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STABILITY AND ELECTRONIC PROPERTIES OF ISOMORPHOUS SUBSTITUTED $Si_{7-x}Mn_x^+$

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Abstract. The optimized geometries, stability, and magnetic properties of cationic clusters Si_7^+, Si_6Mn^+, and $Si_5Mn_2^+$ have been determined by the method of density functional theory using the B3P86/6-311+G(d) functional/basis set. Their electronic configurations have been analyzed to understand the influence of substituting Si atoms by Mn atoms on the structural and magnetic aspects of Si_7^+. It is shown that the manganese dopant does not alter the structure of the silicon host but significantly changes its stability and magnetism. In particular, while the magnetic moment of Si_7^+ is 1 μ_B, $Si_5Mn_2^+$ exhibits a strong magnetic moment of 9 μ_B and that of Si_6Mn^+ takes a relatively high value of 4 μ_B. Among studied clusters, the pentagonal bipyramid $Si_5Mn_2^+$ is assigned as the most stable one.

Keywords: cluster silicon, density functional theory.

Classification numbers: 4.10.1; 4.10.4.

1. INTRODUCTION

Investigations of the geometries, electronic structures, energetics, and reactivity of atomic clusters have attracted significant interest in recent years. Among the atoms clusters that have been studied, the silicon clusters are of particular interest to scientists [1 - 2]. Silicon has been and continues to be one of the most widely used elements in various semiconductor applications such as solar cells and microelectronics. For some small Si_n clusters, the ground-state geometries have been studied by using many experimental techniques, confirming the theoretically proposed ones [3 - 6]. Transition metal atoms are usually magnetic due to their half-filled *d* orbitals. Doping transition metal atoms into silicon clusters is expected to create species which have prolific magnetic properties [7 - 10]. Many studies on the small cationic silicon clusters doped with transition metals, for instance copper and vanadium Si_nCu^+ and Si_nV^+ (n = 6 - 8), have been performed for optimizing their geometrical structures. Among 3*d* transition metal-silicon systems, manganese doped silicon clusters have been of particular interest. The Mn atom has an electronic configuration of $3d^5 4s^2$ with a high magnetic moment. Several reports on structures and magnetism of small silicon clusters doped with manganese atom have also been performed [8 - 9]. However, the influence of Mn-substitution into the Si_7 cluster on its geometrical and electronic structures as well as its magnetism has not been studied yet.

In this study, we investigate the structure, stability, magnetism of the Si_7^+, Si_6Mn^+, $Si_5Mn_2^+$ and the effect of Mn substitution in the cationic silicon cluster Si_7^+ using density functional theory with the B3P86/6-311+G(d) functional/basis set.

2. METHOD OF CALCULATIONS

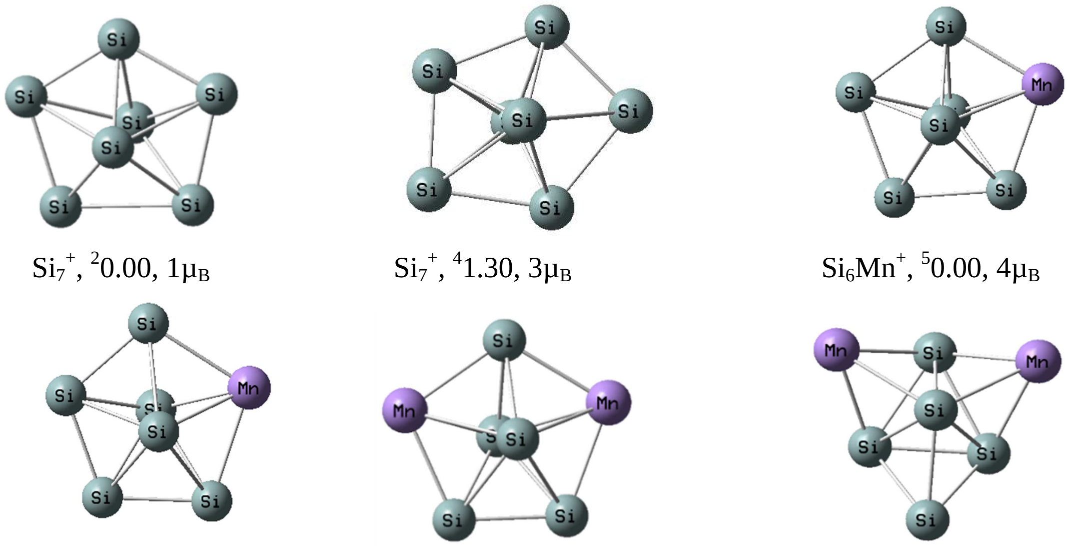
We use the method of density functional theory (DFT) which is implemented in the Gaussian 09 software [11-12] to investigate the manganese doped silicon cationic clusters Si_7^+, Si_6Mn^+, and $Si_5Mn_2^+$.

