Chapter 3

Transition Metal Doped $Ge_n$ Clusters

3.1 Introduction

The clusters at nanoscale have attracted lot of interest among scientific community due novel structural, electronic and magnetic properties. The semiconductor clusters have created lot of interest among researchers due to size dependant electronic and magnetic properties. The experimental advancement in incorporating magnetic impurities in non-magnetic semiconductors have attracted great interest due to their potential to create new class of spin-dependant electronic devices.

The dilute magnetic semiconductors (DMS) continues to get immense attention [5-7] due to their novel functionalities beyond conventional semiconductors, utilizing both the charge and spin of electrons [10–14]. The conventional semiconductor devices use s and p electrons and magnetic devices use d electrons to perform their functions. The DMS based spintronic devices are supposed to use both s and p electrons of host semiconductors and d electrons of transition metal impurities to perform their semiconducting and magnetic functions. In recent past, the room temperature DMS have been prepared experimentally by incorporating magnetic ions Mn, Fe with host semiconductors based mainly on IV, III-IV, III-V, II-IV and II-VI group compounds. The origin of ferromagnetism in DMS is still debated.

The doping have proven to be effective to tune the opto-electronic, magnetic properties and stability of the host clusters [10,15–17]. Among the group IV clusters, silicon clusters doped with TM dopants (Cr, Mn, W, Mn, Cu, Zn) [18-23]
have been studied extensively both theoretically and experimentally to explore the possibility of inducing magnetism in semiconducting clusters. When TMs are encapsulated into large sized silicon cages results in tunability of HOMO (Highest occupied molecular orbital)-LUMO (Lowest unoccupied molecular orbital) gap. The geometries of the relaxed TM doped semiconductor clusters are easy to distort when filled or empty molecular orbitals are close in energy according to Jahn Teller theorem [19]. The magnetic moment of few TM dopants is completely quenched in Si [13, 24, 25]. Therefore, search for group-IV based DMSs has been extended to higher mass congeners such as Germanium Ge and Tin Sn [12, 23, 26].

The Cr doped Ge single bulk crystal using vertical gradient solidification method has shown ferromagnetic ordering at 126 K [27] where as Cr doped Ge film using molecular beam epitaxy (MBE) has shown weak paramagnetic behavior between 1.8 K and 300 K [27]. Therefore, possibility of realizing IV DMS with room temperature $T_c$ is yet to be fully understood and requires further investigation. In the recent past, room temperature Ferromagnetism (FM) have been reported in Ge$_{1-x}$Mn$_x$ nanocolumns [28]. The FM have also been observed upto 115 K in MnGe prepared using molecular beam epitaxy (MBE) growth [29]. Further, FM at $T_c = 285$ K [30] is also reported in high Mn doped Ge single crystals obtained by solid solutions.

The magnetic moment (MM) do not show signs of quenching for Co doped Ge$_n$ clusters [31]. Ferromagnetism have been reported in Mn$_x$Ge$_{1-x}$ and Cr$_x$Ge$_{1-x}$ single crystals grown by MBE [30, 41] and Cr, Fe doped bulk Ge single crystals. These developments have created a strong interest in search for room temperature Ge based compounds [10].

However, despite various theoretical attempts, the origin of the observed magnetism in TM doped Ge$_n$ clusters is yet to be explored. The isolated investigations reported in literature fails to explain comprehensively the magnetic properties due to TM doping. In this chapter, we have investigated the electronic and magnetic properties of Cr, Mn, Co and Ni doped Ge$_n$ cluster for $n = 1-13$ with plane wave basis sets or localized basis sets to understand the origin of magnetism.

### 3.2 Computational details

The calculations are performed using Spin polarized Density Functional Theory (DFT) within the pseudopotential plane wave method as implemented in VASP
(Vienna Ab-initio Simulation Package) [30] and Spanish Initiative for Electronic Simulation with thousands of atoms (SIESTA) [31,32]. The valence shell electronic configuration used for potential generation of Ge is $4s^2,4p^2$ and for Cr, Mn, Co and Ni it is $3d^54s^1$, $4s^1\,3d^5,4s^1\,3d^5$ and $4s^1\,3d^5$ respectively.

The projector augmented wave method with PW-91 exchange correlation functional is used for spin polarized generalized gradient approximation (GGA) [33]. The energy cutoff 300 eV is used for the expansion of plane wave basis set. The reciprocal space integration is carried out at the gamma point. Symmetry unrestricted geometry and spin optimizations are done using conjugate gradient and quasi Newtonian methods until all the forces are less than 0.01 eV/Å. Simple cubic super-cells are used with the periodic boundary conditions, where two neighboring clusters are kept separated by at least 15 Å vacuum space. For each size, several initial geometrical structures have been considered.

The spin polarized calculations are carried out using generalized gradient approximation (GGA) that implements Perdew, Burke and Ernzerhof (PBE) exchange-correlation functional [33]. Core electrons are replaced by non-local, norm-conserving pseudo potentials factorized in the Kleinman-Bylander form [34], whereas valence electrons are described using DZP (double-$\zeta$ + polarization) basis set. We have used $3d^54s^1$ configuration for Cr and $4s^24p^1$ for Ge. The structures are obtained by minimization of the total energy using Hellmann-Feynman forces, including Pulay like corrections. Structural optimizations are performed using conjugate gradient algorithm until the residual forces in the optimization are smaller than 0.001 eV/Å.

To get the ground state magnetic moment we have explicitly considered all possible spin configurations for each geometrical structure. For transition metals, the PAW method seems to be more appropriate (as good as the AE calculations) than the US-PP approach [49]. The US-PP overestimates the magnetization energies and this overestimation is even more large for GGA calculations than local spin density approximation (LSDA). This is due to the fact that the GGA functionals are more sensitive to the shape of the wave functions than the LSDA functionals. However, the difference between these two methods, US-PP and PAW, are solely related to the pseudization of the augmentation charges in the US-PP approach, which can be removed by choosing very accurate pseudized augmentation function, which is then computationally expensive.

In order to obtain the global minimum structures of Ge$_n$Cr clusters, we considered large number of possible isomeric structures by (a) taking all structures
reported in the previous papers [10–12, 35–47]; (b) substituting one Ge atom by Cr atom from the ground state structures and isomers of \( Ge_{n+1} \) clusters; (c) adopting from those known structures for TM doped \( Ge_n \) and \( Si_n \) clusters such as \( Ge_n Mn, Ge_n Co, Si_n Fe, Si_n Cr \) and \( Si_n Co \). The spin unrestricted calculations are performed for all allowable spin multiplicities of \( Ge_n Cr \) clusters to reveal the possible magnetism of the clusters. The on-site charges and magnetic moments are obtained from Mulliken charge analysis.

### 3.3 Pure \( Ge_n \) Clusters

Firstly, we have obtained the ground state (GS) structures for pure \( Ge_n \) clusters. Pure \( Ge_n \) clusters for \( n = 1-4 \) adopt planar geometries as their ground state structures. For \( Ge_3 \), the triangle with \( C_2v \) symmetry, for \( Ge_4 \), the rhombus structure with \( D_2h \) symmetry and \( Ge_5 \), trigonal structure with \( D_{3h} \) symmetry are found to be the global minimum structures.

When \( n \geq 5 \), \( Ge_n \) clusters have a tendency to form three dimensional (3D) configurations as minimum energy structures. \( Ge_6 \) shows a bicapped quadrilateral with \( D_{2h} \) symmetry, \( Ge_7 \) forms a pentagonal bipyramid structure (\( D_{2d} \) symmetry). \( Ge_9 \) gives a bernal structure with \( C_2v \) symmetry, \( Ge_{10} \) adopts a tetracapped trigonal prism having \( C_{3v} \) symmetry, \( Ge_{11} \) and \( Ge_{14} \) show \( D_4h \) symmetry whereas \( Ge_{12} \) and \( Ge_{13} \) show \( C_{2h} \) and \( C_{2v} \) symmetries respectively. The obtained structures as shown in Figure-3.1.3.2 and bond-length given in Table 3.1 are in agreement with the existing theoretical results. The equilibrium properties of \( Ge_n \) clusters such as binding energy/atom, ionization potentials and electron affinities are in agreement with available experimental results [32, 33].

