

# Electronic, magnetic and optical properties of Cu, Ag, Au-doped Si clusters

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**Abstract** The structural, optical and magnetic properties of Cu, Ag, Au-doped Si<sub>7</sub> Clusters have been systematically investigated using density functional theory calculations. The global optimized structures of Cu, Ag, Au-doped Si clusters are predicted to have a lower HOMO–LUMO gap and higher magnetic moment. M-doping (M=Cu, Ag, Au) in Si cluster widens a range of adsorption wavelength, especially Au-doping. The characteristics in electronic density of states (DOSs) show that C<sub>5v</sub>-Si<sub>6</sub>Cu has a big asymmetrical spin-up and spin-down. The average atomic moment is 0.428 m<sub>B</sub> per atom for the Si<sub>6</sub>Cu cluster with C<sub>5v</sub> symmetry, while the average paramagnetic moment is 0.143 m<sub>B</sub> per atom for other M-doped (M=Cu, Ag, Au) Si<sub>7</sub> clusters.

**Keywords** Absorption spectrum · Cluster · Density functional theory · Magnetic moment

## Introduction

Silicon has become one of the most important semiconductors, which is due to its unique electrical properties and widespread applications. The material with the size of nano-scale demonstrates remarkable physical and chemical properties. Silicon clusters, as a transition state from a Si atom to bulk silicon, have

attracted much attention both theoretically and experimentally. Specifically, pure and heteroatom-doped silicon clusters [1–11] have been extensively investigated in certain areas of chemistry and physics. The doped clusters have exhibited unique optical and electronic properties [12]. Additionally, potential applications of materials with novel properties based on metal doped silicon clusters are of significant importance to materials engineers working in the semiconductor industry [13].

Recently, the physical and chemical properties of Si clusters can be easily adjusted by changing their sizes [14], shapes [15], and impurity [16]. The doping often provides an approach in designing the novel silicon-based functional nanomaterials as follows. The transition-metal doped silicon clusters have attracted growing attention because of their enhanced stabilities as compared with the pure silicon clusters [17, 18]. Some metal-doped Si clusters, including many transition-metal doped Si clusters [19, 20], MSi<sub>n</sub> clusters (M=Sc–Zn) [21], anionic clusters MSi<sub>12</sub> (M=3d transition-metal) [22], MSi<sub>12</sub> clusters (M=Hf–Au) [23], MSi<sub>16</sub> clusters (M=Sc<sup>−</sup>, Ti, and V<sup>+</sup>) [24, 25], MSi<sub>14</sub> clusters (M=Sc–Ni) [26], YbSi<sub>n</sub> (n=7–13) clusters [15] were also disclosed in physical and chemical properties by theoretical calculations and/or experimental results. Despite the general interest in metal-doped silicon cluster, the number of studies devoted to group IB metals is surprisingly limited compared to similar systems involving metal-doped silicon clusters [27]. Some structures of metal–silicon clusters, as MSi<sub>n</sub><sup>+</sup> (M=Cu, Ag, Cr; n=7–10) [28], charged and neutral Cu@Si<sub>n</sub> clusters (n=9–14) [29], AgSi<sub>n</sub> (2<n<13) species [30, 31], Ag-doped Si<sub>n</sub> (n=1–13) clusters [3], Au-doped Si<sub>n</sub> (n=1–16) [32], have been reported. In view of the seeming lack of understanding optical and magnetic properties, it is still highly desirable to perform an extensive and perhaps conclusive study on Cu,

