A theoretical study of the first-row transition metal doped germanium clusters $Ge_{14}M$

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ABSTRACT

Geometry, stability, electronic structure, and magnetic properties of $Ge_{14}M$ clusters with M being a 3d transition metal atom, from Sc to Zn, were studied using density functional theory (DFT) calculations at B3PW91/6-311+G(d) level. The obtained results found that $Ge_{14}M$ clusters preferentially exist in their lowest possible spin state, except for M being Fe and Cr. The thermodynamic stability of the structures has been evaluated through the average binding and embedded energies. $Ge_{14}Ti$ and $Ge_{14}V$ clusters are considered to be the most stable in the $Ge_{14}M$ series (M = Sc - Zn) with the geometry of the C_2 point group where M is located in the center of the Ge_{12} hexagonal prism along with two Ge-atoms capping on two Ge_6 faces. In this series $Ge_{14}M$ clusters, only $Ge_{14}Fe$ cluster is stable at the high spin state, with a magnetic moment of $2_{\mu B}$.

Keywords: Doped germanium clusters; Density functional theory; Binding energy; Embedded energy.

1. INTRODUCTION

Similar to silicon, germanium is one of the important elements in semiconductor material and the microelectronics industry [1]. Over the past several decades, many theoretical and experimental investigations on the geometric and electronic structures of semiconductor nanoclusters based on these elements have been widely carried out [2], [3] and the obtained results have provided a deeper understanding of stability, growth mechanism, as well as application possibilities of materials based on atomic clusters containing chemical elements silicon and germanium. It was found that doping a metal atom into germanium clusters, generated by dual laser vaporization experiments, remarkably altered their chemical and physical properties [2].

In 2011, a study of Kapila *et al.* using DFT calculation found that Ge_n clusters doped by Ni atom are more stable than those doped by Co or Mn atoms [2]. Recently, our theoretical investigation on the first-row transition metals doped into Ge_{16} cluster in both neutral and anionic states found that both $Ge_{16}Sc$ and $Ge_{16}Cu$ neutral clusters can be considered as superhalogens because of their high electron affinity (≥ 3.6 eV) and the total magnetic moment of $Ge_{16}Mn$ reaches a maximum value of 3 μ_B [5]. Many studies indicated that doping transition metals into a pure atomic cluster may increase their stability. Based on the energetic parameters, highest occupied molecular orbitals - lowest unoccupied molecular orbitals (HOMO-LUMO) energy gap, and chemical hardness, Siouani *et al.* showed that the $Ge_{14}V$ cluster possesses the highest stability in the Ge_nV series, with n = 1 - 19 [6]. Among Ge_nMn clusters (n = 2 - 16), Ge_5Mn, Ge_9Mn, $Ge_{12}Mn$, and $Ge_{14}Mn$ were evaluated to be more stable than the rest, and remarkably, $Ge_{14}Mn$ was found as a “magic cluster” [7]. Similarly, the $Ge_{14}Fe$ cluster has the highest stability in the Ge_nFe (n = 9 - 16) series [8]. Along with $Ge_{10}Cr$, the $Ge_{14}Cr$ cluster was found to have enhanced stability in the Ge_nCr (n = 1 - 17) series [9]. Most recently, Wang *et al*. found that the structures of $Ge_{14}M^-$ clusters, with M = V, Nb, Ta, had the complete closed cage structure with high stability and these clusters can be considered as potential building blocks for novel nanomaterials [10]. These studies have shown that doping the transition metal into germanium cluster, in particular Ge_{14}, can lead to significant changes in their structure, stability, and properties and thus, this has attracted the attention of scientists. Motivated by that, we carried out an investigation using DFT calculation on $Ge_{14}M$ clusters, with M being the first-row transition metal to critically examine their stability, geometrical and electronic structures, and magnetic properties.

2. COMPUTATIONAL METHODS

The possible initial structures of $Ge_{14}M$ clusters are generated in two ways: first, by adding an M-doped metal atom to all possible positions both around and into the most stable Ge_{14} isomers, and another way, by substituting a Ge-atom in Ge_{15} isomers with M-atom. The geometrical structures of Ge_{14} and Ge_{15} isomers are taken from previous reports [6, 8]. Many previous theoretical studies on germanium clusters doped with the first-row transition metals proved the reliability of using the B3PW91 hybrid functional in geometrical optimization as well as energetic parameters calculations [1, 11]. Thus, these initial structures are geometrically optimized using the B3PW91 functional with the basis set LanL2DZ effective core potential. The most stable structures obtained at this level having relative energies less than 3.0 eV are further optimized using the B3PW91 functional but with a larger basis set of 6-311+G(d) in various spin states. To ensure the optimized geometries are local minima, the vibrational frequencies and zero-point energy correction (ZPE) of $Ge_{14}M$ clusters are determined at the same theoretical level B3PW91/3-311+(d) and the correction of zero point energy is also included in relative energy calculation. All quantum chemical calculations are carried out using Gaussian 09 package [12]. The electronic structure and magnetic properties of the most stable $Ge_{14}M$ clusters are analyzed based on natural bond orbital (NBO) calculation using the NBO 3.0 program also implemented in the Gaussian 09 program.