### 3.4 Results and Discussion

Using the computational procedure described above we optimized a large number of low-lying isomers and determined the ground state structures for TM doped \( Ge_n \) clusters up to \( n = 13 \) as shown in Figures 3.3-3.6 for \( Cr, Mn, Co \) and \( Ni \) respectively. To study the comparative stabilities of the clusters, binding energy per atom and the second difference of energies and dissociation energies are given in Table 3.2.
Figure 3.1: Optimized ground state structures of Ge\(_n\) clusters for \(n = 1-8\)
Figure 3.2: Optimized ground state structures of Geₙ clusters for n = 9-14
Table 3.1: The bond length of \((Ge)_n\), \(n = 1-14\) clusters.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>(R_{Ge-Ge})</th>
<th>(R_{Ge-Ge})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ge_2)</td>
<td>2.55</td>
<td>2.47</td>
</tr>
<tr>
<td>(Ge_3)</td>
<td>2.38</td>
<td>2.62</td>
</tr>
<tr>
<td>(Ge_4)</td>
<td>2.56</td>
<td>2.46</td>
</tr>
<tr>
<td>(Ge_5)</td>
<td>2.59</td>
<td>2.42</td>
</tr>
<tr>
<td>(Ge_6)</td>
<td>2.60</td>
<td>2.19</td>
</tr>
<tr>
<td>(Ge_7)</td>
<td>2.70</td>
<td>2.60</td>
</tr>
<tr>
<td>(Ge_8)</td>
<td>2.53</td>
<td>2.60</td>
</tr>
<tr>
<td>(Ge_9)</td>
<td>2.60</td>
<td>2.19</td>
</tr>
<tr>
<td>(Ge_{10})</td>
<td>2.63</td>
<td>2.63</td>
</tr>
<tr>
<td>(Ge_{11})</td>
<td>2.60</td>
<td>2.58</td>
</tr>
<tr>
<td>(Ge_{12})</td>
<td>2.56</td>
<td>2.51</td>
</tr>
<tr>
<td>(Ge_{14})</td>
<td>2.50</td>
<td>2.58</td>
</tr>
</tbody>
</table>

3.4.1 Structural Growth of \(TMGe_n\) clusters

\(Ge_2Cr\) clusters

\(GeCr\) dimer with a bond length of 2.54 \(\text{Å}\) having antiferromagnetic (AFM) interaction is found more stable than with ferromagnetic (FM) interaction by 0.03 eV. The bond length of 2.54 \(\text{Å}\) for \(GeCr\) is in good agreement with the theoretical value of 2.52 \(\text{Å}\) [12]. For \(Ge_2Cr\), the planar structure with \(C_{2v}\) symmetry (Figure 3.3) is the lowest energy structure and the Cr atom have AFM interaction with two Ge atoms. The Ge-Cr bond distance in \(Ge_2Cr\) increases to 2.60 \(\text{Å}\) which is higher than in \(GeCr\) dimer, indicating its relative weak nature. In \(Ge_3Cr\), the ground state (GS) structure shows a non-planar structure with \(C_{3v}\) symmetry having Ge-Cr and Ge-Ge bond distance of 2.80 \(\text{Å}\) and 2.48 \(\text{Å}\). The obtained GS structure is similar to \(Ge_3Mn\) cluster but different from the planar structure with \(C_{2v}\) symmetry predicted as GS by Hou et al. [12] and is found less stable by 0.55 eV. The \(Ge_4Cr\) cluster forms a 3D pyramidal GS structure with \(C_{2v}\) symmetry as shown in Figure 3.3. The Ge-Cr bond distance have increased to 2.76 \(\text{Å}\)-2.90 \(\text{Å}\) and the Ge-Ge bond distance is found to be 2.53 \(\text{Å}\). The obtained structure is in agreement with Hou et al. [12]. Interestingly, similar GS structures have been reported for Mn and Co doped \(Ge_n\) clusters. For \(Ge_5Cr\) cluster, the GS structure forms a square bipyramidal geometry having \(C_{3v}\) symmetry as shown in Figure 3.3. The Ge-Cr bond distances vary.
from 2.71-2.84 Å and Ge-Ge bond distance is found to be 2.55 Å. The obtained GS structure is different from GS structure with $C_4$ symmetry proposed by Hou et al. [12], and is found less stable by 0.21 eV but similar to $Gc_5Mn$ and $Gc_5Co$.

At this stage, we would like to add that as per our knowledge the magnetic properties of $Ge_nCr$ clusters for $n > 5$ are being reported for the first time. For $Ge_9Cr$, the structure having pentagonal bipyramid geometry and structure with $C_{5v}$ symmetry are nearly isoenergetic and differ by a small energy 0.01 eV. However, the structure with magnetic moment $6 \mu_B$ is slightly more stable. The capped tetragonal bipyramid structure predicted as the GS structure for $Gc_7Co$ is less stable by 0.52 eV. For $Gc_7Cr$, the structure with Cr attached to pentagonal bipyramid ($C_{5v}$) of $Ge_7$ cluster is found to be the GS structure. The distorted cube structure with $C_{3v}$ symmetry has been predicted as ground state structure for $Gc_7Mn$ and $Gc_7Co$, and is found to less stable by 0.74 eV. For $Gc_9Cr$, we found a tricapped trigonal prism geometry with $C_{3v}$ symmetry as the global minimum structure. The structure which has been reported as ground state structure for $Gc_8Co$ is less stable by 0.47 eV.

So far a trend has emerged in which the GS structure for a particular cluster size Cr prefers to occupy the surface position. For $n \geq 9$, 3d TMs such as Mn, Fe, Co and Cu when doped in $Ge_n$ clusters, have shown tendency to occupy internal encapsulated positions. However, due to weak bonding of Cr-Ge, the Cr atom is expected to show different growth behavior.

For $n = 9$, the structure with $C_{3v}$ symmetry is found to be the GS structure. This may be envisaged to have been formed by Cr adsorption on $Ge_9$ structure. The Ge-Cr bond distance varies in the range 2.73-2.81 Å and Ge-Ge bond distance has increased to 2.70 Å. We observe that structures with Cr atom at the surface position are lower in energy than Cr at encapsulated position. The structure with Cr at central encapsulated site is found to be higher in energy by 2.2 eV showing its less stability. For $Ge_{10}Cr$, the tricapped trigonal prism of $Ge_9$ capped with one Cr and one Ge atom with $C_5$ symmetry is the ground state structure. The structure with Cr encapsulated in Ge structure which is predicted to be GS structure for $Ge_{10}Mn$ is less stable by 3.16 eV. For $Gr_{11}Cr$, the Cr atom tends to stabilize at the surface rather than at the central encapsulated position.

For $Gc_{12}Cr$ and $Gc_{13}Cr$ clusters, as shown in Figure-3.3, the Cr atom have shown a tendency to settle at peripheral position of Ge cluster with increased coordination number. For $Gr_{12}Cr$, the ground state may be understood as $Gc_{13}$ structure with $C_{2v}$ symmetry with one Ge atom replaced by Cr. The structure with Cr encapsulated at
Figure 3.3: The calculated lowest-energy structures for Ge$_n$Cr ($n = 1$-13) clusters. Purple circles represent germanium atoms, and blue circles represent chromium atoms.
the center of Ge cage with $I_h$ symmetry which is the GS structure for $MnGe_{12}$ [11] is less favored by 0.84 eV. For $Ge_{13}Cr$, the structure with Cr absorbed on the $Ge_{14}$ unit is more stable than other isomer structures by 0.29 eV, 0.61 eV, 0.63 eV, 1.63 eV and 1.86 eV respectively. The structural stability of $Ge_{1n}Cr$ clusters are investigated by calculating the binding energy per atom w.r.t pure $Ge_n$ clusters which is plotted in Figure-3.7. The binding energy of $Ge_nCr$ clusters increases with increase in cluster size which indicates that these clusters can continuously gain energy during the growth process. This is consistent with the experimental observation of $Ge_{14}Cr^+, Ge_{15}Cr^+$ and $Ge_{16}Cr^+$ [33]. Further, we observe Cr doped clusters show a small decrease in binding energy per atom w.r.t $Ge_n$ clusters implying that Cr does not enhance cluster stability. At this point we would like to draw attention to the interesting pattern shown by structural stability of various 3d TM doped $Ge_n$ and $Si_n$clusters reported in literature [11, 25, 43 47]. From the binding energy per atom variation as a function of cluster size for Mn, Fe, Ni, Co and Cu doped Ge clusters, we find that the binding energy per atom tends to increase with TM doping and the TM atom prefers to stabilize at the endohedral positions for $n > 8$. Similar pattern is observed for $Si_nTM$ clusters except for Ag doped $Si_n$ clusters for $n = 1-13$ which shows decrease in binding energy and Ag atom prefers to stabilize at the exohedral position [15]. Similar behavior of decrease in binding energy with Cr doping have been reported $Ge_nCr$ for $n = 3-5$ by Hon et al. [12]. The binding energy curve as plotted in Figure 3.7 shows a small reduction in binding energy and Cr atom have also shown a tendency to stabilize at the exohedral position. Further, the decrease in the binding energy due to Cr doping is consistent with behavior of Ge-Ge and Ge-Cr bond distances which tend to increase with increase in cluster size.

