Structures and magnetic properties of $Fe_{6-x}Si_x$ clusters

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Article Information	Abstract

The structures and magnetic properties of $Fe_{6-x}Si_x$(x=0-5) clusters have been systematically studied at the BPW91 level in density-functional theory (DFT). Calculated results show that the Fe atoms of the lowest-energy structures of $Fe_{6-x}Si_x$ clusters tend to go together, and Si atoms tend to occupy surface site bonding with iron atoms as many as possible. The total magnetic moments of $Fe_{6-x}Si_x$ clusters decrease monotonously with increasing Si atom. The natural population and natural electron configuration reveal that the decrease of the total magnetic moment is directly relevant to the hybridization between Si-3p and Fe-4s.

1. Introduction

The study of atomic clusters started from the past century. As a new field, it has attracted considerable interest. In the past several decades, theoretical and experimental physicists devoted themselves to the physical and chemical properties of the clusters, such as geometric and electronic structures, ionization potentials, electron affinities, chemisorptions, photoelectron spectroscopy and so on[1-6]. Magnetism, as one of the most important properties of matter, has been bringing scientists' attention all the time. Recently, many scientists focus attention on the magnetism of the atomic clusters rather than the bulks.

Transition-metal (TM) clusters are a subject of particular interest due to the strong environment dependence of their magnetic properties and their possible applications in magnetic recording and storage technology. However, physical and chemical properties of TM clusters show remarkable size-dependent variations that cannot be explained by the shell model of s valence electrons due to the existence of d electrons with complicated electronic ground-state structures and different spin multiplicities, which presents a tremendous challenge to both experimental and theoretical investigations on transition-metal clusters [7]. Recently, with the

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appearance of the DFT theory, which has the ability to directly explore and assign cluster geometries and discriminate between possible isomers, some meaningful improvements have been achieved. DFT theoretical studies have shown that the magnetic moments of Fe_n, Co_n and Ni_n clusters are significantly larger than the corresponding bulk magnetizations[8-12]. Moreover, non- vanishing magnetic moments have been recently observed in clusters of some 4d TMs like $Rh_n(n \leq 50)$ which are non-magnetic in the bulk[13-15].

Recently, the interest in studying mixed clusters including transition-metal atoms has grown rapidly, especially involving 3d TMs. For instance, theoretical studies of $(Cr_xFe_{1-x})_n$ have revealed interesting transitions from ferromagnetic to antiferromagnetic-like order as a function of increasing Cr concentration x, which are accompanied by important changes in the average magnetic moments per atom[16]. In Ref[17], a density functional method BPBE is selected to study $Ni_xTi_y(x+y \leq 5)$ clusters, and the theoretical results obtained show that the geometry and shape depend on the Titanium composition. For Al-doped Fe_n clusters, we have studied the magnetic behavior of $Fe_{n-1}Al$ and $Fe_{6-x}Al_x$ clusters using the DFT method, and found the Al impurity decreases the total magnetic moments of iron clusters, moreover, as the number of Al atom increases, the total magnetic moments gradually decrease [18-19].

Although these mixed clusters have become a matter of increasing interest in cluster research, the study on Si-doped iron clusters, to the best of our knowledge, has not been found in the literature to data. Motivated by the above and the potential technological application of Fe-Si alloy, in this article, we choose Si atoms as impurity and study the geometric structures and

electronic properties of Fe-Si bimetallic clusters.

2. Computational method

All geometry optimizations without symmetry constrains are performed by the BWP91 method in Gaussian 98 program package[20]. In the optimization process, all possible configurations and spin multi-plicities are considered and searched unbia-sedly. Moreover, the optimized structures are further verified by frequency calculations (no negative frequency).

In terms of basis sets, the Lanl2dz basis sets[21] and the 6-31G(d) basis sets[22] are selected to describe Fe atoms and Si atom, respectively. Those basis sets combined with the BPW91 method result in bond lengths of 2.01 Å and 2.30 Å for Fe_2 and Si_2 which are in agreement with the corresponding experimental values of 2.02 Å[23] and 2.25 Å[24]. Good agreement between theoretical and experimental values indicates that the present computational method and basis sets are feasible.