3. RESULTS AND DISCUSSION

3.1. Lowest-energy structures of $Ge_{14}M$ cluster

To evaluate the reliability of the calculation method, the parameters of bond length, and first ionization potential (IP) of Ge_2, Cu_2, and Cr_2 molecules were calculated using different DFT functionals including B3PW91, B3P86, M06-2X, B3LYP and PBE with the same 6-311+G(d) basis set. The results of theoretical calculations and experimental data are presented in table 1. For B3PW91 functional, the bonding lengths of Ge_2, Cu_2, and Cr_2 are predicted to be 2.390, 2.264, and 1.556 Å, respectively, which are consistent with the experimental values of 2.44, 2.22, and 1.679 Å, respectively. Moreover, the calculated IP using B3PW91 functional is also in good agreement with experimental data. The calculated IP value of Ge_2 obtained at B3PW91/6-311+G(d) level is of 7.620 eV, which approximates the experimental IP value of 7.8 eV. These confirm that the calculated results of $Ge_{14}M$ clusters system, with M being 3*d* transition metal, obtained at the B3PW91 functional in conjunction with the 6-311+G(d) basis set level are reliable. The notation $Ge_{14}M$-X is used to denote the isomers under consideration, where M = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn and X = A, B, C, etc. refer to different isomers with increasing relative energies. Parameters including symmetry point group (PG), electronic state (ES), average Ge-M bonding length d_{TB}(Ge-M), a total of covalent radii of Ge and M atoms (r_{Ge} + r_M), the difference $\Delta_{d\text{-}r}$ of d_{TB}(Ge-M) and (r_{Ge} + r_M), the coordination number of M, the electronic configuration of the M-atom, and the natural charge on M obtained in the NBO analysis are listed in table S1 of the SI file. Due to geometrical optimizing calculations found a large number of isomers for each $Ge_{14}M$ cluster, only the most stable isomers and a few isomers considered of the $Ge_{14}M$ at B3PW91/6-311+G(d) level are shown in figure 1 while lower-lying isomers are displayed in figure S1 of the Supplemental Information (SI) file (https://online.jmst.info/index.php/jmst/article/view/784/595). The main geometrical features of the $Ge_{14}M$ clusters can be briefly summarized as follows:

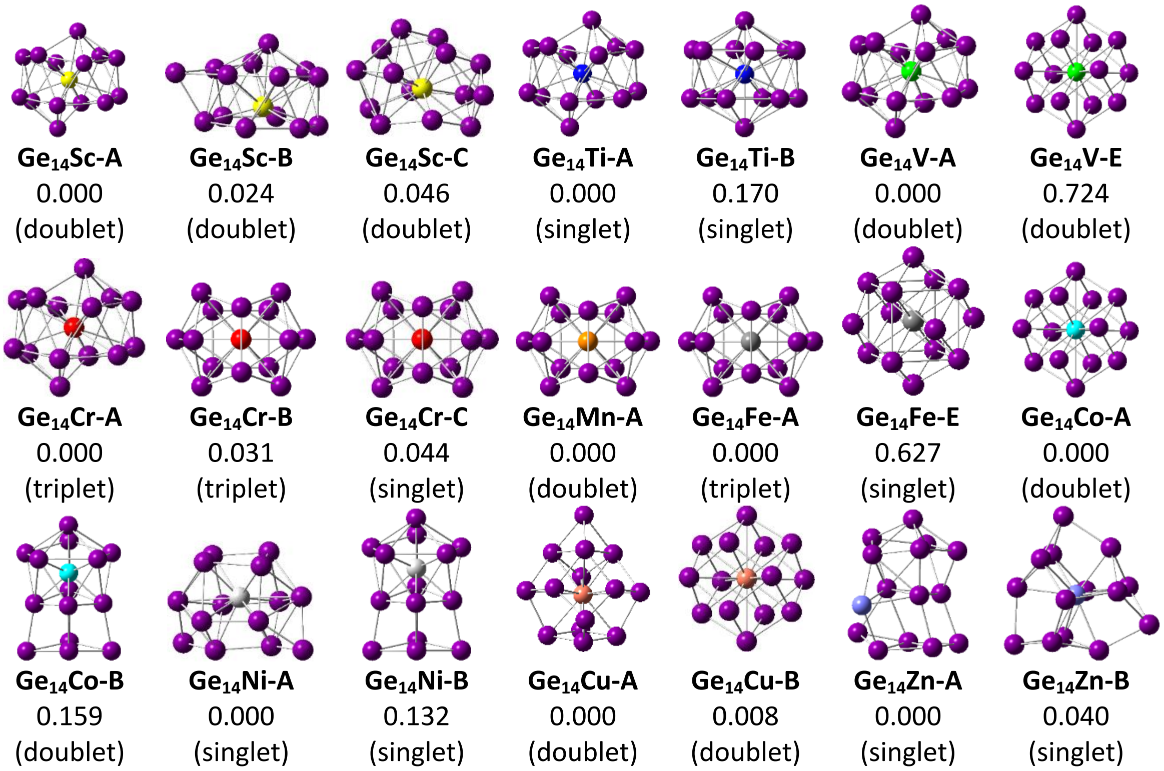
The most stable structures of **$Ge_{14}M$-A** (M = Sc, Ti, V, Cr) belong to C_2 point group in which M dopant locates at the center of the hexagonal prism Ge_{12} and two remaining Ge-atoms locates above and below two Ge_6 faces. The $Ge_{14}Sc$, $Ge_{14}Ti$, and $Ge_{14}V$ structures exist in the lowest possible spin state that is ^2A, ^1A and ^2B, respectively. Only $Ge_{14}Cr$ favors a higher spin state that is triplet ^3B. The next isomers of $Ge_{14}Sc$, including **$Ge_{14}Sc$-B** and **$Ge_{14}Sc$-C**, are also in the doublet spin state and have very low relative energies of 0.024 and 0.046 eV, respectively. They thus can be considered energetic quasi-degenerate isomers and may co-exist in the experimental beam under subtle conditions.