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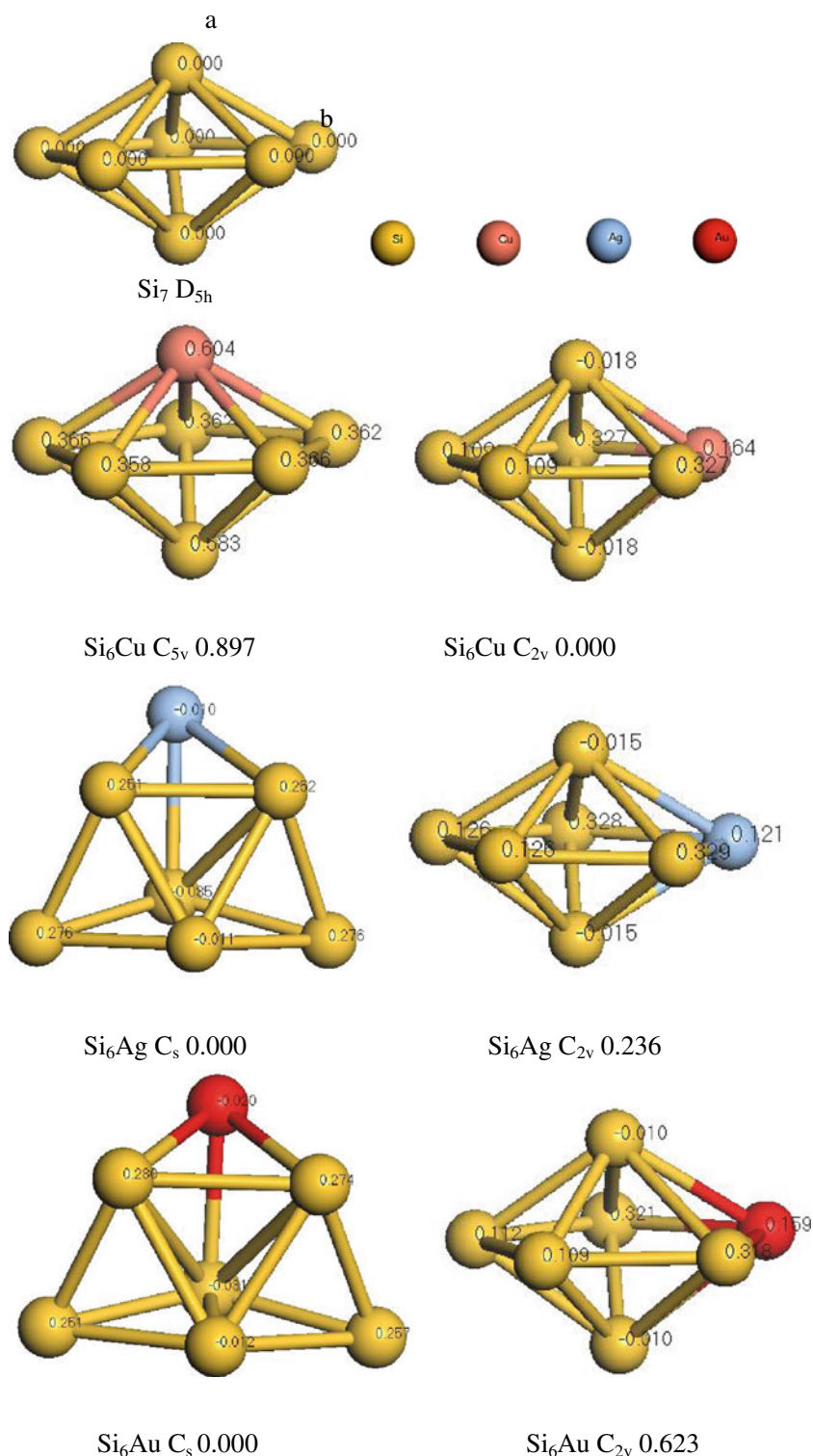
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Ag, Au-doped Si clusters due to potential applications in magneto-optics and photovoltaic cells.