$MnGe_n$

The optimized structures of $MnGe_n$ are shown in Figure 3.4. For $GeMn$ dimer, cluster with bond length 2.29 Å is found to be the ground state structure which is in agreement to Wang et al. [11]. For $MnGe_2$ cluster, the planer triangular structure with $C_{2v}$ symmetry having bond lengths 2.36 Å ($Ge-Mn$) and 2.42 Å ($Ge-Ge$), is found to be the ground state structure. The linear isomers ($Mn-Ge-Ge, Ge-Mn-Ge$) are found less stable by 1.3 eV and 2.13 eV respectively. The $Ge-Mn$ bond distance is higher than its dimer indicating comparatively weak interaction. For $MnGe_3$
Table 3.2: The binding energy per atom (\(B.E./A\)), Dissociation energy (DE) and second difference of energy \(\Delta^2E\) for \(Ge_{x}TM\) (\(TM = \text{Cr, Mn, Co, Ni}\)). The positive and negative signs represents energy gain and loss respectively.

<table>
<thead>
<tr>
<th>(TMGe_n)</th>
<th>Cr</th>
<th>Mn</th>
<th>Co</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>(TMGe_1)</td>
<td>0.06</td>
<td>0.33</td>
<td>-1.47</td>
<td>-3.48</td>
</tr>
<tr>
<td>(TMGe_2)</td>
<td>1.32</td>
<td>3.68</td>
<td>-2.25</td>
<td>-3.82</td>
</tr>
<tr>
<td>(TMGe_3)</td>
<td>1.72</td>
<td>3.50</td>
<td>-2.67</td>
<td>-3.92</td>
</tr>
<tr>
<td>(TMGe_4)</td>
<td>2.16</td>
<td>3.53</td>
<td>-3.02</td>
<td>-4.27</td>
</tr>
<tr>
<td>(TMGe_5)</td>
<td>2.46</td>
<td>4.75</td>
<td>-3.27</td>
<td>-4.69</td>
</tr>
<tr>
<td>(TMGe_6)</td>
<td>2.78</td>
<td>3.59</td>
<td>-3.38</td>
<td>-1.04</td>
</tr>
<tr>
<td>(TMGe_7)</td>
<td>2.83</td>
<td>3.25</td>
<td>-3.44</td>
<td>-3.85</td>
</tr>
<tr>
<td>(TMGe_8)</td>
<td>2.93</td>
<td>3.50</td>
<td>0.0</td>
<td>-3.53</td>
</tr>
<tr>
<td>(TMGe_9)</td>
<td>3.02</td>
<td>3.42</td>
<td>-0.33</td>
<td>-3.63</td>
</tr>
<tr>
<td>(TMGe_{10})</td>
<td>3.09</td>
<td>3.88</td>
<td>1.0</td>
<td>-3.71</td>
</tr>
<tr>
<td>(TMGe_{11})</td>
<td>3.08</td>
<td>2.80</td>
<td>-0.34</td>
<td>-3.73</td>
</tr>
<tr>
<td>(TMGe_{12})</td>
<td>3.08</td>
<td>3.00</td>
<td>-0.72</td>
<td>-3.75</td>
</tr>
<tr>
<td>(TMGe_{13})</td>
<td>3.13</td>
<td>3.50</td>
<td>-3.76</td>
<td>-3.93</td>
</tr>
</tbody>
</table>
cluster, the three dimensional (3D) geometry having $C_{3v}$ symmetry is found to be the ground state structure. The rhombic structure is found to be less stable by 1.39 eV. $MnGe_3$ is the smallest cluster with three dimensional (3D) structure having a pyramidal geometry with $MnGe$ and $Ge-Ge$ bond lengths equal to 2.28 Å and 2.69 Å respectively. The obtained optimized structure is similar to that reported in literature [11,50].

For $MnGe_4$ cluster, a distorted rhombus geometry with $C_s$ symmetry is found to be the ground state structure (GS). The obtained GS is in agreement with Wang et al. [11]. The calculated Ge-Mn and Ge-Ge bond lengths lie in between 2.19 Å-2.65 Å and 2.51 Å-2.84 Å respectively. For $MnGe_5$ cluster, a square bipyramidal geometry with $C_{3v}$ symmetry is found to be the ground state structure. The Ge-Mn and Ge-Ge bond lengths are 2.35 Å and 2.64 Å-2.68 Å respectively. For $MnGe_6$ cluster, a bicapped pentagonal geometry with $C_{3v}$ symmetry is found to be the GS structure. The Ge-Mn and Ge-Ge bond lengths are 2.59 Å and in the range 2.53 Å-2.79 Å respectively. The capped tetragonal bipyramid structure is less stable by 0.03 eV. For $MnGe_7$ cluster, a distorted cubic geometry with $C_{3v}$ symmetry is found to be the GS structure, which is in agreement to [11]. The Ge-Mn and Ge-Ge bond lengths lie in the range 2.45 Å-2.85 Å and 2.60 Å-2.72 Å respectively. For $MnGe_8$ cluster, a cage structure having $C_{3v}$ symmetry with Mn atom on the surface is obtained as GS state structure. The Ge-Mn and Ge-Ge bond lengths lie in the range 2.49 Å-2.95 Å and 2.67 Å-2.73 Å respectively. The obtained optimized GS structure is in agreement to available literature [11,50].

For $MnGe_9$ cluster, a tetracapped trigonal prism with $C_{3v}$ symmetry is found to be the GS structure. The GS structure may be visualized as $Ge_{10}$ cluster being substituted by one $Mn$ atom at the convex position. At this point we would like to mention that Zhao et al. using DFT [50] have reported structure with $C_4$ symmetry as the ground state structure which is found as one of the isomer less stable by 0.19 eV in our calculation. The 1-5-3 layer structure is found to be less stable by 0.02 eV. The Ge-Mn and Ge-Ge bond-lengths lie in the range 2.34 Å-2.66 Å and 2.68 Å-2.77 Å respectively. $MnGe_{10}$ cluster, a multi rhombic structure with $C_s$ symmetry as shown in Figure-3.4. It is found to be the GS, which is in agreement to Wang et al. [11] and the Ge-Mn and Ge-Ge bond-lengths are 2.52 Å-2.73 Å and 2.64 Å-2.71 Å respectively. For $MnGe_{11}$ cluster, a structure with $C_5$ point group symmetry is obtained as the ground state structure, in agreement with Wang et al. [11]. The Ge-Mn and Ge-Ge bond-lengths are found to be 2.57 Å-2.96 Å and 2.49 Å-2.53 Å respectively.
Figure 3.4: The calculated lowest-energy structures for \( Ge_nMn \) (\( n = 1-13 \)) clusters. Pink circles represent germanium atoms, and green circles represent manganese atoms.
A respectively. The structure with $C_1$ symmetry which has been reported as the ground state structure in $TMSi_{13}$ [13], is found to be less stable by 0.13 eV in our calculations.

For $MnGe_{12}$ cluster, a perfect hexagonal prism geometry with Mn atom lying inside the cage is found to be the ground state structure, which is in agreement to work done by Zhao et al. [50]. The Ge-Mn and Ge-Ge bond-lengths are 2.57 A-2.96 A and 2.49 A-2.53 A respectively. The structure with $I_h$ symmetry reported as GS by Wang et al. is found to be less stable by 0.40 eV in our calculations. For $MnGe_{13}$ cluster, a cage like structure with $C_1$ point group symmetry is found to be the GS structure, in agreement to Zhao et al. [50]. The Ge-Mn and Ge-Ge bond-lengths are in the range 2.66 A-2.95 A and 2.55 A-2.72 A respectively. Wang et al. [11] reported structure with $C_s$ symmetry as the GS which is found to be one of the isomers less stable by 0.24 eV in our calculations.

$CoGe_n$

The optimized structures of $CoGe_n$ are shown in Figure 3.5. $GeCo$ dimer with bond-length 2.14 A is found to be the ground state configuration. For $CoGe_2$, the planar triangular structure having $C_3v$ symmetry with bond length lying between 2.25 A-2.45 A is found to be the ground state structure as shown in Figure-3.5. The linear structures of $Co-Ge-Ge$ and $Ge-Co-Ge$ are less stable by 1.36 eV and 2.37 eV respectively. The larger Ge-Co bond length in $Ge_2Co$ than GeCo dimer implies comparatively weaker interaction. For $CoGe_3$, a pyramidal structure similar to $MnGe_3$ having $C_2v$ symmetry with $Co-Ge$ and $Ge-Ge$ bond-lengths ranging between 2.29 A-2.30 A is found to be the most stable structure. The rhombic structure which is reported as the GS structure by Jing et al. [10] is found to be less stable by 0.61 eV. In $CoGe_4$ cluster, the distorted rhombus structure with $C_s$ symmetry is found to be the GS structure which is in agreement with the reported GS structure [10]. The $Co-Ge$ and $Ge-Ge$ bond-lengths are found to be 2.32 A-2.79 A and 2.63 A-2.83 A respectively. For $CoGe_5$ cluster, the square bipyramidal geometry with $C_4v$ symmetry is found to be the GS structure. The $Co-Ge$ and $Ge-Ge$ bond-lengths are found to vary in the range 2.36 A-2.38 A and 2.58 A-2.70 A respectively. The results are in agreement with Jing et al. [10].