3. Results and discussion

3.1 Geometric structure

The ground-state geometric structures of the $Fe_{6-x}Si_x$ clusters are determined by full geometric optimization. For each different composition, a number of stable structures are obtained. The structures corresponding to the lowest total energy is presented in Fig.1 according to the energy order. For Fe_6, the lowest-energy structure obtained is the rectangular bipyramid. The ground-state structure for Fe_5Si is the same rectangular bipyramid as that of Fe_6 cluster. Other three stable configurations (2b, 2c and 2d) that the cap atom or the side atom of the capped trigonal bipyramid is replaced by a Si atom are represented in Figure 1. The 2b structure

is 0.17 eV and 0.29 eV more stable than 2c and 2d, respectively, while the structure 2d with four Fe-Si bonds is energetically less
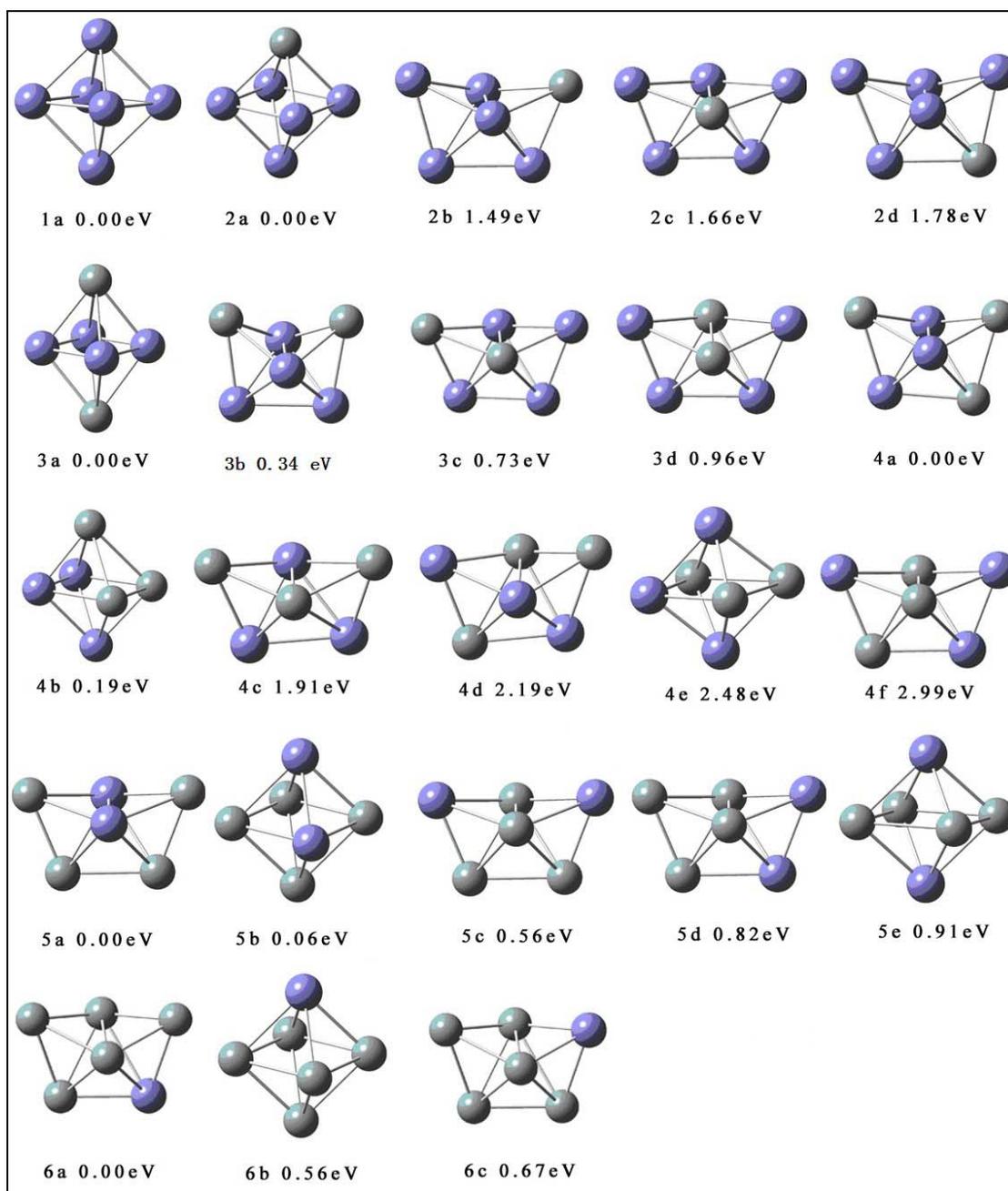

