

Journal of Molecular Structure: THEOCHEM 718 (2005) 165-173

www.elsevier.com/locate/theochem

THEO

# A computational investigation of the Ni-doped $Si_n(n=1-8)$ clusters by a density functional method

Zhao-Yu Ren<sup>a</sup>, Feng Li<sup>a,b</sup>, Ping Guo<sup>a</sup>, Ju-Guang Han<sup>a,c,\*</sup>

<sup>a</sup>Institute of Photonics and Photon-Technology, Northwestern University, Xi'an 710069, People's Republic of China

<sup>b</sup>Shang Luo Teachers' College, Shang Luo, ShaanXi 726000, People's Republic of China

<sup>c</sup>National Synchrotron Radiation Laboratory, University of Science and Technology of China, Jin Zhai Rd 96, Hefei 230026, People's Republic of China

Received 23 November 2004; revised 4 January 2005; accepted 4 January 2005

#### Abstract

The NiSi<sub>n</sub> (n=1-8) clusters are investigated computationally using a Density Functional approach. Geometry optimizations of the NiSi<sub>n</sub> (n=1-8) units are carried out under the constraint of well-defined symmetries at the B3LYP level employing a pseudopotential method in conjunction with Los Alamos double zeta basis sets. Consequently, the resulting total energies, natural populations, fragmentation energies, and equilibrium geometries of the NiSi<sub>n</sub> (n=1-8) clusters are presented and discussed. Theoretical results show that the Ni atom in the small NiSi<sub>n</sub> clusters absorbs on the surface site, and that the Ni atom in the NiSi<sub>8</sub> cluster prefers being encapsulated into the Si frame. The most stable NiSi<sub>n</sub> (n=1, 2) and NiSi<sub>n</sub> (n=3-8) clusters correspond to the triplet and singlet spin configurations, respectively. The natural population of the Ni atom in the most stable NiSi<sub>n</sub> (n=1-8) clusters varies from positive to negative. The relative stabilities are discussed; the calculated results reveal that the NiSi<sub>8</sub> cluster is the most stable structure.

© 2005 Elsevier B.V. All rights reserved.

Keywords: NiSin clusters; Geometry and stability; Charge-transfer; Density functional method calculation

# 1. Introduction

The technically important transition metal silicon clusters have attracted attention [1-15], both theoretically and experimentally. In particular, the clusters of the group-14 elements in the Periodic Table with interesting electronic properties and important practical applications have been the topics of many studies in recent years [1-6], because this information is very important for the fine processing of semiconductor material, for generating new materials with unusual and novel properties, for investigating the possible rule in surface growth processors and for the interesting comparison with the bulk solids.

The experimental investigations of the small mixed transition metal-silicon clusters ( $MSi_n$ ; M=Cr, Mo, W;

 $n \leq 18$ ) have been produced by mass spectrometry [9] and mixed transitional metal silicides have been generated by time-of-flight mass spectroscopy [16]. The electronic states of the CuSi and AuSi dimers [17] have been predicted by measuring their laser absorption spectra. In addition, the VSi and NbSi dimers have been investigated by matrixisolated ESP spectroscopy while bond energies are detected experimentally [18–20]. In the case of silver silicides, the previous gas phase work consists of measurement of the dissociation energy of the AgSi diatom deduced in the mass spectrometric studies of Rieker et al. [21] and computational investigations of the AgSi<sub>n</sub> (n=1-5) clusters by a density functional method [22]. Under the motivations of experimental results, the charge-transfer mechanisms and the equilibrium geometries of  $MSi_n$  (M=Ir, Ta, Ru, Cr, Mo, and W),  $\text{ReSi}_{x}$  (x=1-12, 16, 20, 24, 28, 32, 36), and  $\text{CuSi}_{n}$ clusters are investigated theoretically [6,11–15,23–28].

The Ni-semiconductor interfaces and, in particular, Ni silicides grown on Si surface have attracted research attentions due to their technological importance in the Si semiconductor fabrication. Transition metal silicides

<sup>\*</sup> Corresponding author. Address: National Synchrotron Radiation Laboratory, University of Science and Technology of China, Jin Zhai Rd 96, Hefei 230026, People's Republic of China. Tel.: +86 1601979 3714; fax: +86 551 5141078.

E-mail address: jghan@ustc.edu.cn (J.-G. Han).