For $CoGe_6$, the bicapped pentagonal structure having $C_{5v}$ symmetry and with bond-lengths 2.32 A-2.44 A ($Co-Ge$) and 2.53 A-2.94 A ($Ge-Ge$) is found to be the
Figure 3.5: The calculated lowest-energy structures for $Ge_nCo$ ($n = 1-13$) clusters. Pink circles represent germanium atoms, and blue circles represent cobalt atoms.
GS structure. The capped tetragonal bipyramid structure is found to be less stable by 0.16 eV. In \(\text{CoGe}_7\) cluster, the distorted cubic geometry with \(C_{3v}\) symmetry and bond lengths in the range 2.29 A-2.60 A (Ge-Co) and 2.49 A-3.77 A (Ge-Ge) is found to be the GS structure. In \(\text{CoGe}_8\) cluster, the tricapped-trigonal prism geometry with \(C_{2v}\) symmetry with Co atom on the surface is found to be the ground state structure. The Co-Ge and Ge-Ge bond-lengths are found to vary from 2.33 A-2.71 A and 2.67 A-2.72 A respectively.

For \(n \geq 9\), there is a significant difference in the position of Co in \(\text{Ge}_n\) clusters. In \(\text{CoGe}_9\) cluster, the GS structure can be described as 1-5-3 layer structure with Co atom lying at the centre of cluster with \(C_5\) symmetry. The tetracapped trigonal prism structure is found to be less stable by 0.02 eV. For \(\text{CoGe}_{10}\), the bicapped square antiprism structure is found to be the ground state structure. The GS is remarkably stable with Co-Ge and Ge-Ge bond-lengths varying in the range 2.38 A-2.76 A and 2.53 A-2.84 A respectively. In \(\text{CoGe}_{11}\) cluster, the GS structure has \(C_{2v}\) point group symmetry with 1-4-4-2 layer structure and bond-lengths 2.38 A-2.76 A and 2.51 A-2.89 A for Co-Ge and Ge-Ge respectively. The structure with \(C_5\) point group symmetry is less stable by 0.22 eV.

For \(\text{CoGe}_{12}\) cluster, the cage like structure is found to be the lowest energy geometry. The GS geometry can be described as multi-pentagonal structure with \(C_s\) symmetry. The hexagonal prism structure with Co inside the cage structure is found to be less stable by 0.60 eV. In \(\text{CoGe}_{13}\) cluster, a cage like structure with \(C_1\) symmetry similar to \(\text{MnGe}_{13}\) with bond-lengths (Co-Ge) 2.46 A-2.79 A and (Ge-Ge) 2.62 A-2.85 A is found to be GS structure. The structure reported as GS by Jing et al. [10] is found to be one of the isomer which is less stable by 0.21 eV.

\(\text{NiGe}_n\)

The optimized structures of \(\text{NiGe}_n\) are shown in Figure 3.6. \(\text{NiGe}\) dimer is stable with a bond length equal to 2.14 A. For \(\text{NiGe}_2\), a planar structure with \(C_{2v}\) symmetry and bond-length of 2.23 A-2.43 A is found to be the ground state structure. The obtained ground state structure is in agreement with structure reported by Bandyopadhyay et al. [51]. The linear structures of \(\text{Ni-Ge-Ge}\) and Ge-Ni-Ge are found to be less stable by energy difference of 1.38 eV and 1.23 eV respectively. Interestingly, the Ge-Ni bond distance in \(\text{NiGe}_2\) is larger than NiGe dimer indicating weak nature of the bonds. In \(\text{NiGe}_3\) cluster, the GS structure is found with planar geometry
having \( C_{2v} \) symmetry as shown in Figure 3.6. The Ge-Ni and Ge-Ge bond lengths are found to be 2.24 Å and 2.37 Å respectively. The obtained GS structure is in agreement with ref. [51].

The GS structure for \( \text{NiGe}_4 \) is found to be a distorted rhombus structure with \( C_4 \) symmetry and having bond lengths in the range 2.30 Å-2.31 Å (Ge-Ni) and 2.47 Å-3.04 Å (Ge-Ge) in agreement with the reported results [51]. For \( \text{NiGe}_5 \) cluster, a square bipyramidal geometry with \( C'_4 \) symmetry is found to be the GS structure. The obtained GS structure is similar to as obtained for \( \text{MnGe}_5 \) and \( \text{CoGe}_5 \). The Ge-Ni and Ge-Ge bond lengths lie in the range 2.31 Å-2.46 Å and 2.33 Å-2.87 Å respectively. For \( \text{NiGe}_6 \) cluster, the GS structure is a tetragonal bipyramid geometry with \( C'_4 \) symmetry. The Ge-Ni and Ge-Ge bond lengths vary in the range 2.38 Å-2.40 Å and 2.48 Å-2.75 Å respectively. The bicapped pentagonal structure is less stable by 0.11 eV. For \( \text{NiGe}_7 \) cluster, a distorted cubic geometry is nearly isoenergetic with structure having \( C'_4 \) symmetry. The distorted cubic structure is favoured to be the GS structure which is similar to the GS of \( \text{MnGe}_7 \) and \( \text{CoGe}_7 \). In \( \text{NiGe}_8 \) cluster, a cage-like structure with Ni atom on the surface having \( C'_4 \) symmetry is the GS structure. The obtained GS structure is consistent with Bandyopadhyay et al. [51]. The Ge-Ni and Ge-Ge bond lengths lie in the range 2.37 Å-2.87 Å and 2.69 Å-2.76 Å respectively.

For \( \text{NiGe}_9 \) cluster, the obtained GS structure can be described as 1-5-3 layer structure with Ni atom lying at the center of cluster having symmetry \( C'_4 \). The bond lengths vary from 2.28 Å-2.78 Å for Ge-Ni and 2.56 Å-2.84 Å for Ge-Ge respectively. However, Wang and Han et al. [52] using DFT have reported a structure with \( C' \) symmetry as the GS structure which is found to be less stable by 0.48 eV in our calculations. The tetracapped trigonal structure is less stable by 0.01 eV. For \( \text{NiGe}_{10} \) cluster, a multi rhombic structure with Ni atom at the endohedral position with \( C'_4 \) symmetry is the ground state structure. The Ge-Ni and Ge-Ge bond lengths vary from 2.42 Å-2.50 Å and 2.61 Å-2.67 Å respectively. The obtained GS structure is in agreement to work done by Bandyopadhyay et al. [51].

For \( \text{NiGe}_{11} \) cluster, structure with 1-4-4-2 layers having \( C'_4 \) point group symmetry is found to be the ground state structure. The bond lengths for Ge-Ni and Ge-Ge varies in the range 2.45 Å-2.64 Å and 2.55 Å-2.90 Å respectively. The obtained GS structure is in agreement with the reported GS by Bandyopadhyay et al. [51]. However, the structure with \( C' \) symmetry which is found as GS structure for \( \text{MnGe}_{11} \) is less stable by 0.15 eV. For \( \text{NiGe}_{12} \) cluster, the GS structure is a
Figure 3.6: The calculated lowest-energy structures for $Ge_nNi$ ($n = 1-13$) clusters. Pink circles represent germanium atoms, and grey circles represent nickel atoms.
perfect hexagonal prism with Ni atom lying inside the cage. The bond lengths of 
Ge-Ni and Ge-Ge vary in the range 2.50 A-3.05 A and 2.53 A-2.55 A. However, the 
GS structure obtained for CoGe$_{12}$ is found to be less stable by 0.76 eV. In NiGe$_{13}$ 
cluster, a cage like structure with $C_1$ symmetry is found to be the ground state 
structure. The optimized structure obtained by Bandyopadhyay et al. [51] is found 
to be less stable by 0.41 eV.

From the above structural analysis of Ge$_n$TM clusters and its comparison with 
available theoretical results many interesting trends can be summarized. If we com­
pare with pure Ge$_n$ clusters, the TM doping leads to substantial structure recon­
structions. The TM have shown tendency to move from convex, to surface and to 
the interior site as the size varies from $n = 2$-13. The TM atoms for a critical size 
of Ge$_n$ cluster completely falls into the center of Ge frame and form cage. This 
critical size of the cluster can be understood on the basis of radius of the TM atoms, 
larger the atom size more number of Ge atoms are needed to encapsulate the bigger 
atom. In present work we find critical size of $n = 11$, $10$ and $9$ for Mn, Co and 
Ni dopants respectively. This is consistent with the order of their covalent radii 
$Mn > Co > Ni$.