Table 1. *The bonding length ($d_{M\text{-}M}$) and ionization potential of Ge_2, Cu_2, and Cr_2.*

Method	Ge_2		Cu_2		Cr_2	
	$d_{M\text{-}M}$ (Å)	IP (eV)	$d_{M\text{-}M}$ (Å)	IP (eV)	$d_{M\text{-}M}$ (Å)	IP (eV)
Experiment	2.44 [a]	7.8 [c]	2.22 [b]	7.899 ± 0.007 [d]	1.679 [b]	6.4 ± 0.2 [e]
B3PW91	2.390	7.620	2.264	7.809	1.556	6.416
B3P86	2.385	8.193	2.252	8.436	1.553	7.136
M062X	2.375	9.256	2.394	7.369	1.515	4.786
B3LYP	2.408	7.644	2.278	7.996	1.565	6.672
PBE	2.298	7.355	2.2507	8.101	1.596	6.969

Ref. [a] [13], [b] [14], [c] [15], [d] [16], [e] [17].

In a previous study, DFT calculations using the PBE function in combination with the double ζ (DZ) basis set for Ge atoms and double ζ basis set with polarization function (DZP) for V-atom showed that the **$Ge_{14}V$-E** structure belonging to the O_h point group and exists in doublet spin state is the most stable structure [6]. To re-evaluate this claim, the **$Ge_{14}V$-A** and **$Ge_{14}V$-E** isomers were calculated at various levels of calculation. At PBE/LanL2DZ level, DFT calculations indicate that **$Ge_{14}V$-E** structure is less stable than **$Ge_{14}V$-A** with a relative energy of 0.256 eV. Next, the optimizing calculations using various DFT functions, including B3PW91, B3LYP, B3P86, and M06-2X, combined with a larger basis set of 6-311+G(d) are performed. The obtained results, displayed in table S2 of the SI file, show that for any function used, **$Ge_{14}V$-E** isomer is much less stable than **$Ge_{14}V$-A** with a relative energy value being higher than 0.7 eV. In addition, these calculations also point out **$Ge_{14}V$-E** structure containing imaginary frequency, although the symmetry of **$Ge_{14}V$-E** is decreasing from O_h to D_{2h}. Therefore, it can be confirmed that the **Ge$_{14}$V-A** structure found in this study is the most stable structure of the Ge$_{14}$V cluster.



Ge$_{14}$Sc-A 0.000 (doublet)
Ge$_{14}$Sc-B 0.024 (doublet)
Ge$_{14}$Sc-C 0.046 (doublet)
Ge$_{14}$Ti-A 0.000 (singlet)
Ge$_{14}$Ti-B 0.170 (singlet)
Ge$_{14}$V-A 0.000 (doublet)
Ge$_{14}$V-E 0.724 (doublet)
Ge$_{14}$Cr-A 0.000 (triplet)
Ge$_{14}$Cr-B 0.031 (triplet)
Ge$_{14}$Cr-C 0.044 (singlet)
Ge$_{14}$Mn-A 0.000 (doublet)
Ge$_{14}$Fe-A 0.000 (triplet)
Ge$_{14}$Fe-E 0.627 (singlet)
Ge$_{14}$Co-A 0.000 (doublet)
Ge$_{14}$Co-B 0.159 (doublet)
Ge$_{14}$Ni-A 0.000 (singlet)
Ge$_{14}$Ni-B 0.132 (singlet)
Ge$_{14}$Cu-A 0.000 (doublet)
Ge$_{14}$Cu-B 0.008 (doublet)
Ge$_{14}$Zn-A 0.000 (singlet)
Ge$_{14}$Zn-B 0.040 (singlet)