(in particular NiSi<sub>2</sub>) constitute prototype systems in surface science studies for understanding the effects of the transition metal atoms in surface reconstruction. However, despite intensive research investigations experimentally, the growth mechanism of transition metal silicides on Si surface has not yet been completely understood. Theoretical works of the Ni-silicide interfaces are usually based upon band structure calculations applied on various slab geometries or structures [29–31]. Some cluster calculations have also been performed and reported for modeling the NiSi<sub>2</sub>/Si(111) interfaces [30]. All these theoretical calculations have been undertaken using either the density functional theory (DFT) within local density approximation (LDA) or the tight-binding (TB) scheme. Also, to our best of knowledge, ab initio calculations at the configuration interaction (CI) level have not been reported for Ni-Si systems besides of the small NiSi and NiSi<sub>2</sub> clusters [5,28]. This is mainly due to the computational difficulties associated with the Ni species even in its free atom state. In particular, the Ni atom exhibits sensitivity to the electron correlation effects (due to its open d-shells) and the results depend strongly on the CI-level used [32,33].

Although some studies of the structures and electronic properties on the series of the  $MSi_n$  (M = Cr, Mo, W, Ag, Ir, Re; n = 1 - 6) clusters and the NiSi<sub>n</sub> (n = 1 - 2) clusters have been carried out theoretically [28]. Surely, there are no systematic investigations of the NiSi<sub>n</sub> (n=1-8) within DFT approach considering exchange-correlation functionals. The main objective of these studies, therefore, is to provide theoretical understanding and interpreting of the geometries, relative stabilities and charge-transfer mechanisms of the Ni silicides. In order to compare with available theoretical and experimental results and to give a reasonable interpretation of the experimental phenomenon of  $NiSi_n$ (n=1-8) clusters, computational investigations of total energies and equilibrium geometries as well as chargetransfer mechanisms, along with natural charges and natural electron populations, are performed by the density functional method in this paper.

#### 2. Computational details

The explicit treatment of all the electrons in a cluster having a large number of atoms constitutes a demanding computational task. One of the best ways to overcome this difficulty is to employ electron core potentials (ECP), also known as pseudopotentials, by means of which only the valence electrons are explicitly treated. ECP calculations can actually provide accurate results for both homo- and heteronuclear clusters having transition metal, nitrogen, germanium or silicon atoms and their various combinations as firmly proven by the previous investigations [10–15, 22–28]. However, the DFT method overestimates the energies [34], and it gives shorter bond lengths than the experimental results. In general, the optimized structures predicted at the UB3LYP level are in good agreement with experimental values. LanL2DZ basis sets are become widely used in quantum chemistry, particularly in the investigation on compounds containing heavy elements (atoms) [10–15, 22-28]. The LanL2DZ basis sets have been employed to calculate the equilibrium geometries and spectroscopic properties of small molecules or clusters containing the transition metals. Therefore, the combination of density functional theory (DFT) methods with ECP's provides a feasible and accurate approach to the electronic structure study of the NiSi<sub>n</sub> (n=1-8) clusters. Hagelberg et al. [24] compared DFT-B3LYP/LanL2DZ calculated geometries of several  $Si_n$  cages with well-established structures of those compounds and found a typical average deviation of 1-4% in bond lengths and angles. Furthermore, DFT-B3LYP/ LanL2DZ ionization potentials of those Si<sub>n</sub> cages agree satisfactorily with the DFT-B3LYP/6-311 + G(d) results.

All computations are carried out with the GAUSSIAN 98 [35] program package. Geometries are optimized at the B3LYP level employing LanL2DZ (Stuttgart/Dresden effective core potential) basis sets with the scalar relativistic effect being considered. A systematic investigation of the NiSi<sub>n</sub> (n=1-8) clusters at the B3LYP level employing LanL2DZ basis sets will provide a general conclusion. For each stationary point of cluster, the stability is examined by the harmonic vibrational frequency calculation. In case of an imaginary is found, a relaxation along the coordination of the imaginary vibrational mode is carried out until the true minimum is reached. Therefore, equilibrium geometry and total energy for each cluster and its isomers are surely the stable structures, and correspond to the local minimum. In our calculation for the NiSi<sub>n</sub> (n=1-8) clusters, as a test, the Ni<sub>2</sub> and Si<sub>2</sub> molecules are analyzed at the B3LYP level employing LanL2DZ basis sets. Our calculated Ni-Ni and Si-Si bond lengths of the Ni2 and Si2 clusters are 2.369 and 2.352 Å, respectively; which are in good agreement with previous theoretical results at B3LYP/6-311G\* (2.239 and 2.286 Å) and CCSD(T)/6-311G\* (2.249 and 2.271 Å) [28] levels as well as experimental results(2.20 and 2.246 Å) [36,37]. On grounds of these findings, the B3LYP/LanL2DZ method is believed to yield an adequate description of the bonding properties of the Ni atom in the small Si units.