To understand the relative stability of Ge$_n$TM clusters, the binding energy per 
atom is calculated. The binding energy per atom is defined as

$$E_b[Ge_nTM] = [nE[Ge] + E[TM] - E[Ge_nTM]]/n + 1, \quad (3.1)$$

where $E[Ge]$, $E[TM]$ and $E[Ge_nTM]$ denotes the total energies of Ge atom, TM atom 
and Ge$_n$TM cluster respectively where TM = Cr, Mn, Co, Ni. The binding energy 
per atom of TM doped Ge$_n$ clusters increases linearly as a function of cluster size as 
shown in Figure-3.7. The figure shows that the binding energy of the Ge$_n$ clusters 
decreases on doping with $Cr$ and increases marginally on doping with Mn, Co and 
Ni. Further, these $TMGe_n$ clusters gain energy during their growth process which 
indicates possibility of their formation experimentally. For $n < 4$, the binding energy 
per atom is found to be maximum for NiGe$_n$ and minimum for MnGe$_n$ clusters. 
However, for $n \geq 4$ the binding energy per atom shows almost similar pattern for 
Co and Ni doped Ge clusters except for $n=11$.

The relative stability is examined by calculating the second difference of energy 
$\Delta^2E$ and the energy needed to dissociate the TM from $TMGe_n$ cluster. The second 
order difference in cluster energy is a sensitive quantity that reflects the relative
stability of a cluster and is defined as


The $\Delta^2 E$ as a function of size is tabulated in Table-I and plotted in figure-7, which shows oscillatory pattern and most stable structure for $n = 10$ in all cases.

The dissociation energy (DE) which is defined as the energy required for dissociation of $Ge_nTM$ into $Ge_{n-1}TM$ and $Ge$ and is calculated as


The dissociation energy varies in the range of 0.33 eV-7.52 eV for $CrGe_n$, 3.18 eV-1.56 eV for $MnGe_n$, 3.70 eV-4.90 eV for $CoGe_n$ and 2.09 eV-5.11 eV for $NiGe_n$.

The higher values of dissociation energy for $n = 5$ and 10 for TM = Cr, Mn, Co and Ni doped $Ge_n$ clusters indicates their extra stability. The binding energy per atom and the second difference of energies are shown in Figure 3.7.

### 3.4.2 Electronic Properties

The HOMO-LUMO gap, Electron Affinity(E.A.), Ionization Potential(I.P.) of pure $Ge$ clusters is presented along with $Ge_nCr$ clusters in Figures 3.8, 3.9.

**$Ge_nCr$ clusters**

The size dependent electronic properties of $Ge_nCr$ clusters are investigated by calculating the Highest occupied molecular orbital (HOMO) and Lowest unoccupied molecular orbital (LUMO) gap, vertical ionization potentials (IP) and electron affinities (EA). The HOMO - LUMO gap for pure $Ge_n$ and $Ge_nCr$ clusters is plotted as function of cluster size in Figure 3.9.

The Figure 3.9 shows local peaks at $n = 1, 3, 6, 8, 10, \text{ and } 13$ for $Ge_nCr$ clusters, implying the stronger chemical stability of these structures relative to their counterparts. The range of HOMO-LUMO gaps for $Ge_nCr$ clusters is lower than the corresponding pure $Ge_n$ clusters which suggests the increase in the metallic nature of Cr doped $Ge_n$ clusters. The IP and EA variation as a function of cluster size of $Ge$ as shown in Figure 3.8, which shows a gradual increase for EA, small decrease in IP up to $n=7$ and oscillatory behavior thereafter.
Figure 3.7: Shows the size dependence of the binding energies per atom and Second difference of energy for GeₙTM clusters.
Figure 3.8: The E.A. and I.P. of $Ge_nCr$ clusters for $n = 1-13$ and $Ge_n$ clusters for $n = 1-14$. 
Figure 3.9: The HOMO-LUMO gap of $Ge_nCr$ clusters for $n = 1$-$13$ and $Ge_n$ clusters for $n = 1$-$14$. 
In order to understand the variation of HOMO-LUMO gap, we have performed a detailed analysis of molecular orbitals by examining the electronic density of states (EDOS) of \( Ge_{n+1} \) and \( Ge_{n}Cr \) clusters for \( n = 2 \) and 7 as representative cases (Figures 3.10, 3.11). It can be seen that the EDOS in the vicinity of the fermi level is changed significantly when \( Ge_{n} \) clusters are doped with Cr.

Figure 3.10: Electron density of states (EDOS) for \( Ge_{3} \) and \( Ge_{2}Cr \) shows a significant change in the EDOS at the Fermi level due Cr doping. The dotted line corresponds to Fermi level; black and red lines denote spin up and spin down density of states. There is significant spin up EDOS at Fermi level, while spin down EDOS are zero at Fermi level. The Projected density of states (PDOS) of 3d, 4s and 4p orbitals at Cr site in \( Ge_{2}Cr \) are also shown.

The difference in the spin up and spin down EDOS for Cr doped \( Ge_{n} \) cluster indicates the presence of strong electronic polarization. The electronic polarization may be explained on the basis of electric field generated due to the charge transfer between Cr and Ge atoms. From the contribution of different orbital components (s,
Figure 3.11: Electron density of states (EDOS) for $Ge$ and $Ge\text{Cr}$ shows a significant change in the EDOS at the Fermi level due Cr doping. The dotted line corresponds to Fermi level; black and red lines denote spin up and spin down density of states. There is significant spin up EDOS at Fermi level, while spin down EDOS are zero at Fermi level. Projected density of states (PDOS) at Cr site in $Ge\text{Cr}$, shows significant contribution at the Fermi level due d and p orbitals.
it can be seen that electronic states in the vicinity of fermi level mainly come from 4p and 3d states. The spin down d states are unoccupied, which indicates that HOMO-LUMO states are mainly localized around the Cr atom and there is a small electronic distribution around the Ge atom. Therefore, the p-d hybridization may be responsible for the size dependence of HOMO-LUMO gap.

In order to elucidate the bonding nature of the Ge-Cr and Ge-Ge bonds in GeₙCr clusters, the Mulliken charge analysis was performed at each atomic site. In all the GeₙCr clusters, the charge transfer takes place from Cr atom to Ge atoms indicating that Cr atom acts as electron donor. Such charge transfers may be explained on the basis of half filled 3d orbital of Cr. This charge transfer behavior is similar to Fe and Mn doped Ge clusters but different from W (another IVB group element) in which charge transfer takes place from Ge unit to W. All the ground state structures of GeₙCr clusters for n = 1 - 13, exhibit high spin electronic states of S = 2 with quintet state (with multiplicity (2S+1 = 5)) and S = 3 with septet state (2S+1 = 7).

The electronic structure and bonding may be explained qualitatively from electronic configuration of Cr atom and Ge₂ atoms. In Cr atom, the electronic configuration is 3d⁴⁴s¹, where the entire valence orbitals are singly occupied and in Ge₂, the ground state is triplet and unpaired electrons occupy the degenerate π MOs, which are Ge-Ge bonding MOs. The Ge₂ unit approach towards Cr atom such that there is maximum orbital overlap and electron pairing. This leads to an electron pairing in the following two MOs (i) the MO formed as a result of overlap between the Cr 4s¹ orbital with one of the singly occupied π MO of Ge₂ and (ii) the MO resulting from the overlap of dₓ²⁻ᵧ² orbital of Cr with the degenerate π MO of Ge₂. This leaves four unpaired electrons in the valence d orbitals of Cr, namely dₓ², dₓ₋ᵧ², dₓz and dᵧz. Note that singly occupied dₓ₂ and dᵧₓ MOs can overlap with antibonding π MOs of Ge₂ unit resulting in a d-π back donation from Cr atom to Ge₂ unit. The Mulliken charge shows a net charge of +0.19 e on Cr atom and -0.09 e is derived for each of Ge atom consistent with Hou et al. [12].

GeₙTMclusters

The electronic properties of TMGeₙ clusters are investigated in terms of the variation in HOMO-LUMO gap as a function of clusters size as shown in figure-3.12. To investigate the change in the electronic density due to TM doping, the change in the...
The HOMO-LUMO gap of TM doped Geₙ clusters predicts their ability to undergo chemical reactions with small molecules. A large HOMO-LUMO gap corresponds to a closed shell electronic configuration with high stability. The HOMO-LUMO gap for spin up (↑) and spin down (↓) states for TM (TM = Mn, Co and Ni) doped Geₙ clusters with increasing atomic number is plotted in figure-3.12. At this point we would like to mention that HOMO-LUMO gap for spin (↑) and spin (↓) is same for pure Geₙ clusters. However, due to TM doping there is a significant variation in the spin up and spin down HOMO-LUMO gap as a function of cluster size. In MnGeₙ clusters, the spin up HOMO-LUMO gap is found to be maximum.
for MnGe dimer which shows sharp decrease to 0.2 eV in MnGe$_2$. For $n > 3$, the HOMO-LUMO gap for spin up electrons increases oscillatory with local maxima at $n = 5$ and $n = 12$. The HOMO-LUMO gap of spin down electrons shows magnitude greater than gap for spin up electrons except for $n = 1$ and 5. The HOMO-LUMO gap is maximum for $n = 6$ and 12 for Mn in agreement with Wang et al. [11]. For both spin-up and spin-down electrons, the HOMO-LUMO gap is close to 1 eV, indicating its metallic behavior.