The  $\text{Si}_7$  cluster with  $D_{5h}$  symmetry is a typical model [33], and P-, B-doped [34] and Cu-doped [35] Si

clusters have different optical and electric properties from  $\text{Si}_7$  cluster. In order to reveal the dopant effects on small Si cluster, we studied structural, optical and magnetic properties of M-doped Si cluster (M=Cu, Ag,

**Fig. 1** The optimized structures for Cu, Ag, Au-doped Si-clusters (Cu, Ag, Au-doped sites are atomic sites with a and b in  $D_{5h}$ - $\text{Si}_7$ ). The local atomic magnetic moment (unit in  $\mu_B$ ) is shown in corresponding atom. Below displays the corresponding point group symmetry and relative energies (unit in eV)



Au). M-doped (M=Cu, Ag, Au) in Si cluster adjusts optical and magnetic properties.

### Computational methods

First-principles density functional spin-polarized calculations using Dmol3 code [36, 37] are performed for energetic structure stabilities and optical properties of pure Si<sub>7</sub>, Cu, Ag, and Au doped Si<sub>7</sub> nanoclusters. The geometric structures of all neutral clusters modeled by global optimization using genetic algorithm are optimized by a Perdew–Burke–Enzerh (PBE) exchange-correlation functional by in density functional theory (DFT) level [38]. The Kohn–Sham equation is expanded in a double numeric quality basis set with polarization functions. The basis set cutoff was chosen to be 5 Å. The Fermi smearing of 0.001 Ha. was used in the calculations. The DFT semi-core pseudopotential [39] is used to treat the electrons of heavy Ag and Cu atoms. In order to obtain well-converged geometrical and electronic structures, the self-consistent field (SCF) convergence tolerance is tightened to 10<sup>-6</sup>, the energy, maximum force, and maximum displacement convergence criterion are set to 10<sup>-6</sup> Ha, 0.002 Ha/Å, and 0.005Å, respectively. The optical excitation spectra are calculated using time-dependent density functional theory (TD-DFT) as implemented in the Dmol3 with adiabatic local density approximation (ALDA) kernel exchange-correlation terms [40].

To study the stability of the cluster, we define average binding energy of the clusters as follows:

$$E_b = [-E_{cluster} + mE_{Si} + nE_{Cu/Ag/Au}]/7, \tag{1}$$

where  $n=0, 1; m=7-n$ .

To study the electronic properties of the cluster, adiabatic ionization potential (IP), and adiabatic electron affinity (EA) is defined as:

$$E_g = HOMO-LUMO \tag{2}$$

$$IP = -E_{cluster} + E_{cluster^+} \tag{3}$$

$$EA = -E_{cluster} + E_{cluster^-} \tag{4}$$

### Results and discussion

#### Geometric structures and energetic stability

Figure 1 shows the relative stable configurations and isomers for Cu-, Ag-, Au-doped Si<sub>7</sub> clusters. Three types of nanoclusters with C<sub>5v</sub>, C<sub>2v</sub> and C<sub>s</sub> symmetry are found by Cu-, Ag-, Au-doping in atomic sites with a and b of D<sub>5h</sub>-Si<sub>7</sub>. We determine the ground state of all the nanoclusters considered by checking their total energies with different spin multiplicity. The pure Si<sub>7</sub> cluster with D<sub>5h</sub> symmetry has a relative structural stability. The results show that the stability of the Si<sub>6</sub>Cu cluster with C<sub>5v</sub> symmetry exceeds that of the Si<sub>6</sub>Cu cluster with C<sub>2v</sub> symmetry by 0.897 eV in total energy; however, in the stability of the Si<sub>6</sub>Ag cluster with C<sub>s</sub> symmetry exceeds that of the Si<sub>6</sub>Cu cluster with C<sub>2v</sub> symmetry by 0.236 eV, and in the Si<sub>6</sub>Au cluster the stability of the C<sub>s</sub>-Si<sub>6</sub>Au cluster exceeds that of the C<sub>2v</sub>-Si<sub>6</sub>Au cluster by 0.623 eV. The cluster with C<sub>s</sub> symmetry has lower structural stability than that with C<sub>2v</sub> symmetry for Si<sub>6</sub>Ag and Si<sub>6</sub>Au as shown in Fig. 1.