# 3. Results and discussions

Computational results of bond lengths (Ni–Si and Si–Si), bond angles, together with total energies, are listed in Table 1. Natural populations and natural electron populations of the Ni atom in the most stable NiSi<sub>n</sub> (n=1-8)clusters are listed in Table 2. The stable NiSi<sub>n</sub> (n=1-8)structures are displayed in Figs. 1 and 2, respectively.

# 3.1. Geometry and stability

In an effort to understand the electronic structures of the NiSi<sub>n</sub> (n=1-8) clusters, geometries, natural populations,

167

Table 1				
The bond lengths and bone	d angles as well a	s total energies of	f the NiSi <sub>n</sub> $(n =$	(1-8) clusters

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	electron state	Eb	а	<i>R</i> 3	R2	<i>R</i> / <i>R</i> 1	Multiplicity	Symmetry	Sys
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\int 1\Sigma$	-173.0838296				2.064	0	$C_{\infty}$ v	NiSi
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\delta = \frac{3\Sigma}{2}$	-173.0900496				2.268	1		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	1	-173.0664977				2.245	2		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	!	-172.9557437				2.461	3		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$^{1}A_{1}$	-176.9466801	60.2		2.219	2.213	0	$C_2$ v	NiSi <sub>2</sub>
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$3^{3}B_{1}$	-176.9807256	58.8		2.240	2.284	1	- 2	2
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$^{5}A_{2}$	-176.9259802	63.4		2.498	2.377	2		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$^{1}\Sigma$	-176.9177674			2.243	2.100	0	$C_{\infty}$ v	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$^{3}\Sigma$	-176.9464669			2.226	2.120	1		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	<sup>5</sup> Σ	-176.8965123			2.328	2.396	2		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	) <sup>1</sup> A'	-176.9156649			2.253	2.104	0	Cs	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	<sup>3</sup> A'	-176.9550896			2.183	2.227	1		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	<sup>5</sup> A″	-176.9228739			2.401	2.278	2		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$^{1}\Sigma g$	-176.7981117				2.081	0	$D_{\infty}h$	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	ι <sup>1</sup> Α,	- 180 8532464	113.1	2 255	2 255	2 240	0	Cav	NiSia
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$^{3}B_{1}$	-180.8422523	98.1	2.235	2.233	2.240	1	C2V	11013
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	DI	-180.6708031	20.1		2.510	2.077	0	D₂h	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$^{1}A_{1}$	-180.7680979		2.548	2.548	2.330	0	Cav	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$^{3}A''$	-180.8306917		2.521	2.521	2.327	1	Cs	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	5 <sup>5</sup> A″	-180.7568848		2.403	2.403	2.819	2		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.	101 5000 500					-		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$A_1$	- 184.7203538		2.445	2.410	2.399	0	$C_2$ v	N1S14
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$A_2$	- 184.668/238		2.409	2.427	2.595	2	<b>T</b> 1	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.	- 184.66/446	100 5		2 100	2.101	0	Td C	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	A 3 D	- 184.00/410	109.5		2.100	2.100	0	$\mathcal{C}_2$	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	В 7 <sup>5</sup> л	- 184.04/984/	130.2		2.455	2.182	1		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	A ()	- 184.0042387	91.5		2.215	2.320	2	$C v(\mathbf{h})$	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1 <sup>3</sup> A /	-184.0074139 -184.7100734		2 368	2 362	2.100/2.101	1	$C_2 v(0)$	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1 A	-184.718269		2.308	2.302	2.234	0	$C_2 v(c)$	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$3\Lambda^{\prime}$	-184.6982709		2.270	2.278	2.220	1	C3	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	A	-184.6745571		2.300	2.308	2.304	2		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	) <sup>1</sup> A'	- 188 5969749		2,375	2.286	2.278	0	Cs	NiSi₅