The B3P86/6-311+G(d) functional/basis set has been used for our calculations [13 - 15]. The optimization calculations which are followed by frequency calculations have been done for searching minima of the clusters. Geometries, electronic energies, zero point energies, relative energies are deduced from these calculations.

3. RESULTS AND DISCUSSIONS

3.1. Equilibrium geometries

Optimized structures of all studied clusters, which are displayed in Fig. 1, are found in form of a pentagonal bipyramid.



Si_7^+, ^{2}0.00, 1μ$_B$ Si_7^+, ^{4}1.30, 3μ$_B$ Si_6Mn^+, ^{5}0.00, 4μ$_B$

Si_6Mn^+, ^{7}0.38, 6μ$_B$ $Si_5Mn_2^+$, ^{10}0.00, 9μ$_B$ $Si_5Mn_2^+$, ^{10}0.39, 9μ$_B$

Figure 1. The geometry of the clusters Si_7^+, Si_6Mn^+ and $Si_5Mn_2^+$.

For the cluster Si_7^+, the most stable structure has a spin state of ^{2}A, corresponding to a magnetic moment of 1 μ$_B$, in C_1 point group. The next isomer is a C_1 symmetric pentagonal bipyramid is 1.30 eV higher in energy than the corresponding doublet state. The structure of

Si_6Mn^+ in C_{2v} point group is found as the most stable isomer with 4 unpaired electrons and a magnetic moment of 4 μ_B. This structure is a pentagonal bipyramid formed by replacing one Si atom in the base plane of pentagonal bipyramid Si_7^+ by one Mn atom. The exactly same structure with 6 unpaired electrons has a relative energy of 0.38 eV. The ground state structure of $Si_5Mn_2^+$ is a pentagonal bipyramid with a dectet spin state, in which the two Mn atoms locate on its base plane and are interspersed by a Si atom. This structure is formed by replacing one Si atom in cluster Si_6Mn^+ by one Mn atom. For this motif of structure the other electronic state ^{10}A has been also found with a relative energy of 0.39 eV, where the Si_5 moiety forms a trigonal bipyramid capped with two Mn atoms onto two different faces or edges of the bipyramid. The obtained geometry structure results of clusters Si_7^+ and Si_6Mn^+ are consistent with some studies of the geometry of previous silicon clusters [16] and consistent with the results of Lievens and coworkers on the structure, electronic, and magnetic moments of manganese-doped silicon clusters cations Si_nMn^+ with n = 6 - 10 [7, 8]. It has been reported that Mn singly-doped silicon clusters prefer planar structures at sizes n = 2 - 4. A transition from 2D to 3D has been found at Si_5Mn^+ and Si_6Mn^+ by forming tetragonal and pentagonal bipyramid structures. To our best knowledge, the structure and electronic properties of $Si_5Mn_2^+$ have been less understood compared to that of its singly-doped counterpart. A recent study on the growth mechanism of neutral and anionic $Si_{1\text{-}8}Mn_2^{0,-}$ clusters has revealed that their structure also favor the pentagonal bipyramid form [17]. It is suggested that the pentagonal bipyramid is the most stable form of Si_5Mn_2 clusters regardless its charge states.

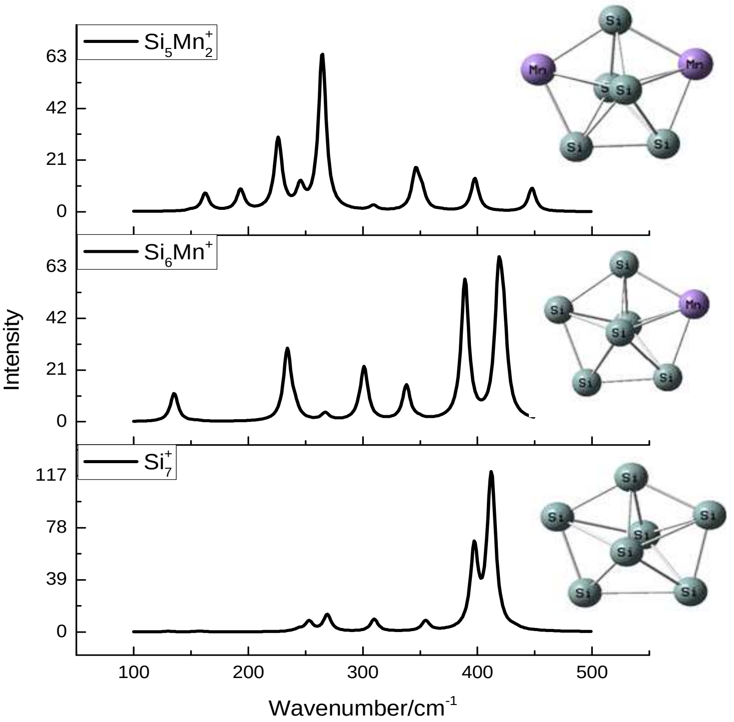


Figure 2. IR spectra of the Si_7^+, Si_6Mn^+, and $Si_5Mn_2^+$.