To evaluate the relative energetic and electronic structure of these clusters, the binding energy (E<sub>b</sub>), vertical ionization potential (IP), electronic affinity (EA) and HOMO–LUMO gap are compared in Table 1. For all the dopant clusters investigated, the C<sub>5v</sub>-Si<sub>6</sub>Cu has a magnetic moment with 3 μ<sub>B</sub>, while the other clusters have a magnetic moment with 1

**Table 1** The geometrical symmetry, spin and the binding energy (E<sub>b</sub>), vertical ionization potential (IP), electronic affinity (EA), HOMO–LUMO gap (E<sub>g</sub>) for Si<sub>7</sub>, and different Si<sub>6</sub>Cu, Si<sub>6</sub>Ag, Si<sub>6</sub>Au clusters

Species	Symmetry	Spin	E <sub>b</sub> (eV)	HOMU (eV)	LUMO (eV)	Energy gap (E <sub>g</sub> , eV)	IP (eV)	EA (eV)
Si <sub>7</sub>	D <sub>5h</sub>	0	3.522	-5.822	-3.693	2.128	7.779	1.836
Si <sub>6</sub> Cu	C <sub>5v</sub>	3	3.135	-5.222	-4.791	0.432	5.904	3.019
Si <sub>6</sub> Cu	C <sub>2v</sub>	1	3.263	-4.937	-4.431	0.505	6.830	2.332
Si <sub>6</sub> Ag	C <sub>s</sub>	1	3.137	-4.683	-4.140	0.543	6.674	2.215
Si <sub>6</sub> Ag	C <sub>2v</sub>	1	3.105	-4.650	-4.166	0.484	6.358	2.105
Si <sub>6</sub> Au	C <sub>s</sub>	1	3.249	-4.955	-4.401	0.553	6.943	2.447
Si <sub>6</sub> Au	C <sub>2v</sub>	1	3.160	-4.834	-4.358	0.477	6.512	2.389

$m\mu_B$ . Compared with  $D_{5h}$ - $Si_7$  cluster with a magnetic moment with  $0 m\mu_B$ . The Cu, Ag, Au-doped  $Si_7$  clusters have a relatively high magnetic moment. So M-doping ( $M=Cu, Ag, Au$ ) in  $Si_7$  increases a magnetic moment.