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$8 \frac{3}{\Delta}$	- 188 58706318		2.373	2.200	2.270	1	05	1 (1015
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5 <sup>5</sup> Δ'	- 188 5516675		2 493	2 451	2.443	2		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	}	-188.5969743		2.427	2.427	2.278	0	C.	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	3	-188.5797488		2.423	2.432	2.218	1	01	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	7	-188.5524857		2.449	2.473	2.340	2		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	-188.5624583			2.360	2.107/2.315	0	$C_1(\mathbf{b})$	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	<sup>3</sup> B	-188.5615257			2.370	2.423/2.481	1	$C_2(\mathbf{b})$	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	<u>}*</u>	-188.5368648*			2.291	2.350/2.893	2	- 2(-)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$i$ $^{1}A_{1}$	-188.5864996			2.650	2.351/2.349	0	$C_2$ v	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	${}^{3}B_{2}$	-188.569550			2.547	2.592/2.246	1		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	/ <sup>1</sup> A/	-192.4704317		2.395	2.386	2.360	0	Cs	NiSic
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	)	-192.4704799		2.475	2.387	2.360	0	$C_1$	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1	-192.4485377		2.470	2.468	2.364	1	-1	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	L	-192.4113401		2.402	2.464	2.382	2		
1         2.350/2.368         2.360         2.360         - 192.4706826           2         2.400/2.400         2.284         2.602         - 192.4229091           Cs(c)         0         2.295/2.070         2.582         2.582         - 192.4414683	)	-192.4659699		2.377	2.436	2.713/2.360	0	$C_{s(b)}$	
2 2.400/2.400 2.284 2.602 -192.4229091 Cs(c) 0 2.295/2.070 2.582 2.582 -192.4414683	Ĵ	-192.4706826		2.360	2.360	2.350/2.368	1		
$C_{S}(c) = 0$ 2.295/2.070 2.582 2.582 $-192.4414683$	l	-192.4229091		2.602	2.284	2.400/2.400	2		
	• <sup>1</sup> A′	-192.4414683		2.582	2.582	2.295/2.070	0	Cs(c)	
$C_2$ 0 2.424/2.328 2.450 -192.454392	${}^{1}A_{1}$	-192.454392			2.450	2.424/2.328	0	$C_2$	
1 2.395/2.192 2.451 -192.4401081	<sup>3</sup> B	-192.4401081			2.451	2.395/2.192	1		
2 2.530/2.233 2.441 -192.4050548	<sup>5</sup> B	-192.4050548			2.441	2.530/2.233	2		
$C_1(b)$ 0 2.461/2.457 2.424 2.851 -192.4552931	L	-192.4552931		2.851	2.424	2.461/2.457	0	<i>C</i> <sub>1</sub> (b)	
1 2.342/2.327 2.443 2.785 -192.4426471	L	-192.4426471		2.785	2.443	2.342/2.327	1		
2 2.477/2.440 2.380 2.925 -192.4303808	5	-192.4303808		2.925	2.380	2.477/2.440	2		
NiSi <sub>7</sub> Cs 0 $2.245/2.245$ $2.407$ $2.826$ $-1963495880$	) ${}^{1}A'$	-196,3495880		2,826	2.407	2.245/2.245	0	Cs	NiSi <sub>7</sub>
$1 \qquad 2.250/2.290 \qquad 2.430 \qquad 2.886 \qquad -196.377330$	••	-196.327330		2.886	2.430	2.250/2.290	1		/
$C_{\rm S}({\rm b}) = 0$ 2.327/2.189 2.514 3.274 -196 3260194	ł	-196.3260194		3.274	2.514	2.327/2.189	0	$C_{s(b)}$	

(continued on next page)

Sys	Symmetry	Multiplicity	<i>R</i> / <i>R</i> 1	<i>R</i> 2	<i>R</i> 3	а	$E_{\mathrm{b}}$	electron state
NiSi <sub>8</sub> Cs Cs	Cs	0	2.223/2.365	3.819	3.391		-200.2433112	
		1	2.411/2.266	2.509	3.353		-200.2239534	<sup>3</sup> A″
		2	2.445/2.436	3.068	2.611		-200.1915247	
	Cs(b)	0	2.199/2.353	2.524	2.478		-200.1870846	
		1	2.256/2.268	2.418	2.483		-200.1818254	

Table 1 (continued)

Unit: Å for bond length, degree for bond angle and hartree for total energy (E<sub>b</sub>).