Figure 1. *Some of the lowest-energy structures of the Ge$_{14}$M (M = Sc – Zn) clusters, relative energy (eV), and spin state at B3PW91/6-311+G(d) level.*

The geometry of **Ge$_{14}$Cr-B** and **Ge$_{14}$Cr-C** belong to the C_s and C_{2v} point group, respectively. Their relative energies, being of 0.031 and 0.044 eV, respectively, are very close to that of **Ge$_{14}$Cr-A** and they thus are considered as energetic degenerate isomers. The most stable shape of **Ge$_{14}$M-A**, with M = Mn, Fe, is a C_{2v} polyhedron with 16 triangular faces, 1 rhombus face and 2 pentagonal faces. The geometry of doublet spin state **Ge$_{14}$Mn-A** was found to be consistent with the previous study [7]. **Ge$_{14}$Fe-A** has the same shape as **Ge$_{14}$Mn-A** but favors the $^3A_1$ triplet spin state. Moreover, in the series of the most stable isomers of **Ge$_{14}$M-A**, with M going from Sc to Zn, only Ge$_{14}$Fe and Ge$_{14}$Cr exist at a high spin state that is a triplet, all remaining of **Ge$_{14}$M-A** isomers favor the low spin states, being singlet or doublet. A previous study reported that **Ge$_{14}$Fe-E** with a point group of O_h in the singlet state $^1A_1$ is the ground state [8]. In this work, however, DFT calculations found the **Ge$_{14}$Fe-E** isomer is much less stable than **Ge$_{14}$Fe-A** with a relative energy gap of 0.627 eV. The calculated results using various functionals, listed in table S3 of the SI file, also indicate that **Ge$_{14}$Fe-A** isomer is significantly more stable than **Ge$_{14}$Fe-E** with the relative energy value being higher than 0.5 eV. Thus, it can be confirmed that the **Ge$_{14}$Fe-A** structure found in this study is the most stable structure of the Ge$_{14}$Fe cluster. The **Ge$_{14}$Co-A** structure has the highest symmetry among the most stable isomers **Ge$_{14}$M-A**. Its geometry belongs to the point group D_{4h} containing 12 rhombohedral faces with the electronic state of $^2B_{1g}$. Although **Ge$_{14}$Ni-A** structure also belongs to C_2 symmetry point group like **Ge$_{14}$M-A** (M = Sc –

Cr), its geometric structure is very different, there are two Ge atoms locating far from the Ni central atom. While the coordination number of M in **Ge_{14}M-A**, with M = Sc, Ti, V, and Cr, is 14, the coordination number of Ni is only 12 in the structure of **Ge_{14}Ni-A**. The stable forms of Ge_{14}Ni are mainly in the singlet state. The geometry of **Ge_{14}Cu-A** is composed of 6 pentagonal faces and 3 rhombus faces, belonging to the group of C_s symmetry points, the coordination number of Cu is only 12, similar to Ni in **Ge_{14}Ni-A**. The most stable structure of Ge_{14}Cu is consistent with the previous study of Bandyopadhyay [18]. The **Ge_{14}Cu-B** isomer with the $^2A_{1g}$ electronic state is only 0.008 eV higher energy than **Ge_{14}Cu-A**, so they can also co-exist and are energetically degenerate states. The **Ge_{14}Zn-A** structure has a symmetry point group of C_1 and the coordination number of Zn is only 5, much lower than that of other Ge_{14}M clusters, being 12 or 14. Unlike other Ge_{14}M clusters, the geometrical structure of **Ge_{14}Zn-A** shows that the Zn-atom is not encapsulated in the framework of Ge_{14}, this structure thus is predicted to be unstable. However, the geometry of the **Ge_{14}Zn-B** structure is significantly different from that of **Ge_{14}Zn-A** in which the Zn-atom in **Ge_{14}Zn-B** is completely enclosed into germanium cage with the geometry belonging to the C_{3h} symmetry. In addition, the relative energy of **Ge_{14}Zn-B** is only 0.04 eV higher than **Ge_{14}Zn-A**, so they are possible co-existence structures of the Ge_{14}Zn cluster. The average bonding length in **Ge_{14}Zn-A** is 2.835 Å, much larger than the sum of the covalent radii of Zn and Ge atoms of 2.42 Å, namely 0.415 Å. This shows that the Ge-Zn bonds in **Ge_{14}Zn-A** are much elongated relative to the sum of the covalent radii. Therefore, it is possible to preliminary evaluate **Ge_{14}Zn-A** to be less stable. In contrast, for the **Ge_{14}M-A** cluster with M = Sc, Ti, and V, the difference between the average Ge-M bonding length and the sum of the covalent radii $\Delta_{d\text{-}r}$ is only from 0.021 to 0.110 Å, which are very small compared to that of the remaining cluster **Ge_{14}M-A**. As a result, in comparison with the sum of the covalent radii, the Ge-Sc, Ge-Ti, Ge-V bonds reach the most perfect degree, and the structures of these Ge_{14}M clusters are predicted to more stable. In **Ge_{14}Ti-A**, the valence shell electron configuration of Ti is [core]$4s^{0.40}3d^{6.26}4p^{1.69}4d^{0.15}6s^{0.01}$. Compared with the configuration of the isolated Ti-atom in the ground state [core]$4s^2 3d^2$, the number of valence shell electrons increases significantly, which is the number of electrons that is delocalized from the Ge_{14} framework into the Ti-atom. This number of delocalized electrons in **Ge_{14}Ti-A** is the greatest in the **Ge_{14}M-A** series and thus the natural charge on Ti is the most negative with the value of -4.514 a.u. Similarly, the values of natural charge on M of **Ge_{14}Sc-A** and **Ge_{14}V-A** are -4.342 and -3.972 respectively, which are also more negative than the charge on M in the remaining clusters. Consequently, when forming bonds with Ge, there is a strong delocalization of the valence electrons of Ge-atoms in the Ge_{14} framework into the empty orbitals of the M-atom with M being Sc, Ti, or V. This leads to the prediction that the Ge_{14}Sc, Ge_{14}Ti, and Ge_{14}V clusters may be more stable than the remaining clusters. In the case of a transition metal M being at the end of the series, such as coopper, the electronic configuration of Cu in Ge_{14}Cu is [core]$4s^{0.47}3d^{9.88}4p^{1.27}5s^{0.03}4d^{0.01}5p^{0.05}$. This configuration alters quite a bit compared to the ground state of isolated Cu-atom which is [core]$4s^1 3d^{10}$. The number of electrons mainly changes only in the 4s orbital and 4p orbital, whereas almost unchanged in the 4d orbital. This is evidenced by the natural charge on the Cu-atom of -0.699 a.u., which is less negative than the metal M at the beginning of the series. This means that the electrons on the Ge_{14} framework are not much delocalized towards the orbitals of Cu-atom, so $Ge_{14}Cu$ is predicted to be less stable.