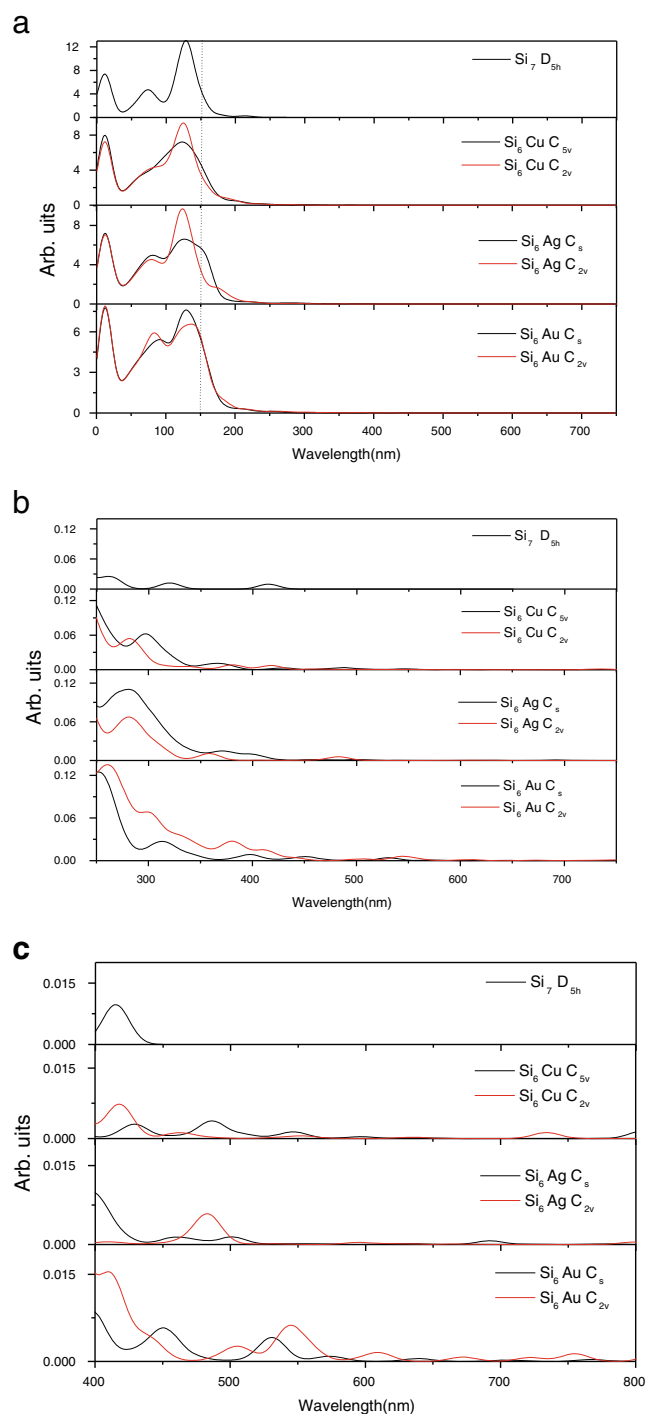
The Cu, Ag, Au-doped Si clusters have an average binding energy with the range from 3.1 eV to 3.3 eV which are obviously lower than 3.522 eV for binding energy of  $D_{5h}$ - $Si_7$  clusters. To some extent, Au (or Ag, or Cu)-doping decreases the stability of the cluster. The HOMO-LUMO gaps of metal-doped clusters are at a range from 0.43 eV to 0.56 eV, and these gaps are lower than 2.123 eV corresponding to the gap of pure  $D_{5h}$ - $Si_7$ . This indicates M-doping ( $M=Cu, Ag, Au$ ) decreases greatly the gap, which is helpful in understanding the  $E_g$  transitions of electrons. The IP (5.904–6.943 eV) of M-doped Si cluster ( $M=Cu, Ag, Au$ ) is lower than that (7.779 eV) of pure  $D_{5h}$ - $Si_7$ , while the EA (5.904–6.943 eV) of M-doped Si cluster is higher than that (7.779 eV) of pure  $D_{5h}$ - $Si_7$ . It is obvious that the M-doping ( $M=Cu, Ag, Au$ ) decreases improves electron ionization and reduce the electron capture.

### Optical spectra

In order to understanding how dopant effects the optical response, we compared the spectra of pure and M-doped Si clusters ( $M=Cu, Ag, Au$ ). The main calculated results are presented in Fig. 2, where the absorption optical spectra of pure and M-doped Si clusters ( $M=Cu, Ag, Au$ ) here considered are shown. Such a comparison is meaningful, for it considers the effect of the dopant differences for clusters. The spectrum of the M-doped Si cluster ( $M=Cu, Ag, Au$ ) shows marked differences from pure  $D_{5h}$ - $Si_7$ . In Fig. 2a, the main adsorption peak of pure Si, and Cu, Ag, Au-doped Si clusters are 12, 74 and 125 nm, respectively. (The origins of the three peaks are listed in Table S1 in supporting materials). The UV spectrum of pure  $D_{5h}$ - $Si_7$  is similar to preview reports [3, 32, 41, 42]. In the range from 200 nm to 400 nm, The Cu, Ag and Au-doped Si clusters have a stronger adsorption than pure  $Si_7$ , as shown in Fig. 2b. So an M-doping ( $M=Cu, Ag, Au$ ) enhances optical adsorption of a range from 200 nm to 400 nm. It is worthy to be mentioned the Au-doped Si cluster takes on a stronger adsorption in 400–800 nm than pure, and Cu, Ag-doped ones, as shown in Fig. 2c. This indicates M-doping ( $M=Cu, Ag, Au$ ) extends the optical adsorption, especially Au-doping. One possible reason is that the M-doping ( $M=Cu, Ag, Au$ ) decreases  $E_g$  value and improves the  $E_g$  transitions of electrons.