\* represents the transition state.

natural electron configurations, and vibrational frequencies of the NiSi<sub>n</sub> (n = 1 - 8) clusters have been calculated by the Density Functional method at the B3LYP level employing LanL2DZ basis sets considering the spin of these species.

#### 3.1.1. NiSi

The (U)B3LYP/LanL2DZ results of the NiSi molecule are shown in Table 1. Resulting values for the Ni-Si bond lengths of the NiSi dimer at the (U)B3LYP/LanL2DZ level with singlet, triplet, and quintet spin configurations are 2.064, 2.268, and 2.245 Å, respectively; the corresponding energies are -173.0838, -173.0900, and -173.0665 hartrees, respectively. On the basis of the total energies of this dimer, one finds that the NiSi dimer with spin triplet configuration is the most stable isomer, and that the corresponding ground state is  ${}^{3}\Sigma$ , which is similar to the those of the WSi and MoSi dimers[11]. However, no detailed theoretical investigation is reported. Our theoretical results show that Ni-Si bond length of the most stable NiSi dimer is in good agreement with 2.124 and 2.142 Å of the NiSi dimer with spin singlet configuration at the B3LYP/ 6-311G\* and CCSD(T)/6-311G\* levels [38], respectively, which give firm supporting to our theoretical results. The coordination number of the Ni in the NiSi dimer is one. The NiSi dimer is calculated at the B3LYP/LanL2DZ level, the Ni-Si bond length in the NiSi<sup>-</sup> diatom with doublet, quartet, and sextet spin configurations is 2.094, 2.355, and 2.572 Å, respectively; the corresponding energies are -173.1179, -173.1264, and -173.0802 hartrees, respectively. It shows that the NiSi<sup>-</sup> diatom with quartet spin configuration is the most stable structure and is selected as the ground state, the electron state is labeled as having  ${}^{4}\Sigma_{g}$  character, the additional charge in the most stable NiSi<sup>-</sup> dimer mainly localizes at the Si atom(-0.78). The EA is predicted to be 0.989.

## 3.1.2. NiSi<sub>2</sub>

The equilibrium geometry of the NiSi<sub>2</sub> cluster is optimized at the (U)B3LYP/LanL2DZ level with  $D_{\infty}h$ ,  $C_{\infty}v$ , Cs, and  $C_2v$  symmetries. This computation is followed by a vibrational frequency analysis. According to the theoretical results of Table 1, we find that the linear  $C_{\infty}v$  isomer is more stable than the linear  $D_{\infty}h$  isomer with the same singlet spin configuration. Furthermore, the linear  $D_{\infty}h$  isomer is the only stable structure. The remarkable Ni-Si bond lengths of the linear  $C_{\infty} v$  NiSi<sub>2</sub> cluster with spin S=0, 1, and 2 are 2.10, 2.120, and 2.396 Å, respectively; one notes that Ni–Si bond length of the  $C_{\infty} v$  NiSi<sub>2</sub> cluster is found to be elongated as the spin S goes from S=0 to S=2, this phenomenon is explained in a previous article [12]. On the basis of the calculated total energy, it obviously shows that the linear  $C_{\infty} v$  NiSi<sub>2</sub> with spin triplet configuration, which is lower in total energy than those of the linear  $C_{\infty} v$  and  $D_{\infty}h$  isomers, corresponds to the most stable structure.

For the NiSi<sub>2</sub> cluster with  $C_2v$  symmetry, as can be seen from the findings related to the geometries of the examined systems, bond lengths and bond angles exhibit strong and obvious dependences on the spin of the species considered. The Ni–Si and Si–Si bond lengths of the  $C_2v$  NiSi<sub>2</sub> cluster increase while SiNiSi bond angle decreases when the spin S goes from S=0 to S=2 monotonically, this variation of bond length is resulted from the charge-transfer (or interaction) among the Ni and silicon atoms. However, the NiSi<sub>2</sub> cluster with S=1 is lower in total energy than those with spin S=0and 2, respectively; therefore, the  $C_2v$  NiSi<sub>2</sub> cluster with spin S=1 is the most stable structure. Furthermore, the Ni–Si bond length of the  $C_2v$  NiSi<sub>2</sub> isomer is in good agreement with the previous theoretical result and experimental measurements [36–38].