3.2. Relative stability of $Ge_{14}M$ clusters

To examine the relative stability of the clusters $Ge_{14}M$ with the change of first-row transition metal M, we calculated different thermodynamic parameters, including average binding energy (E_b) and embedded energies (E_e). These values of the most stable $Ge_{14}M$ clusters are calculated as follows:

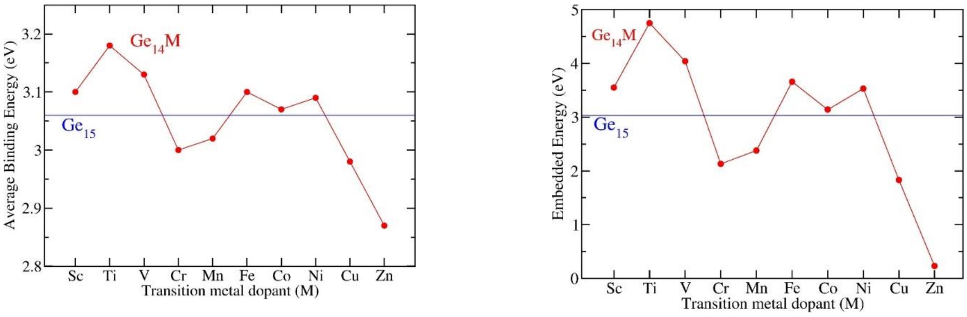
$$E_b(Ge_{14}M) = [14E(Ge) + E(M) - E(Ge_{14}M)]/15 \tag{1}$$

where $E(Ge)$, $E(M)$, and $E(Ge_{14}M)$ represent the total energies of Ge atom, M atom, and the most stable isomer of the $Ge_{14}M$, respectively. Similarly, for the Ge_{15}, the E_b can be defined by Eq. (2) as follows:

$$E_b(Ge_{15}) = [15E(Ge) - E(Ge_{15})]/15 \tag{2}$$

where $E(Ge_{15})$ is the total energy of the pure cluster Ge_{15}. The embedded energy is defined as the energy obtained when the M-atom is incorporated into the pure Ge_{14} cluster. This can also be seen as the dissociation energy of $Ge_{14}M$ to produce Ge_{14} and M. The embedded energy (E_e) is determined by Eq. (3):

$$E_e(Ge_{14}M) = E(Ge_{14}) + E(M) - E(Ge_{14}M) \tag{3}$$



(a) (b)

Figure 2. *Dopant dependence of average binding energies (a), embedded energies (b) for the most stable isomers of $Ge_{14}M$ (M = Sc – Zn) clusters.*