Figure 1. Low-energy isomers for $Fe_{6-x}Si_x$ clusters at the BPW91 level. The blue and gray balls represent iron atoms and silion atoms, respectively. The number under the structure is relative energies (in eV) with respect to that of the corresponding lowest-energy isomers.

favorable than 2c with five Fe-Si bonds. For Fe_4Si_2, the lowest-energy structure is still a rectangular bipyramid, which is segregated by two Si atoms completely. Structure 3b, 3c and 3d are three different capped trigonal bipyramids replaced by two Si atoms, of which the energy of 3b structure with two Si atoms capped a tetrahedral configuration is lowest, while the energy of 3d structure with two Si atoms located on the triangle is highest. It becomes evident that the Si atoms prefer to occupy the surface position, while

the Fe atoms tend to be gathered together. For Fe_3Si_3, the ground state is a capped trigonal bipyramid that three Si atoms are located around three iron atoms. While the 4c

Table 1 Natural population and natural electron configurations of the $Fe_{6-x}Si_x$ clusters found most stable at the BPW91 level.

Cluster	Total magnetic moment/μ_b	Atom number	NP	NEC
Fe_6	20	Fe(1)	-0.00085	$4s^{1.03}3d^{6.89}4p^{0.06}5s^{0.01}4d^{0.01}$
		Fe(2)	0.00017	$4s^{1.03}3d^{6.89}4p^{0.06}5s^{0.01}4d^{0.01}$
		Fe(3)	-0.00138	$4s^{1.03}3d^{6.89}4p^{0.06}5s^{0.01}4d^{0.01}$
		Fe(4)	-0.00051	$4s^{1.03}3d^{6.89}4p^{0.06}5s^{0.01}4d^{0.01}$
		Fe(5)	0.00068	$4s^{1.03}3d^{6.89}4p^{0.06}5s^{0.01}4d^{0.01}$
		Fe(6)	0.00188	$4s^{1.03}3d^{6.89}4p^{0.06}5s^{0.01}4d^{0.01}$
Fe_5Si	14	Fe(1)	0.11196	$4S^{0.84}3d^{6.98}4p^{0.06}5S^{0.01}4d^{0.01}$
		Fe(2)	0.09636	$4S^{0.87}3d^{6.97}4p^{0.04}5S^{0.01}4d^{0.01}$
		Fe(3)	0.06775	$4S^{0.78}3d^{7.09}4p^{0.05}5S^{0.01}4d^{0.01}$
		Fe(4)	0.06739	$4S^{0.78}3d^{7.09}4p^{0.05}5S^{0.01}4d^{0.01}$
		Fe(5)	0.09725	$4S^{0.87}3d^{6.97}4p^{0.04}5S^{0.01}4d^{0.01}$
		Si(6)	-0.44070	$3S^{1.83}3p^{2.59}3d^{0.01}4p^{0.01}$
Fe_4Si_2	10	Fe(1)	0.16399	$4S^{0.73}3d^{7.05}4p^{0.05}4d^{0.01}$
		Fe(2)	0.16611	$4S^{0.73}3d^{7.05}4p^{0.05}4d^{0.01}$
		Fe(3)	0.07628	$4S^{0.70}3d^{7.17}4p^{0.04}4d^{0.01}$
		Fe(4)	0.07577	$4S^{0.69}3d^{7.17}4p^{0.04}4d^{0.01}$
		Si(5)	-0.24104	$3S^{1.83}3p^{2.39}3d^{0.01}$
		Si(6)	-0.24111	$3S^{1.83}3p^{2.39}3d^{0.01}$
Fe_3Si_3	8	Si(1)	-0.23141	$3S^{1.87}3p^{2.36}$
		Fe(2)	0.27292	$4S^{0.57}3d^{7.10}4p^{0.04}4d^{0.02}$
		Fe(3)	0.19175	$4S^{0.71}3d^{7.04}4p^{0.04}5s^{0.01}4d^{0.01}$
		Fe(4)	0.27189	$4S^{0.57}3d^{7.10}4p^{0.04}4d^{0.02}$
		Si(5)	-0.32355	$3S^{1.76}3p^{2.56}4p^{0.01}$
		Si(6)	-0.18161	$3S^{1.80}3p^{2.38}4p^{0.01}$
Fe_2Si_4	6	Si(1)	-0.09939	$3S^{1.72}3p^{2.36}3d^{0.02}4p^{0.01}$
		Fe(2)	0.16830	$4S^{0.57}3d^{7.21}4p^{0.04}4d^{0.01}$
		Fe(3)	0.17406	$4S^{0.48}3d^{7.28}4p^{0.06}4d^{0.02}$
		Si(4)	-0.09012	$3S^{1.56}3p^{2.49}3d^{0.02}4p^{0.02}$
		Si(5)	-0.04771	$3S^{1.73}3p^{2.29}3d^{0.02}4p^{0.01}$
		Si(6)	-0.10515	$3S^{1.74}3p^{2.34}3d^{0.01}$
$FeSi_5$	4	Si(1)	-0.03017	$3S^{1.66}3p^{2.36}4p^{0.01}$
		Si(2)	-0.03242	$3S^{1.66}3p^{2.36}4p^{0.01}$
		Fe(3)	0.18478	$4S^{0.47}3d^{7.29}4p^{0.05}4d^{0.02}$
		Si(4)	-0.05957	$3S^{1.69}3p^{2.35}4p^{0.02}$
		Si(5)	-0.03228	$3S^{1.66}3p^{2.36}4p^{0.01}$
		Si(6)	-0.03034	$3S^{1.66}3p^{2.36}4p^{0.01}$