The NiSi<sub>2</sub> cluster with *C*s symmetry, which is the distortion of the  $C_{\infty}v$  or  $C_2v$  isomers, is obtained. Geometry Table 2

The natural populations and natural electron configurations of the most stable NiSi<sub>n</sub> clusters at the B3LYP/LanL2DZ level

System	Sym- metry	Multiplicity	Natural population	Natural electron configuration
NiSi	$C_{\infty}$ v	1	0.0695	$[core]4s^{1.09}3d^{8.81}$ $4p^{0.02}5s^{0.01}$
NiSi <sub>2</sub>	$C_2$ v	1	0.3557	$[core]4s^{0.59}3d^{9.01}$ $4p^{0.03}5s^{0.01}4d^{0.01}$
NiSi3	$C_3$ v	0	0.2704	$[core]4s^{0.48}3d^{9.22}$ $4d^{0.01}4p^{0.01}5p^{0.01}$
NiSi4	$C_2$ v(b)	0	0.2620	$[core]4s^{0.35}3d^{9.34}$ $4p^{0.02}4d^{0.01}5p^{0.02}$
NiSi5	Cs	0	0.2175	[core] $4s^{0.39}3d^{9.35}$ $4d^{0.01}5p^{0.04}$
NiSi <sub>6</sub>	$C_1$	0	0.2078	$[core]4s^{0.39}3d^{9.32}$ $4p^{0.07}4d^{0.01}$
NiSi7	Cs	0	0.2023	$[core]4s^{0.38}3d^{9.36}$ $4p^{0.03}4d^{0.01}5p^{0.03}$
NiSi <sub>8</sub>	Cs	0	-0.1546	$[core]4s^{0.52}3d^{9.44}$ $4d^{0.01}5p^{0.19}$



Fig. 1. Structures of the NiSi<sub>x</sub> (x = 1 - 5) clusters.

optimization of the bending Cs NiSi<sub>2</sub> (S=0, 1 and 2) cluster shows that this is a stable structure. According to the calculated SiSiNi bond angle (Table 1), one finds that the Cs ReSi<sub>2</sub> can be described as a slight distorted C<sub>2</sub>v NiSi<sub>2</sub> cluster; furthermore, Ni–Si bond length in the Cs isomer correlates with spin of these species considered. Theoretical result shows that the Cs isomer with spin triplet configuration is the most stable structure.

On the basis of the calculated total energies of the NiSi<sub>2</sub> isomers, theoretical results show that the C<sub>2</sub>v NiSi<sub>2</sub> isomer with triplet spin configuration is a lowest-energy structure, and is the most stable isomer and the ground state, the corresponding electron state is labeled as having <sup>3</sup>B<sub>1</sub> character. However, the ground states of the WSi<sub>2</sub>, MoSi<sub>2</sub>, and CrSi<sub>2</sub> isomers correspond to singlet spin configurations, which are different from that of the C<sub>2</sub>v NiSi<sub>2</sub> isomer. In addition, the *C*s NiSi<sub>2</sub> can be seen as the intermediate of the C<sub>∞</sub>v and C<sub>2</sub>v forms, this finding is similar to the ReSi<sub>2</sub> cluster, and the Ni atom in the NiSi<sub>2</sub> cluster tries to saturate the dangling bonds of the Si atoms.

# $\begin{array}{c} & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\$

Fig. 2. Structures of the NiSi<sub>x</sub> (x=6-8) clusters.

3.1.3. NiSi3

In analogy to the optimization results of the MoSi<sub>3</sub> [11], CrSi<sub>3</sub> [15], and ReSi<sub>3</sub> isomers, four stable isomeric structures of the NiSi<sub>3</sub> isomers with  $C_3v$ ,  $D_3h$ ,  $C_8$ , and  $C_2v$  symmetries are found, all of them are selected as candidates of the ground-state configuration.