The average binding energy (E_b) and embedded energy (E_e) values in eV of the lowest energy isomer of the $Ge_{14}M$ cluster (M = Sc – Zn) are presented in table S4 of the SI file. The plot of the dependence of E_b and E_e values of these clusters on the M-doped atom is shown in figure 2. The shape of the plots shows that the dependence of E_b and E_e on the M-doped atom is completely similar. The E_b and E_e of the Ge_{15} cluster are 3.061 and 3.026 eV, respectively. The E_b and E_e of $Ge_{14}M$ clusters with M being Sc, Ti, V, Fe, Co, and Ni are all larger than those of the pure cluster Ge_{15}. That is, doping an M atom into Ge_{14} makes the new structure more stable than adding a Ge-atom. The $Ge_{14}Ti$ cluster has the largest E_b of about 3.176 eV compared to all other clusters. The E_b value of $Ge_{14}V$ is 3.129 eV, which is only smaller than that of $Ge_{14}Ti$. The E_e of $Ge_{14}Ti$ and $Ge_{14}V$, being of 4.754 and 4.042 eV, respectively, are also larger than that of the remaining $Ge_{14}M$. This reveals these are more stable clusters. The next clusters including $Ge_{14}Fe$, $Ge_{14}Sc$, and $Ge_{14}Ni$ with E_b values in the range of 3.095 – 3.104 eV, and E_e in the range of 3.532 – 3.665 eV, the stabilities of these clusters are thus significantly greater than that of $Ge_{14}M$ clusters, with M being Cr, Mn, and Cu, that possess E_b values in the range of 2.982 – 3.018 eV. The $Ge_{14}Zn$ structure with the smallest E_b and E_e, being of 2.875 and 0.234 eV, respectively, is the least stable in the $Ge_{14}M$ series. Thus, the trends of E_b and E_e in $Ge_{14}M$ show that doping the first-row transition metals M, except Cr, Mn, Cu and Zn, into Ge_{14} enhances the stability compared to the pure germanium cluster Ge_{15}. This variation trend is similar to the results of previous studies for $Ge_{16}M$ [5].

3.3. Magnetic moments

According to NBO analysis, the value of the total magnetic moment (TMM) of the cluster and local magnetic moment (LMM) of each atom is defined as the difference between the number of spin-up and spin-down electrons occupied on the molecular orbitals of the cluster or on the atomic orbitals of each atom. The transition metals in 3*d* series such as V, Cr, Mn, Fe, Co,... with the corresponding basic electron states of $^4F_{3/2}$, $^7S_3$, $^6S_{5/2}$, $^5D_4$, $^4F_{9/2}$,… possess magnetic properties because of containing unpaired electrons. By doping M-atom in the Ge_{14} framework, the overlapping of the 3*d* and 4*s* orbitals of M atom with the valence orbitals of Ge atom can change the magnetic property of all $Ge_{14}M$ cluster. Table 2 shows LMMs at each atom and TMMs of the most stable isomers of the $Ge_{14}M$ (M = Sc – Zn) clusters. Obviously, the magnetic moments of the $Ge_{14}M$ clusters are mainly generated on the transition metal atoms. The LMMs are 2.4, 2.4, 1.8, and 1.0 μ_B corresponding to M being Cr, Mn, Fe, and Co respectively. In general, the magnetic moment of M atom decreases when it endohedrally doped in the Ge_{14} cage. In $Ge_{14}V$ and $Ge_{14}Cu$ clusters, the LMMs of V and Cu is approximately zero. In particular for $Ge_{14}Mn$, despite having a rather high LMM of Mn, being of 2.4 μ_B, the total magnetic moment is only 1.0 μ_B. The NBO calculation shows that, for $Ge_{14}Mn$, the electron configurations of the alpha and beta spin orbitals in Mn atom are $[core]4s^{0.22}3d^{4.84}4p^{0.62}4d^{0.29}5p^{0.01}$ and $[core]4s^{0.21}3d^{2.66}4p^{0.62}4d^{0.14}5p^{0.01}$, respectively. The difference between *3d*-alpha spin and *3d*-beta spin is 2.18. Thus the electrons in *3d* orbitals contribute a value of 2.18 μ_B to the LMM, being of 2.4 μ_B, of Mn atom. These are the spin-up electrons whereas the Ge atoms contribute spin-down electrons and this cause the TMM to decrease to 1.0 μ_B. As analyzed above, $Ge_{14}Fe$ in the triplet state is stable, which has the highest total magnetic moment, 2μ_B. Meanwhile, the $Ge_{14}Cr$ cluster also exists in the triplet state and has a total magnetic moment of 2μ_B but is less stable. Table 2 also shows the values of both LMMs of Cr and Mn is 2.4 μ_B and LMM value of Fe is 1.8 μ_B but the total magnetic moments of $Ge_{14}Cr$ and $Ge_{14}Fe$ do not decrease as much as in the case of $Ge_{14}Mn$ because the number of spin-down and spin-up electrons of Ge atoms contributing to the magnetic moments of these clusters are not much different.