In CoGe$_n$ clusters, the HOMO-LUMO gap for spin up ($\uparrow$) electrons is maximum for $n = 9$. For $n > 3$, the HOMO-LUMO gap for spin up electrons increases oscillatory with local maxima at $n = 9$ and $n = 11$. The HOMO-LUMO gap for spin down ($\downarrow$) electrons shows magnitude less than gap for spin up electrons except for $n = 11$. The HOMO-LUMO gap is maximum for $n = 10$. The magnitude of the HOMO-LUMO gap for spin-up electrons is close to 1.0 eV and for spin-down electrons is less than 1.0 eV which is smaller as compared to MnGe$_n$.

In NiGe$_n$ clusters, the HOMO-LUMO gap for spin up ($\uparrow$) and spin down ($\downarrow$) electrons exists only for $n = 2$, 4 and 8. The HOMO-LUMO gap is maximum for $n = 2$ which decreases sharply for $n = 1$ and 3. For $n = 8$, there is overlap of HOMO-LUMO gap of spin up and spin down electrons. The HOMO-LUMO gap as a function of cluster size shows maximum value for $n = 2$ and 10 which is in agreement with Bandyopadhyay et al. [51]. The HOMO-LUMO gap remains close to 1.0 eV for all the cases. A spin arrangement in any magnetic cluster is magnetically stable only if both the spin gaps are positive [28]. In our calculation of HOMO-LUMO gap for TM doped Ge$_n$, these gaps are positive for all the clusters.

In order to further elucidate the origin and change in the electronic properties due to TM doping, we calculated the spin electronic density of states (EDOS) of TMGe$_n$ clusters. The EDOS of few representative cases are shown in Figure 3.13. Figure shows a significant change in EDOS of TMGe$_n$ clusters w.r.t pure Ge$_n$ clusters. At this point we would like to mention that there is no polarization in EDOS of pure Ge$_n$. In MnGe$_3$ and MnGe$_6$ clusters, the spin polarization results in change of EDOS near Fermi level as shown in Figure 3.13(a,b). For MnGe$_3$, the EDOS shows finite value at Fermi level for spin down electrons. In MnGe$_6$ cluster, there is finite EDOS at Fermi level with unequal magnitude. The EDOS profile of spin up and spin down electrons below Fermi level shows significant variation in EDOS profile. For CoGe$_9$ and CoGe$_{10}$ clusters, the EDOS is plotted in Figure 3.13(c,d), both shows finite value of EDOS at Fermi level. However, there is a significant
Figure 3.13: The Electron Density of States (EDOS) for MnGe, CoGe and NiGe. Red line denotes the spin-up electronic charge density and black denotes the spin-down electronic charge density. The dotted vertical line indicates the Fermi level in Kohn-Sham eigen values.
change in EDOS profile below Fermi level for spin up and down channels. In case of 
NiGe$_7$, Figure 3.13(e,f), the EDOS for spin up and down electrons is same suggesting 
no spin polarization is induced, both spin up and spin down EDOS are zero at Fermi 
level resulting into magnetic insulator. For NiGe$_x$, there is a finite value of EDOS 
at Fermi level and unequal EDOS for spin up and spin down electrons below Fermi 
level resulting into half metallic magnetic cluster. Therefore, the Ge$_n$TM clusters 
which shows half metallic behavior capable of retaining magnetism.

### 3.4.3 Magnetic Properties

The magnetic properties of pure and TM doped Ge$_n$ clusters have been calculated 
using spin-polarized DFT. The magnetic moment (MM) is calculated from the differ­ 
ence of spin up and spin down electrons. From the EDOS of pure Ge clusters ($n= 
3$ and 8) as plotted in figure 3.10 and 3.11 there is no polarization of spin up and 
spin down electrons, resulting in zero magnetic moment.

**Ge$_n$Cr clusters**

The total magnetic moment along with local magnetic moment (LMM) at Cr site 
and the contribution of 3d, 4p and 4s orbital towards LMM as well as the induced 
magnetic moment at Ge site are tabulated in Table 3.3. The total magnetic moment 
of Ge$_n$Cr clusters for $n = 1-13$ is not a monotonic function of the cluster size and 
interestingly only two magnetic states with 4 $\mu_B$ and 6 $\mu_B$ are observed. The 
high magnetic moments observed in all the GS structures are consistent with the 
empirical rule relating Cr-Ge distance with magnetic moment i.e. the larger is 
the average distance between TM impurity and the atom of the host cluster the 
larger is the multiplicity [23]. The high spin states of Ge$_n$Cr may be explained 
on the basis of the unpaired electrons in the system. The total magnetic moment 
arise mainly due to localized magnetic moment at Cr site, small induced magnetic 
moment on Ge atoms and magnetic interaction with Ge atoms. The charge transfer 
occurs in the same direction i.e. from Cr atom to the Ge atoms. The maximum 
induced magnetic moment of 1.21 $\mu_B$ is developed on Ge atom in GeCr. The induced 
magnetic moment on Ge atom varies from 0.55-0.38 $\mu_B$ for $n = 2-5$. For $n > 5$, the 
small magnetic moment of 0.02-0.36 $\mu_B$ is induced on Ge atoms some them which 
aline antiferromagnetically w.r.t to Cr atom. At Cr atom in Ge$_n$Cr clusters, the 
spin magnetic moment comes mainly from the unpaired electrons of the 3d state and
Table 3.3: The total spin magnetic moment of the Ge\textsubscript{n}Cr clusters, \(\mu_{Cr}\) is the local magnetic moment on Cr atom; and \(\mu_{3d}\), \(\mu_{4s}\) and \(\mu_{4p}\) are magnetic moments of the 3d, 4s, 4p states of Cr atom respectively. \(\mu_{ind}\) is the maximum induced magnetic moment on nearest Ge atoms.

<table>
<thead>
<tr>
<th>CrGe\textsubscript{n}</th>
<th>(\mu_{total})</th>
<th>(\mu_{Cr})</th>
<th>(\mu_{3d})</th>
<th>(\mu_{4s})</th>
<th>(\mu_{4p})</th>
<th>Ge (\mu_{in})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge\textsubscript{1}Cr</td>
<td>1.52</td>
<td>1.65</td>
<td>0.06</td>
<td>0.58</td>
<td>1.21</td>
<td></td>
</tr>
<tr>
<td>Ge\textsubscript{2}Cr</td>
<td>1.53</td>
<td>1.62</td>
<td>0.09</td>
<td>0.33</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>Ge\textsubscript{3}Cr</td>
<td>1.42</td>
<td>1.57</td>
<td>0.01</td>
<td>0.11</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>Ge\textsubscript{4}Cr</td>
<td>1.90</td>
<td>1.62</td>
<td>0.02</td>
<td>0.26</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>Ge\textsubscript{5}Cr</td>
<td>1.92</td>
<td>1.61</td>
<td>0.07</td>
<td>0.21</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>Ge\textsubscript{6}Cr</td>
<td>1.57</td>
<td>1.69</td>
<td>0.01</td>
<td>0.20</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>Ge\textsubscript{7}Cr</td>
<td>1.98</td>
<td>1.61</td>
<td>0.09</td>
<td>0.18</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>Ge\textsubscript{8}Cr</td>
<td>1.02</td>
<td>1.65</td>
<td>0.10</td>
<td>0.17</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>Ge\textsubscript{9}Cr</td>
<td>5.03</td>
<td>1.73</td>
<td>0.10</td>
<td>0.20</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>Ge\textsubscript{10}Cr</td>
<td>5.44</td>
<td>1.70</td>
<td>0.09</td>
<td>0.55</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>Ge\textsubscript{11}Cr</td>
<td>4.98</td>
<td>1.67</td>
<td>0.17</td>
<td>0.14</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>Ge\textsubscript{12}Cr</td>
<td>5.01</td>
<td>1.66</td>
<td>0.21</td>
<td>0.13</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>Ge\textsubscript{13}Cr</td>
<td>1.88</td>
<td>1.64</td>
<td>0.10</td>
<td>0.22</td>
<td>0.25</td>
<td></td>
</tr>
</tbody>
</table>

very small contribution from 4s. As in free Cr atom, the valence configuration is 3d\textsuperscript{6}4s\textsuperscript{1} with 6 \(\mu_{B}\) magnetic moment and a careful investigation of magnetic moment in Table 3.3, shows a charge transfer from Cr to Ge beside a internal charge transfer with in the Cr atom. Therefore, for the Ge\textsubscript{n}Cr cluster, the charge transfer mainly happens between the 4s, 3d and 4p orbitals of Cr and the 4s, 4p orbitals of Ge. Thus, there exits s-p-d hybridization in Cr, s-p hybridization of Ge and p-d hybridization between the Cr and Ge atoms, whose combined effect may explain the observed FM in group IV DMSs. Therefore, the present work have predicted the presence of high magnetic moment in Cr doped Ge clusters in intermediate size clusters \((n = 1-13)\), which might be further explored as a possible DMS. The magnetic properties of Ge\textsubscript{n}TM clusters are investigated in terms of total MM calculated for the GS structure and the local MM of TM atom. The magnetic moment is calculated from the difference of spin up and spin down electrons \(Q(\uparrow - \downarrow)\). The total MM of TMGe\textsubscript{n} clusters, local MM of TM atoms, MM contribution of s and d orbital of TM and p orbital of Ge atoms, along with total charge on TM atom \((Q_{T,M})\) are summarized in Tables 3.4, 3.5.
**GenMn Clusters**