### Magnetic properties

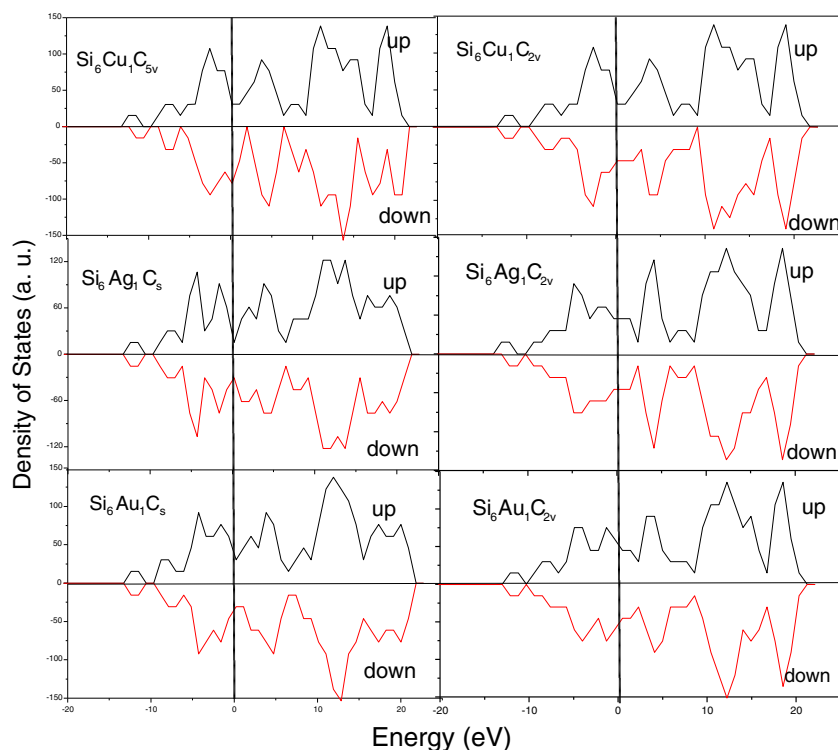
We investigated the cluster electronic properties by calculating the electronic density of states (DOSs). The spin-resolved DOS of pure  $Si_7$  and  $Si_6M$  cluster ( $M=Cu, Ag, Au$ ) are shown



**Fig. 2** The optical absorption spectra of  $Si_7$ ,  $Si_6Cu$ ,  $Si_6Ag$ ,  $Si_6Au$  clusters

in Fig. 3. A asymmetrical spin-up and spin-down can be observed for the M-doped Si clusters, indicating all  $MSi_6$  clusters are magnetic ones [43, 44]. A big asymmetrical spin-up and spin-down can be observed for  $C_{5v}$ - $Si_6Cu$  in Fermi level. So  $C_{5v}$ - $Si_6Cu$  clusters have a relatively big magnetic moment with  $3 m\mu_B$ . A little asymmetrical spin-up and spin-down can be observed for the  $C_s$ - $Si_6Ag$ ,  $C_s$ - $Si_6Au$ ,  $C_{2v}$ -

**Fig. 3** The spin-resolved electronic density of states (DOSs) of  $\text{Si}_6\text{Cu}$ ,  $\text{Si}_6\text{Ag}$ ,  $\text{Si}_6\text{Au}$  clusters. The dashed vertical line represents the Fermi level