Table 2. *TMM (μ_B) and LMM (μ_B) of $Ge_{14}M$ clusters.*

Atom	**$Ge_{14}Sc$**	**$Ge_{14}V$**	**$Ge_{14}Cr$**	**$Ge_{14}Mn$**	**$Ge_{14}Fe$**	**$Ge_{14}Co$**	**$Ge_{14}Cu$**
Ge (1)	0.0	0.7	0.0	-0.2	0.0	0.1	0.1
Ge (2)	0.0	0.0	0.0	-0.1	0.1	0.0	0.0
Ge (3)	0.1	0.1	-0.2	-0.1	0.0	0.1	0.1
Ge (4)	0.2	0.1	-0.1	-0.1	0.0	0.0	0.0
Ge (5)	0.2	-0.1	0.1	-0.1	0.0	0.1	0.0

Ge (6)	0.0	0.0	-0.1	-0.1	0.0	0.0	0.0
Ge (7)	0.0	0.0	0.1	-0.1	0.0	0.1	0.1
Ge (8)	0.0	0.0	-0.1	-0.1	0.1	0.0	0.5
Ge (9)	0.0	0.0	-0.2	0.0	0.0	0.0	0.1
Ge (10)	0.0	0.0	0.0	-0.1	0.0	0.0	0.0
Ge (11)	0.0	0.0	-0.1	-0.1	0.0	0.0	0.0
Ge (12)	0.0	0.0	0.1	-0.2	0.0	0.0	0.0
Ge (13)	0.1	0.1	0.0	-0.1	0.0	-0.2	0.1
Ge (14)	0.1	0.0	0.1	0.0	0.0	-0.2	0.0
M (15)	0.3	0.1	2.4	2.4	1.8	1.0	0.0
TMM	1.0	1.0	2.0	1.0	2.0	1.0	1.0

4. CONCLUSIONS

In this work, we carried out a systematic investigation using density functional theory calculations on the geometry, stability, electronic structure, and magnetic properties of $Ge_{14}M$ clusters with M being 3d transition metal atoms. The obtained results show that substituting a Ge-atom with an M-atom in the Ge_{15} cluster makes the stability of the cluster increase with M being Sc, Ti, V, Fe, Co, and Ni. The values of average binding and embedded energies of the $Ge_{14}Ti$ structure are the highest in comparison to those of the remaining $Ge_{14}M$ clusters. The lowest energy structures together with some low-lying isomers are assigned and discussed in detail. DFT calculation also indicated some quasi-degenerate forms strongly compete for the ground state; hence, they may co-exist in the experimental beam under subtle conditions. Among all of the $Ge_{14}M$ clusters, the $Ge_{14}Cr$ and $Ge_{14}Fe$ clusters have the highest total magnetic moment values, being of $2\mu_B$. However, the calculations of average binding and embedded energies revealed that $Ge_{14}Fe$ is more stable than Ge_{15} whereas $Ge_{14}Cr$ is less stable than that.

REFERENCES

[1]. J. Atobe, K. Koyasu, S. Furuse, and A. Nakajima, *“Anion photoelectron spectroscopy of germanium and tin clusters containing a transition- or lanthanide-metal atom; MGe_n^- (n = 8–20) and MSn_n^- (n = 15–17) (M = Sc–V, Y–Nb, and Lu–Ta),”* Physical Chemistry Chemical Physics, vol. 14, no. 26, pp. 9403–9410, (2012).

[2]. Q. Jing, F. Tian, and Y. Wang, *“No quenching of magnetic moment for the Ge_nCo (n=1–13) clusters: First-principles calculations,”* The Journal of Chemical Physics, vol. 128, no. 12, p. 124319, (2008).

[3]. M. Shibuta, T. Niikura, T. Kamoshida, H. Tsunoyama, and A. Nakajima, *“Nitric oxide oxidation of a Ta encapsulating Si cage nanocluster superatom ($Ta@Si_{16}$) deposited on an organic substrate; a Si cage collapse indicator,”* Physical Chemistry Chemical Physics, vol. 20, no. 41, pp. 26273–26279, (2018).

[4]. M. Kumar, N. Bhattacharyya, and D. Bandyopadhyay, *“Architecture, electronic structure and stability of TM@ Ge (n)(TM= Ti, Zr and Hf; n= 1-20) clusters: a density functional modeling,”* Journal of molecular modeling, vol. 18, no. 1, pp. 405–418, (2012).

[5]. H. T. Nguyen, N. T. Cuong, N. T. Lan, N. T. Tung, M. T. Nguyen, and N. M. Tam, *“First-row transition metal doped germanium clusters $Ge_{16}M$: some remarkable superhalogens,”* RSC Advances, vol. 12, no. 21, pp. 13487–13499, (2022).

[6]. C. Siouani, S. Mahtout, S. Safer, and F. Rabilloud, *“Structure, Stability, and Electronic and Magnetic Properties of VGe_n (n = 1–19) Clusters,”* The Journal of Physical Chemistry A, vol. 121, no. 18, pp. 3540–3554, (2017).