For \( \text{MnGen} \) clusters, the magnitude of total MM oscillates between 1 \( \mu_B \) and 3 \( \mu_B \). The calculations are performed for all possible spin combinations (1 \( \mu_B \), 3 \( \mu_B \), 5 \( \mu_B \)) for all GS structures of \( \text{MnGen} \) clusters. For \( n = 1, 2, 4, 5, 6 \) and 11, the total MM is found to be 3 \( \mu_B \) where as it is 1 \( \mu_B \) for other clusters. However, MM of 3 \( \mu_B \) and 1 \( \mu_B \) have been reported [50] for \( n = 7 \) and 11 respectively. The total MM is mainly located at the TM site and the main contribution is from \( d \) orbital. The \( s \) and \( p \) orbital contribution is very small. A small MM of the order of 0.001-0.28 \( \mu_B \) is induced on the nearest Ge atoms which interacts AFM with Mn atom except for \( n = 9 \) and 11. The origin of magnetism may be attributed to the presence of unpaired electrons of the \( 3d \) states and \( p-d \) hybridization between Ge and TM atoms as it is clear from the PDOS plot shown in Figure 3.14. The maximum value of 4 \( \mu_B \) local MM on Mn is less than 5 \( \mu_B \) of the Mn atom in small Mn clusters. The valence shell configuration of Mn atom is \( 3d^54s^2 \), therefore according to Hund’s Rule the MM for Mn is 5 \( \mu_B \). However, the hybridization between \( 3d \) and \( 4p \) orbital induces the anti-parallel interaction between the Ge atoms and Mn resulting in reduction of MM of the Mn atom. The local MM of TM is delocalized and distributed over the surrounding Ge atoms.

**GenCo Clusters**

For \( \text{CoGe}_n \), the magnetic moments are tabulated in Table-5.5 for \( n = 1-13 \). We have considered all the possible spin combinations (1, 3, 5) for all the GS structures of \( \text{CoGe}_n \) clusters. Table 3.5 shows a total MM of 1 \( \mu_B \) for all size except for \( n = 2, 3 \) and 9. However, the MM of 3 \( \mu_B, 1 \mu_B \) and 3 \( \mu_B \) have been reported for \( n = 1, 3 \) and 7 [10] respectively. A small MM of the order 0.004-0.17 \( \mu_B \) is induced on Ge atoms and is aligned parallel to Co atom for \( n = 2, 3, 6-8, \) and 10-13. However, induced MM of 0.04 \( \mu_B \) is aligned anti-parallel w.r.t. Co for \( n = 1, 4 \) and 5.

The valence shell electronic configuration for Co is \( 3d^74s^2 \) and according to Hund’s rule the atomic MM of Co atom is 3 \( \mu_B \) however due to hybridization between Co \( 3d \) and \( 4p \) orbitals with Ge \( 4s, 4p \) orbitals, as shown in projected DOS plots Figure 3.14, there is a reduction in local MM of Co atom in \( \text{CoGe}_n \) clusters. The induced MM on Ge is aligned ferromagnetically w.r.t. to Co atom except for \( n = 1, 4 \) and 5 which favours anti-parallel alignment. The local MM is less than the total MM implying the FM alignment which is opposite to magnetic behavior.
Table 3.4: The Total magnetic moment $\mu_{\text{total}}$, $\mu_{\text{3d}}$, $\mu_{\text{4s}}$ and $\mu_{\text{4p}}$ are the magnetic moments of the 3d,4s,4p states of Mn atom respectively. $\mu_{\text{Mn}}$ and $Q_{\text{Mn}}$ are the Local magnetic moment and charge of Mn atom. $Q_1$ and $Q_2$ are the spin-up and spin-down gaps.

<table>
<thead>
<tr>
<th>MnGe</th>
<th>$\mu_{\text{total}}$</th>
<th>$\mu_{\text{3d}}$</th>
<th>$\mu_{\text{4s}}$</th>
<th>$\mu_{\text{4p}}$</th>
<th>$\mu_{\text{Mn}}$</th>
<th>$Q_{\text{Mn}}$</th>
<th>$Q_1$</th>
<th>$Q_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnGe</td>
<td>3</td>
<td>3.82</td>
<td>0.14</td>
<td>0.03</td>
<td>3.94</td>
<td>5.49</td>
<td>2.28</td>
<td>1.48</td>
</tr>
<tr>
<td>MnGe</td>
<td>3</td>
<td>3.40</td>
<td>0.09</td>
<td>0.00</td>
<td>3.48</td>
<td>5.59</td>
<td>0.29</td>
<td>1.04</td>
</tr>
<tr>
<td>MnGe</td>
<td>3</td>
<td>2.86</td>
<td>0.06</td>
<td>-0.03</td>
<td>2.88</td>
<td>5.64</td>
<td>0.33</td>
<td>0.97</td>
</tr>
<tr>
<td>MnGe</td>
<td>3</td>
<td>3.50</td>
<td>0.06</td>
<td>-0.03</td>
<td>3.53</td>
<td>5.60</td>
<td>0.51</td>
<td>0.76</td>
</tr>
<tr>
<td>MnGe</td>
<td>3</td>
<td>3.55</td>
<td>0.06</td>
<td>0.00</td>
<td>3.61</td>
<td>5.57</td>
<td>1.44</td>
<td>0.76</td>
</tr>
<tr>
<td>MnGe</td>
<td>3</td>
<td>3.03</td>
<td>0.04</td>
<td>0.00</td>
<td>3.07</td>
<td>5.57</td>
<td>1.09</td>
<td>1.23</td>
</tr>
<tr>
<td>MnGe</td>
<td>1</td>
<td>1.99</td>
<td>0.03</td>
<td>0.00</td>
<td>2.00</td>
<td>5.77</td>
<td>0.15</td>
<td>1.30</td>
</tr>
<tr>
<td>MnGe</td>
<td>1</td>
<td>2.11</td>
<td>0.03</td>
<td>0.00</td>
<td>2.14</td>
<td>5.78</td>
<td>0.44</td>
<td>1.27</td>
</tr>
<tr>
<td>MnGe</td>
<td>1</td>
<td>0.78</td>
<td>0.03</td>
<td>0.03</td>
<td>0.85</td>
<td>5.92</td>
<td>0.30</td>
<td>1.18</td>
</tr>
<tr>
<td>MnGe</td>
<td>1</td>
<td>1.26</td>
<td>0.01</td>
<td>0.01</td>
<td>1.27</td>
<td>6.03</td>
<td>0.11</td>
<td>1.30</td>
</tr>
<tr>
<td>MnGe</td>
<td>1</td>
<td>2.47</td>
<td>0.02</td>
<td>0.02</td>
<td>2.51</td>
<td>5.88</td>
<td>0.84</td>
<td>0.97</td>
</tr>
<tr>
<td>MnGe</td>
<td>1</td>
<td>1.76</td>
<td>0.02</td>
<td>0.02</td>
<td>1.80</td>
<td>5.74</td>
<td>1.35</td>
<td>1.60</td>
</tr>
<tr>
<td>MnGe</td>
<td>1</td>
<td>1.87</td>
<td>0.02</td>
<td>0.02</td>
<td>1.91</td>
<td>5.74</td>
<td>0.61</td>
<td>0.73</td>
</tr>
</tbody>
</table>

in MnGe$_n$ clusters. In CoGe$_n$ clusters there is an electronic charge transfer from Ge atom to Co atom. There is internal charge transfer from s orbital to d orbital of Co atom. However, the MM is mainly contributed by d orbital of Co atom. Interestingly, similar behavior has been reported for W doped Ge$_n$ clusters, where the charge transfer takes place from Ge to W. At this point we would like to mention that Co have shown magnetic quenching for Si$_n$Co [26] but no quenching is observed in our calculation in agreement with other ab initio studies [10].