structure with one Si atom occupying the core site is 1.91 eV less stable than the ground state. The similar phenomenon also occurs for Fe_2Si_4 cluster. For $FeSi_5$ cluster,

the 6a structure with 4 Fe-Si bonds is 0.67 eV energetically lowers than structure 6c with Fe atoms tend to be gathered together, and Si atoms prefer to occupy the surface position and to be located around a Fe core with a

3.2 Magnetic and electronic properties

Based on the lowest-energy structures, the total magnetic moments of $Fe_{6-x}Si_x$ clusters are computed, which are given in Table 1. It is seen that the total magnetic moments of $Fe_{6-x}Si_x$ clusters decrease monotonously as a function of Si atom.

To further understand the interaction between Fe and Si, natural population (NP) and natural electron configurations (NEC) are performed and the corresponding results are summarized in Table 1. It can be clearly seen that the charges on Fe atoms are always positive, and the charges on Si atoms are always negative, which implies the electrons transfer from Fe to Si.

Nextly, let us to analyze the natural electron configurations of $Fe_{6-x}Si_x$ clusters. The electronic configuration of the Fe atom and Si atom is $3d^64s^2$ and $3s^23p^2$, respectively. It can be seen from Table 1 that the electrons occupying the 3d orbital of Fe increase as the number of Si atom increases, conversely, the electrons occupying the 4s orbital of Fe decrease as the number of Si atom increases. It implies that there are some 4s electrons are transferred to the 3d orbital. However, the natural electron configurations also reveal that the 3d electrons increase from 6.89 to 7.29 with the increasing of Si atom, while corresponding 4s electrons change from 1.03 to 0.47. Clearly, the 3d electrons captured are much less than the 4s electrons lost.

In addition, Table 1 also shows that the electrons of 3p orbital of Si captured are more than that of 3s orbital lost, which indicates some 4s electrons are transferred to 3p orbital of Si atom. Obviously, the hybridization between Fe-4s and Si-3p brings

three Fe-Si bonds.

To summarize, it can be concluded that the maximum of Fe-Si bonds for all $Fe_{6-x}Si_x$ (x=0-5) clusters.

out. In a word, the hybridization between Fe-4s and Si-3p decreases the total magnetic moments of $Fe_{6-x}Si_x$ clusters. It should also be noted that an increase of Fe-Si coordination means the decreasing of the magnetic moments, thus the total magnetic moments of $Fe_{6-x}Si_x$ clusters will certainly decrease monotonously with increasing Si atom.

4. Conclusion

To summary, the structures and magnetic properties of $Fe_{6-x}Si_x$ clusters have been studied by the density functional method. The calculated results suggest the following conclusion.

(1) For $Fe_{6-x}Si_x$ clusters, the Fe atoms tend to be gathered, and the silicon atoms are located around a Fe core with a maximum of Fe-Si bonds.
(2) The total magnetic moments of $Fe_{6-x}Si_x$ clusters decrease monotonously as the number of Si atom increases.
(3) The natural population and natural electronic configuration show that there are some 4s electrons of Fe atoms are transferred to the 3p orbital of Si atoms, and the hybridization between Fe-4s and Si-3p results in the decrease of the total magnetic moments.

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