[7]. W.-J. Zhao and Y.-X. Wang, *“Geometries, stabilities, and magnetic properties of MnGe$_n$ (n=2–16) clusters: Density-functional theory investigations,”* Journal of Molecular Structure: THEOCHEM, vol. 901, no. 1, pp. 18–23, (2009).

[8]. W.-J. Zhao and Y.-X. Wang, *“Geometries, stabilities, and electronic properties of FeGe$_n$ (n=9–16) clusters: Density-functional theory investigations,”* Chemical Physics, vol. 352, no. 1, pp. 291–296, (2008).

[9]. K. Dhaka and D. Bandyopadhyay, *“Study of the electronic structure, stability and magnetic quenching of CrGe$_n$ (n = 1–17) clusters: a density functional investigation,”* RSC Advances, vol. 5, no. 101, pp. 83004–83012, (2015).

[10]. K. Wang, Z.-Z. Jia, R.-Y. Wang, X.-D. Zhu, R. Moro, and L. Ma, *“TMGe$_{8-17}^{-}$ (TM = Ti, Zr, Hf, V, Nb, Ta) clusters: group determined properties,”* The European Physical Journal Plus, vol. 137, no. 8, p. 949, (2022).

[11]. X.-J. Deng, X.-Y. Kong, H.-G. Xu, X.-L. Xu, G. Feng, and W.-J. Zheng, *“Photoelectron Spectroscopy and Density Functional Calculations of VGe$_n^{-}$ (n = 3–12) Clusters,”* The Journal of Physical Chemistry C, vol. 119, no. 20, pp. 11048–11055, (2015).

[12]. M.J. Frisch et al., *“Gaussian 09 Revision C.01, Gaussian Inc. Wallingford CT.,”* Computer program. (2010).

[13]. G. V Gadiyak, Y. N. Morokov, A. G. Mukhachev, and S. V Chernov, *“Electron density functional method for molecular system calculations,”* Journal of Structural Chemistry, vol. 22, no. 5, pp. 670–674, (1982).

[14]. J. R. Lombardi and B. Davis, *“Periodic Properties of Force Constants of Small Transition-Metal and Lanthanide Clusters,”* Chemical Reviews, vol. 102, no. 6, pp. 2431–2460, (2002).

[15]. A. Neckel and G. Sodeck, *“Bestimmung der Dissoziationsenergien der gasförmigen Moleküle CuGe, AgGe und AuGe,”* Monatshefte für Chemie / Chemical Monthly, vol. 103, no. 1, pp. 367–382, (1972).

[16]. A. D. Sappey, J. E. Harrington, and J. C. Weisshaar, *“Resonant two- photon ionization-photoelectron spectroscopy of Cu$_2$: Autoionization dynamics and Cu$_2^+$ vibronic states,”* The Journal of chemical physics, vol. 91, no. 7, pp. 3854–3868, (1989).

[17]. K. Hilpert and R. Ruthardt, *“Determination of the dissociation energy of the Cr$_2$ molecule,”* Berichte der Bunsengesellschaft für physikalische Chemie, vol. 91, no. 7, pp. 724–731, (1987).

[18]. D. Bandyopadhyay, *“Architectures, electronic structures, and stabilities of Cu-doped Ge$_n$ clusters: density functional modeling,”* Journal of Molecular Modeling, vol. 18, no. 8, pp. 3887–3902, (2012).

TÓM TẮT

Nghiên cứu lý thuyết sự pha tạp của kim loại chuyển tiếp chu kỳ 4 vào cluster của germanium Ge$_{14}$M

Hình học, độ bền, cấu trúc electron và tính chất từ của các cụm Ge$_{14}$M với M là nguyên tử kim loại chuyển tiếp 3d, từ Sc đến Zn, được nghiên cứu bằng lý thuyết phiếm hàm mật độ với phiếm hàm B3PW91 và bộ hàm cơ sở 6-311+G(d). Các kết quả cho thấy cụm Ge$_{14}$M ưu tiên tồn tại ở trạng thái spin thấp nhất có thể có của nó trừ các trường hợp M là Fe, Cr. Độ bền nhiệt động của các cấu trúc được đánh giá qua các giá trị năng lượng liên kết trung bình và năng lượng pha tạp. Các cụm Ge$_{14}$Ti và Ge$_{14}$V được xem là bền nhất trong dãy Ge$_{14}$M (M = Sc – Zn) với kiểu hình học thuộc nhóm điểm C$_2$ có M nằm ở tâm lăng trụ lục giác của cluster Ge$_{12}$ có gắn thêm hai nguyên tử Ge nằm hơi lệch phía trên và dưới hai mặt Ge$_6$. Chỉ duy nhất cấu trúc Ge$_{14}$Fe ở trạng thái spin cao với moment từ 2μ_B là bền trong dãy này.

Từ khoá: Cluster germanium pha tạp; Lý thuyết phiếm hàm mật độ; Năng lượng liên kết; Năng lượng pha tạp.