Ge$_n$Ni clusters

For NiGe$_n$ cluster, the magnetic properties are different as compared to Mn and Co. The quenching of MM is observed for all $n$ considered except for $n = 2, 4$ and 8. This magnetic behavior is similar to as reported for NiSi$_n$ [53]. At this point we would like to mention that magnetic properties of NiGe$_n$ clusters have not been reported in the literature. The quenching of MM implies a nonmagnetic cluster which may be explained on the basis of charge transfer between Ni and Ge atoms and strong hybridization between 3d orbital of Ni and 4p orbital of Ge. Here all the
Figure 3.14: The Projected Density of States (PDOS) for MnGe and CoGe. The upper panel shows 2p-PDOS for Ge atoms and the lower panel shows 3d-PDOS for Mn and Co respectively. The vertical line indicates the Fermi energy which is shifted to 0.0 eV.
Table 3.5: The Total magnetic moment $\mu_{\text{total}}$, $\mu_{3d}$, $\mu_{4s}$ and $\mu_{4p}$ are the magnetic moment of the 3d, 4s, 4p states of Co atom respectively. $\mu_{C_C}$ and $Q_{C_C}$ are the Local magnetic moment and charge of Co atom. $(\delta_1)$ and $(\delta_2)$ are the spinup and spindown gaps.

<table>
<thead>
<tr>
<th>CoGe$_n$</th>
<th>$\mu_{\text{total}}$</th>
<th>$\mu_{3d}$</th>
<th>$\mu_{4s}$</th>
<th>$\mu_{4p}$</th>
<th>$\mu_{C_C}$</th>
<th>$Q_{C_C}$</th>
<th>$(\delta_1)$</th>
<th>$(\delta_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoGe</td>
<td>1.74</td>
<td>0.01</td>
<td>-0.03</td>
<td>1.76</td>
<td>7.92</td>
<td>1.57</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>CoGe$_3$</td>
<td>3.18</td>
<td>0.06</td>
<td>0.02</td>
<td>1.87</td>
<td>7.80</td>
<td>1.40</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>CoGe$_4$</td>
<td>3.88</td>
<td>0.07</td>
<td>0.02</td>
<td>1.98</td>
<td>7.91</td>
<td>1.43</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>CoGe$_5$</td>
<td>1.12</td>
<td>-0.02</td>
<td>0.01</td>
<td>1.10</td>
<td>8.13</td>
<td>0.70</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>CoGe$_6$</td>
<td>1.19</td>
<td>-0.16</td>
<td>0.00</td>
<td>1.21</td>
<td>8.15</td>
<td>1.0</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>CoGe$_7$</td>
<td>0.89</td>
<td>-0.01</td>
<td>0.01</td>
<td>0.89</td>
<td>8.21</td>
<td>0.86</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>CoGe$_8$</td>
<td>0.85</td>
<td>0.01</td>
<td>0.01</td>
<td>0.90</td>
<td>8.23</td>
<td>0.48</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>CoGe$_9$</td>
<td>0.92</td>
<td>0.00</td>
<td>0.01</td>
<td>0.92</td>
<td>8.24</td>
<td>0.81</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>CoGe$_{10}$</td>
<td>1.32</td>
<td>0.04</td>
<td>0.04</td>
<td>1.40</td>
<td>8.34</td>
<td>1.85</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>CoGe$_{11}$</td>
<td>0.65</td>
<td>0.01</td>
<td>0.00</td>
<td>0.66</td>
<td>8.61</td>
<td>1.33</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>CoGe$_{12}$</td>
<td>0.33</td>
<td>0.00</td>
<td>0.03</td>
<td>0.36</td>
<td>8.34</td>
<td>1.26</td>
<td>1.52</td>
<td></td>
</tr>
<tr>
<td>CoGe$_{13}$</td>
<td>0.43</td>
<td>0.00</td>
<td>0.00</td>
<td>0.43</td>
<td>8.29</td>
<td>0.79</td>
<td>0.52</td>
<td></td>
</tr>
</tbody>
</table>

Spin up states are occupied but spin down states are empty, therefore induced MM on Ge atoms is antiparallel w.r.t. Ni resulting in zero MM. However, for $n = 2, 4$ and 8 there is FM coupling between Ni and neighbouring Ge atoms. The Magnetic behaviour in Si$_n$Ni have shown MM quenching for $n = 3-8$ [53].

From the magnetic properties of Mn, Co and Ni doped Ge$_n$ clusters, it can be concluded that the total MM is mainly contributed by TM atom and magnetic interaction with nearest Ge atoms. The local MM decrease gradually in the following the order $Mn > Co > Ni$, conforming the gradual reduction in their number of unpaired d-electrons. For Ge$_n$TM clusters the Ge atoms are aligned anti-parallel except in CoGe$_n$ for $n = 2, 3, 6-8, 10-13$ which interacts ferromagnetically. The total MM oscillates between 3 $\mu_B$ and 1 $\mu_B$ for both Mn and Co doped Ge$_n$ clusters where as for NiGe$_n$ it oscillates between 0 $\mu_B$ and 2 $\mu_B$. The quenching of MM is observed only for Ni doped Ge$_n$ clusters for all $n$ except for $n = 2, 4$ and 8.
3.5 Summary and Conclusions

The structural growth behavior, electronic and magnetic properties have been calculated using first principle calculation of TM (Cr, Mn, Co, and Ni) doped Ge$_n$ clusters. The results are summarized as follows:

(1) The Cr atom tends to stabilize at exohedral position and do not show tendency to fall into center of Ge outer frame. The ground state structures of TMGe$_n$ (Mn, Co, Ni) for $n < 9$ show preference to occupy surface positions while for $n \geq 9$ the TM's show tendency to move towards endohedral positions. There is a critical size of the cluster above which TM tends to form endohedral complexes which is $n = 11$, 10 and 9 for Mn, Co and Ni respectively. The TM-Ge bond length decreases in the order of Mn, Co and Ni in accordance to their size. The ground state geometries of Cr doped Ge clusters exhibits lower symmetry as compared to pure Ge$_n$ clusters. This may be explained on the basis of 2nd Jahn Teller theorem i.e. the geometries of the relaxed clusters are easy to distort when the filled and empty molecular orbitals are close in energy.

(2) The binding energy per atom increases in the TMGe$_n$ clusters as a function of cluster size, suggesting gain in their structural stability. The binding energy does not vary significantly w.r.t pure Ge$_n$ clusters. However, for CrGe$_n$ clusters the magnitude of the binding energy shows a small decrease w.r.t pure Ge$_n$ clusters thereby indicating its lesser stability though changing magnetic properties significantly.

The second difference in energies predict the extra relative stability for Ge$_5$TM except for Co and Ge$_{11}$TM than their neighboring clusters. The analysis of possible fragmentation channels for Ge$_n$TM clusters show that the most probable channel for dissociation of Ge$_n$TM clusters is to dissociate into TM atom and Ge$_n$ unit, for Mn, Co and Cr but for Ge$_n$Ni cluster the dissociation energy is less to remove a Ge atom than the Ni atom.

(3) The TM doping alters the HOMO-LUMO gap of pure Ge$_n$ clusters significantly. The HOMO-LUMO gap for spin up electrons varies from 0.29 eV-2.28 eV, 0.43 eV-1.85 eV, 0.0 eV-1.71 eV for Mn, Co and Ni respectively whereas for spin down electrons the HOMO-LUMO gap varies from 0.73 eV-1.60 eV, 0.05 eV-1.52 eV and 0.0 eV-0.91 eV for Mn, Co and Ni respectively.

(4) The magnetic behavior of TMGe$_n$ clusters is due to TM dopant. The MM is mainly localized at the TM site and nearest Ge atoms. The local MM at TM
site decreases gradually in the order Mn, Co, Ni in accordance to their number of unpaired $d$-electrons. The MM is mainly localized on TM atom however a small MM is induced on nearest Ge atoms.

(5) All the ground state structures of $Ge_nCr$ clusters exhibit high spin quintet or septet states. The magnetic moment value is $1 \mu_B$ or $6 \mu_B$ for Cr, $3 \mu_B$ or $1 \mu_B$ for Mn and Co and $0 \mu_B$ or $2 \mu_B$ for Ni doped clusters. The Mn and Cr atoms interact AFM with some of the nearest Ge atoms but the Co atom interacts AFM only for $n = 1, 4, 5$ and $9$. The Mulliken charge analysis suggest donor nature of Mn and Cr atoms as there is uniform charge transfer from Mn and Cr to Ge atoms.

The magnetic properties of the TM doped Germanium clusters offers a direction for injecting spin in group-IV semiconductor clusters. However, before their potential can be realized, other crucial issues such as low solubility of the TM impurities in semiconducting matrix and clustering of TMs must be resolved. The effect of TM as co-dopants in Ge clusters and thin films ought to be explored for its complete understanding of the role of magnetic impurities in Germanium.
Bibliography


[30] cms.mpi.univie.ac.at/vasp