Figure 2 shows the calculated vibrational IR spectra of the ground-state clusters. The spectrum of Si_7^+ exhibits two primary absorption peaks between 380 and 420 cm^{-1} regarding to the vibrational modes of Si-Si bonds. The experimental spectrum of Si_7^+ is in good agreement with our calculations with several peaks appearing at 385 and 408 cm^{-1} [16]. For the cluster

Si_6Mn^+, several absorption peaks between 240 and 430 cm^{-1}, which are comparable with experimental data with major peaks between 280 and 430 cm^{-1} [7,8]. While the most two pronounced peaks at 370 and 430 cm^{-1} could be generated from Si-Si bonds, the emerging peaks at 240, 300, and 340 cm^{-1} are resulted from the introduction of Mn dopant and could represent Si-Mn vibration modes. The experimental IR spectrum of $Si_5Mn_2^+$ has not been found in literature yet. Our calculations show that it contains two major peaks at 230 and 260 cm^{-1}, which could be due to the Si-Mn and Mn-Mn vibrational modes, respectively. These two peaks are followed by three smaller peaks at 350, 400, and 450 cm^{-1} in the region of Si-Si bonds. Given the excellent fit between computational and experimental spectrum for Si_7^+ and Si_6Mn^+, we believe the calculated IR spectrum for $Si_5Mn_2^+$ would serve as a reliable fingerprint for future vibrational IR spectroscopic measurements.

3.2. Dissociation behavior

In general, the stability of a cluster can be reflected in their dissociation behavior. The cluster having higher dissociation energy will be more stable. On the basis of the results of the electronic energies of the most stable isomers, we have calculated dissociation energies of the parent clusters into daughter clusters for selected potential dissociation channels. The results are represented in Tables 1.

Table 1. Dissociation energies (De, in eV) of Si_7^+ for selected potential dissociation channels.

Dissociation channels	Dissociation energies (eV)
$Si_7^+ \rightarrow Si + Si_6^+$	**3.96**
$Si_7^+ \rightarrow Si_6 + Si^+$	4.50
$Si_7^+ \rightarrow Si_2 + Si_5^+$	6.22
$Si_7^+ \rightarrow Si_5 + Si_2^+$	5.88
$Si_7^+ \rightarrow Si_3 + Si_4^+$	5.18
$Si_7^+ \rightarrow Si_4 + Si_3^+$	5.31
$Si_6Mn^+ \rightarrow Si_6^+ + Mn$	2.80
$Si_6Mn^+ \rightarrow Si_6 + Mn^+$	**2.38**
$Si_6Mn^+ \rightarrow Si_5 + SiMn^+$	4.62
$Si_6Mn^+ \rightarrow Si_5^+ + SiMn$	5.35
$Si_6Mn^+ \rightarrow Si_4 + Si_2Mn^+$	4.72
$Si_6Mn^+ \rightarrow Si_4^+ + Si_2Mn$	5.35
$Si_5Mn_2^+ \rightarrow Si + Si_4Mn_2^+$	4.52
$Si_5Mn_2^+ \rightarrow Si^+ + Si_4Mn_2$	6.10
$Si_5Mn_2^+ \rightarrow Si_5 + Mn_2^+$	4.22
$Si_5Mn_2^+ \rightarrow Si_5^+ + Mn_2$	6.02
$Si_5Mn_2^+ \rightarrow SiMn^+ + Si_4Mn$	5.38
$Si_5Mn_2^+ \rightarrow SiMn + Si_4Mn^+$	5.20
$Si_5Mn_2^+ \rightarrow Mn + Si_5Mn^+$	**2.78**
$Si_5Mn_2^+ \rightarrow Mn^+ + Si_5Mn$	4.06

The potential dissociation channels to remove a neutral/cation Si/Mn atom or bigger fragments are considered. It is shown that the preferred dissociation channels of Si_7^+, Si_6Mn^+,

