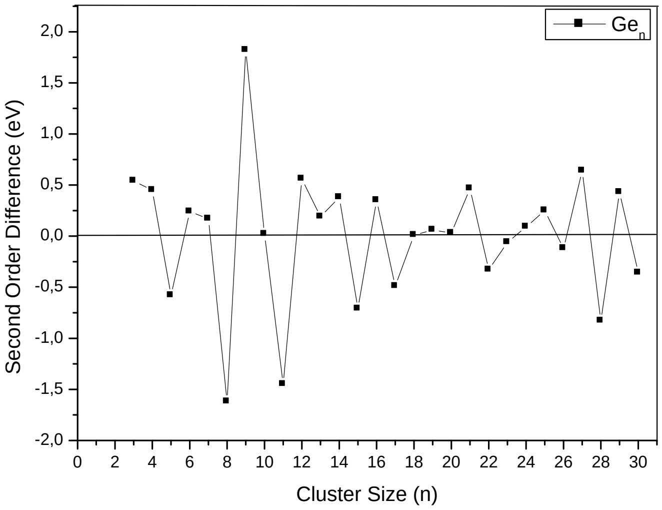


Figure. 04: Size dependence of the second order energy difference of Ge$_n$ (n=2-30) clusters.

Table. 01: Average bond length *a* (Å) and Binding energy E_b (eV)) for Ge_2 and Ge_3 clusters.

Clusters	Our Works		Bibliographic data	
	a (Å)	Eb (eV)	*a* (Å)	Eb (eV)
Ge_2	2.503	1.445	2.450[a] 2.413[b] 2.540[c] 2.610[e] 2.570[g] 2.422[h] 2.421[i]	1.446[a] ~1.430[b] 1.620[d] 1.812[e] ~1.350[f] 1.410[j] 1.320[l] 1.230[m]
Ge_3	2.370	2.110	2.546[a] 2.400[m]	2.059[a] 2.240[k] 2.150[i] 2.040[b]

[a] Ref. [3]

[b] Ref. [10]

[c] Ref. [16]

[d] Ref. [9]

[e] Ref. [1]

[f] Ref. [17]

[g] Ref. [18]

[h] Ref. [19]

[i] Ref. [20]

[j] Ref. [21]

[k] Ref. [22]

[l] Ref. [23]

[m] Ref. [24]

Table. 02: Symmetry group, binding energy per atom E_b (eV/atom) and average bond length ($\mathring{A}$) for pure Ge_n (n=2-30) clusters.

Cluster size (n)	Symmetry	Eb (eV/atom)	a_{Ge-Ge} ($\mathring{A}$)
2	**$D_{\infty h}$**	**1.445**	**2.503**
3	$D_{\infty h}$	2.048	2.339
	C_{2v}	2.109	2.370
	C_{2v}	**2.110**	**2.370**
4	D_{4h}	2.228	2.550
	D_{2h}	2.556	2.576
	D_{2h}	**2.557**	**2.597**
	C_{3v}	2.078	2.479
	$D_{\infty h}$	2.061	2.346
5	C_2	2.518	2.606
	C_{2v}	2.450	2.564
	C_{2v}	2.499	2.618
	C_{2v}	2.504	2.775
	D_{3h}	**2.707**	**2.547**
6	D_{4h}	2.847	2.782
	C_{2h}	2.668	2.760
	C_2	2.672	2.606
	C_{2v}	**2.848**	**2.710**
7	C_{3v}	2.877	2.734
	C_1	2.687	2.647
	C_2	2.843	2.754
	D_{5h}	**2.974**	**2.747**
	C_2	2.843	2.754
	C_S	2.617	2.701
8	**C_{2v}**	**2.866**	**2.776**
	C_2	2.735	2.658
	C_S	2.739	2.730
	C_S	2.422	2.651
9	**C_{2v}**	**2.985**	**2.782**
	C_1	2.700	2.570
	D_{3d}	2.574	2.798
	C_{3v}	2.827	2.686
10	C_s	2.848	2.742
	C_s	3.002	2.779
	C_{2v}	2.968	2.785
	C_{3v}	**3.082**	**2.775**
	C_1	2.953	2.738
	C_s	3.013	2.794
	C_s	3.003	2.771
11	C_{3v}	2.792	2.714
	D_{4h}	2.715	2.816
	C_s	2.907	2.748
	C_s	2.892	2.724
	C_s	**3.029**	**2.770**
12	C_s	2.936	2.798
	C_1	2.955	2.784
	C_1	2.964	2.801
	C_s	2.979	2.793
	C_{2v}	**3.032**	**2.744**
13	**C_{2v}**	**3.050**	**2.760**
	C_2	3.007	2.792
	C_1	3.015	2.835
	C_s	2.990	2.769
	C_1	3.015	2.831
14	C_{3v}	2.922	2.696
	C_s	3.026	2.700
	O_h	2.977	2.659
	C_1	2.986	2.784

	C_s	**3.092**	**2.797**
15	D_{3d}	2.864	2.666
	C_1	2.999	2.829
	C_s	2.959	2.785
	C_1	3.022	2.812
	C_1	3.023	2.786
	C_{2v}	**3.082**	**2.814**
16	C_{2h}	3.027	2.715
	C_1	3.020	2.755
	C_2	3.034	2.808
	C_{2h}	**3.095**	**2.780**
17	C_s	3.050	2.781
	C_1	3.043	2.772
	C_1	3.038	2.762
	C_s	**3.077**	**2.823**
18	C_2	3.014	2.869
	C_s	3.013	2.790
	C_s	3.009	2.782
	C	**3.062**	**2.729**
19	**C_1**	**3.053**	**2.843**
	C_1	3.019	2.771
	C_1	3.019	2.771
20	**C_1**	**3.046**	**2.735**
	C_1	3.033	2.768
	C_1	3.001	2.781
21	C_1	3.041	2.769
	C_1	**3.061**	**2.735**
	C_1	3.050	2.761
22	C_1	3.059	2.750
	C_1	3.040	2.763
	C_1	**3.061**	**2.747**
23	C_1	2.999	2.744
	C_1	3.023	2.785
	C_1	**3.057**	**2.766**
24	C_1	3.056	2.728
	C_1	3.048	2.805
	C_1	**3.057**	**2.763**
25	**C_1**	**3.068**	**2.737**
	C_1	3.046	2.749
	C_1	3.061	2.792
26	C_1	3.035	2.812
	C_1	**3.073**	**2.761**
	C_1	3.065	2.724
27	C_1	3.058	2.769
	C_1	**3.101**	**2.792**
	C_1	3.079	2.737
28	C_1	3.053	2.736
	C_1	**3.097**	**2.709**
	C_1	3.078	2.759
29	C_1	3.081	2.744
	C_1	**3.109**	**2.702**
	C_1	2.866	2.736
30	**C_1**	**3.107**	**2.739**
	C_1	3.064	2.762
	C_1	3.100	2.700