$\text{Si}_6\text{Cu}$ ,  $\text{C}_{2v}\text{-Si}_6\text{Au}$ , which indicating all four clusters are weak magnetic ones. Figure 1 exhibits the local atomic magnetic moment of the pure  $\text{Si}_7$ , and  $\text{Si}_6\text{M}$  cluster ( $\text{M}=\text{Cu}$ ,  $\text{Ag}$ ,  $\text{Au}$ ), too. We can see that the average atomic moment is  $0.428 \text{ m}\mu_{\text{B}}$  per atom for the  $\text{Si}_6\text{Cu}$  cluster with  $\text{C}_{5v}$  symmetry while the average paramagnetic moment is  $0.143 \text{ m}\mu_{\text{B}}$  per atom for other dopant clusters in Fig. 1.

## Conclusions

The structural, electronic and optical properties of  $\text{Cu}$ ,  $\text{Ag}$ ,  $\text{Au}$ -doped  $\text{Si}$  nanoclusters have been investigated using DFT. The  $\text{Si}_6\text{M}$  clusters ( $\text{M}=\text{Cu}$ ,  $\text{Ag}$ ,  $\text{Au}$ ) have a greater change of the structure due to their lower binding energy. The global optimized structures of  $\text{Cu}$ ,  $\text{Ag}$ ,  $\text{Au}$ -doped  $\text{Si}$  clusters are predicted to have a lower HOMO–LUMO gap and a higher magnetic moment. Compared with the pure  $\text{Si}_7$ ,  $\text{Si}_6\text{M}$  ( $\text{M}=\text{Cu}$ ,  $\text{Ag}$ ,  $\text{Au}$ ) clusters have a relatively wide range of adsorption wavelength, especially  $\text{Au}$ -doped  $\text{Si}$  cluster. That is to say, the  $\text{Si}_6\text{M}$  ( $\text{M}=\text{Cu}$ ,  $\text{Ag}$ ,  $\text{Au}$ ) cluster has obviously an optical absorbance at lower energy state than the pure  $\text{Si}_7$ .

From the analyses of the DOS for  $\text{Cu}$ ,  $\text{Ag}$ ,  $\text{Au}$ -doped  $\text{Si}$  cluster, we found that the  $\text{C}_{5v}\text{-Si}_6\text{Cu}$  has the highest magnetic moment. The average atomic moment is  $0.428 \text{ m}\mu_{\text{B}}$  per atom for the  $\text{C}_{5v}\text{-Si}_6\text{Cu}$  cluster while the average paramagnetic moment is  $0.143 \text{ m}\mu_{\text{B}}$  per atom for other  $\text{Cu}$ ,  $\text{Ag}$ ,  $\text{Au}$ -doped  $\text{Si}$  cluster. In all cases studied, the  $\text{Si}_6\text{M}$  ( $\text{M}=\text{Cu}$ ,  $\text{Ag}$ ,  $\text{Au}$ )

clusters have attractive properties of structure and electronic and optical spectra, which indicate their potential application in magneto-optics and photovoltaic cells.

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## References

1. Nigam S, Majumder C, Kulshreshtha SK (2006) *J Chem Phys* 125:074303
2. Majumder C, Kulshreshtha SK (2004) *Phys Rev B* 69:115432
3. Chuang FC, Hsieh YY, Hsu CC, Albao MA (2007) *J Chem Phys* 127:144313
4. Ma L, Zhao JJ, Wang JG, Wang BL, Lu QL, Wang GH (2006) *Phys Rev B* 73:125439
5. Wang JG, Zhao JJ, Ma L, Wang BL, Wang GH (2007) *Phys Lett A* 367:335
6. Han JG, Hagelberg F (2001) *Chem Phys* 263:255
7. Koyasu K, Akutsu M, Mitsui M, Nakajima A (2005) *J Am Chem Soc* 127:4998
8. Ho KM, Shvartsburg AA, Pan B, Lu ZY, Wang CZ, Wacker JG, Fye JL, Brown WL (1998) *Nature* 392:582
9. Shvartsburg AA, Liu B, Lu ZY, Wang CZ, Jarrold MF, Ho KM (1999) *Phys Rev Lett* 83:2167
10. Zdetsis AD (2007) *J Chem Phys* 127:014314
11. Lan YZ (2012) *Chem Phys Lett* 545:95
12. Alivisatos AP (1996) *Science* 271:933