$Si_5Mn_2^+$ are different. In particular, Si_7^+ cluster favor to decay one Si atom to form Si_6^+ daughters with an energy amount of at least 3.96 eV, which is found similar to that of neutral Si_7 clusters [18]. This result in good agreement with the data obtained from collision-induced dissociation experiments by Jarrold and Bower [18,19], where the main product of clusters smaller than Si_9^+ arises from loss of a single atom. In our calculations, the lowest-energy dissociation channel of Si_6Mn^+ is to decay via Si_6 and Mn^+ ion with a required energy of 2.38 eV. For the $Si_5Mn_2^+$ cluster, the loss of one neutral Mn atom is the most fragile dissociation channel corresponding to a dissociation energy of 2.78 eV. The results of calculated dissociation energies imply that Si_7^+ cluster is the most stable species and the Si_6Mn^+ is the least stable one, which needs only 2.38 eV to fragment into Si_6 cluster and a cation Mn^+. To our best knowledge, dissociation measurements have not been performed for Mn doped small silicon clusters so far and the presented dissociation behavior of Si_6Mn^+ and $Si_5Mn_2^+$ would be useful in guiding future experimental studies.

3.3. Magnetic properties

The magnetic nature of clusters can be reflected through their electronic configuration of the magnetic impurity. Thus, we have performed calculations on Natural Bond Orbital (NBO) to reveal the electronic configurations and occupancies of orbitals of Mn atoms in the clusters. The results are represented in Table 2.

Table 2. Electronic configurations of Mn atoms in the $Si_5Mn_2^+$and Si_6Mn^+ clusters and the occupancies of 3d orbitals of Mn atoms.

(1)		(2)	(3)	(4)
$Si_5Mn_2^+$	Mn (1)	[core]4s(0.27)3d(4.94)4p(0.18)4d(0.02)	[core]4s(0.15)3d(0.62)4p(0.15)4d(0.02)	4.32
	Mn (2)	[core]4s(0.27)3d(4.94)4p(0.18)4d(0.02)	[core]4s(0.15)3d(0.62)4p(0.15)4d(0.02)	4.32
Si_6Mn^+	Mn	[core]4s(0.22)3d(4.93)4p(0.15)4d(0.01)	[core]4s(0.14)3d(0.70)4p(0.14)4d(0.02)	4.23

(1) Clusters; (2) Electron Configuration (Alpha spin orbital); (3) Electron Configuration (Beta spin orbital); (4) Occupancy of 3d(Mn) alpha spin orbital - Occupancy of 3d(Mn) beta spin orbital (electron).

As shown in Figure 1, the magnetic moments of the ground-state Si_7^+, Si_6Mn^+, and $Si_5Mn_2^+$ are 1, 4, and 9 μ_B, respectively. The magnetic moments of the ground-state Si_7^+ and Si_6Mn^+ are in line with othe findings in literature [7, 8]. It is obvious that the substitution of one or two Mn atoms into the Si_7^+ clusters does not alter the pentagonal bipyramid structure but significantly enhances the magnetic moment of the cation Si_7^+. The $Si_5Mn_2^+$ has highest magnetic moment (9 μ_B), Si_6Mn^+ has the magnetic moment of 4 μ_B and Si_7^+ possesses the lowest one (1 μ_B). The results obtained in Table 2 show that for $Si_5Mn_2^+$, the ferromagnetically ordered Mn atoms play a key role on the magnetism of the cluster since each Mn atom contributes 4.32 μ_B to the total magnetic moment of 9 μ_B. The ferromagnetic order is also found for neutral Si_5Mn_2 clusters, resulting in a magnetic moment of 8 μ_B [17]. For Si_6Mn^+, the Mn atom donates 4.23 μ_B to the total magnetic moment of 5 μ_B. The unpaired 3d electrons of Mn atoms are approximately equal to those in the individual Mn atom (5 electrons). The magnetic behavior of the doped species is strongly governed by the magnetic properties of the dopant. The total magnetic moment of the clusters is largely localized in the Mn atom provided by the 3d state electrons and controlled by the magnetic ordering between two dopant atoms.

4. CONCLUSION

The method of density functional theory using the B3P86 functional and the 6-311+G(d) basis set has been employed to optimize geometrical structures following by frequency calculations of the clusters Si_7^+, Si_6Mn^+ and $Si_5Mn_2^+$. Dissociation energies are calculated and the most preferred decay paths of the clusters have been identified. The process of manganese substitution into silicon cluster Si_7^+ does not alter its pentagonal bipyramid structure but changes its stability and changes significantly magnetic moment of the cationic cluster Si_7^+, namely the $Si_5Mn_2^+$ has highest magnetic moments (9 μB), Si_6Mn^+ has the magnetic moment of 4 μB and Si_7^+ has lowest one (1 μB).

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