13. Don Dasitha Gunaratne K, Berkdemir C, Harmon CL, Castleman AW (2013) *Phys Chem Chem Phys* 15:6068
14. Lin CS, Cheng WD, Wang JY, Zhang RQ (2011) *Chem Phys Lett* 509:124
15. Zhao RN, Han JG, Bai JT, Liu FY, Sheng LS (2010) *Chem Phys* 372:89
16. Koyasu K, Atobe J, Akutsu M, Mitsui M, Nakajima A (2007) *J Chem Phys A* 111:42
17. Kumar V, Briere TM, Kawazoe Y (2003) *Phys Rev B* 68:55412
18. Khanna SN, Rao BK, Jena P (2002) *Phys Rev Lett* 89:016803
19. Beck SM (1987) *J Chem Phys* 87:4233
20. Ohara M, Koyasu K, Nakajima A, Kaya K (2003) *Chem Phys Lett* 371:490
21. Guo LJ, Zhao GF, Gu YZ, Liu X, Zeng Z (2008) *Phys Rev B* 77:195417
22. Reveles JU, Khanna SN (2005) *Phys Rev B* 72:165413
23. Uchida N, Miyazaki T, Kanayama T (2006) *Phys Rev B* 74:205427
24. Torres MB, Fernández EM, Balbás LC (2007) *Phys Rev B* 75:205425
25. Koyasu K, Atobe J, Furuse S, Nakajima A (2009) *J Chem Phys* 129:214301
26. He JG, Wu KH, Liu CP, Sa RJ (2009) *Chem Phys Lett* 483:30
27. Hiura H, Miyazaki T, Kanayama T (2001) *Phys Rev Lett* 86:1733
28. Jaeger JB, Jaeger TD, Duncan MA (2006) *J Phys Chem A* 110:9310
29. Lan YZ, Feng YL (2009) *Phys Rev A* 79:033201
30. Zhang PF, Han JG, Pu QR (2003) *Theochem* 634:25
31. Gueorguiev GK, Pacheco JM, Stafstrom S, Hultman L (2006) *Thin Solid Films* 515:1192
32. Wang J, Liu Y, Li YC (2010) *Phys Lett A* 374:2736
33. Fischer SA, Madrid AB, Isborn CM, Prezhdo OV (2010) *J Phys Chem Lett* 1:232
34. Fischer SA, Prezhdo OV (2011) *J Phys Chem C* 115:10006
35. Xu HG, Wu MM, Zhang ZG, Yuan JY, Sun Q (2012) *J Chem Phys* 136:104308
36. Delley B (1990) *J Chem Phys* 92:508
37. Delley B (2000) *J Chem Phys* 113:7756
38. Perdew JP, Burke K, Ernzerhof M (1996) *Phys Rev Lett* 77:3865
39. Delley B (2002) *Phys Rev B* 66:155125
40. Gross EKV, Kohn W (1990) *Adv Quantum Chem* 21:255
41. Isborn CM, Prezhdo OV (2009) *J Phys Chem C* 113:12617
42. Isborn CM, Kilina SV, Li X, Prezhdo OV (2008) *J Phys Chem C* 112:18291
43. Pereiro M, Baldomir D, Arias JE (2007) *Phys Rev A* 75:063204
44. Luo WD, Pennycook SJ, Pantelides ST (2007) *Nano Lett* 7:3134