As for the  $C_3v$  and  $D_3h$  symmetries, theoretical results indicate that the  $C_3v$  and  $D_3h$  isomers with singlet spin configuration are the stable structures. However, the  $C_3v$ isomer is lower in total energy than the  $D_3h$  isomer, reflecting that the  $C_3v$  isomer is more stable than the  $D_3h$ isomer. After a distortion of the  $C_3v$  isomer, the stable Cs isomer with triplet and quintet spin configurations is yielded. According to the calculated total energies of the Cs,  $C_3v$  and  $D_3h$  isomers, the Cs isomer with triplet spin configuration is the most stable structure; the corresponding electron state is predicted to be  ${}^3A''$ .

From our results of the  $C_2v$  NiSi<sub>3</sub> cluster (Table 1), the harmonic vibrational frequency analysis indicates that the  $C_2v$  isomer with quintet spin configuration is an unstable isomer. The theoretical results on  $C_2v$  isomer with singlet and triplet spin configurations manifest that Ni–Si and Si–Si bond lengths, total energies, and bond angle depends on the spin of these species considered, therefore, the  $C_2v$  isomer with singlet spin configuration is the most stable structure. The corresponding electron state is  ${}^1A_1$ .

According to the calculated total energies of the NiSi<sub>3</sub> isomers, the circle-like  $C_2v$  isomer with spin singlet configuration is a lowest-energy structure, indicating that the  $C_2v$  isomer with spin singlet configuration is the ground state, with the corresponding electron state being  ${}^1A_1$ .

#### 3.1.4. NiSi<sub>4</sub>

Geometric structures of the NiSi<sub>4</sub> isomers, maintaining Td,  $C_s$ ,  $C_2v$ , and  $C_2$  symmetries, have been considered as the possible candidates of the ground-state configurations. The theoretical result reveals that the Td isomer with doublet spin configuration is the only stable structure; Ni–Si bond length of 2.101 Å is in good agreement with that of the NiSi dimer. The C<sub>4</sub>v NiSi<sub>4</sub> cluster, which is yielded after the Ni atom is capped on the rhombus Si<sub>4</sub> isomer, is optimized at the B3LYP/LanL2DZ level; the vibrational frequency calculation proves that the C<sub>4</sub>v isomer with triplet spin configuration is a stable structure.

The C<sub>2</sub> isomer, which can be described as the slight distortion of the Td isomer, is yielded. The Ni atom in the C<sub>2</sub> isomer interacts with four Si atoms simultaneously with nonequivalent Ni–Si bond lengths. Theoretical results show that Ni–Si and Si–Si bond lengths (2.100 Å) in the C<sub>2</sub> isomer are in good agreement with those of the Td isomer. On the basis of the calculated equilibrium geometry, which is summarized in Table 1, one should notice that Ni–Si and Si–Si bond lengths correlate with spin of these species considered. In other words, Ni–Si and Si–Si bond lengths of the C<sub>2</sub> isomer increase as the spin S varies from S=0 to S=2. However, according to the calculated total energies, it obviously reveals that the  $C_2$  isomer with singlet spin configuration is the most stable structure; the corresponding electron state is labeled as having <sup>1</sup>A character.

Guided by previous theoretical result of the  $C_4v \text{ ReSi}_4$ cluster, geometry optimization of the  $C_2v(b)$  isomer is performed. Specifically, the equilibrium geometry can be seen as the Re atom being capped the distorted rhombus  $C_2v$ Si<sub>4</sub> cluster. The final theoretical result of harmonic vibrational frequency proves that the NiSi<sub>4</sub> isomer with triplet spin configuration is a stable structure. The  $C_2v(b)$ isomer, which can be depicted as the distortion of the  $C_4v$ isomer, is yielded. The optimized geometry shows that the  $C_2v(b)$  isomers with singlet and quintet spin configurations are the stable structures. On the basis of the calculated total energies of the NiSi<sub>4</sub> isomers with  $C_4v$  and  $C_2v(b)$ symmetries, it apparently shows that the  $C_2v(b)$  isomer with singlet spin configuration is the most stable structure.

The  $C_2v(c)$  NiSi<sub>4</sub> isomer, which can be seen as Ni atom being capped the  $C_2v$  Si<sub>4</sub> isomer, is considered. Theoretical result shows that the  $C_2v(c)$  isomer with singlet spin configuration is a stable isomer. The stable Cs(c) isomer with triplet spin configuration, which can be depicted as the distortion of the  $C_2v(c)$  isomer, is obtained after geometry optimization, the Cs(c) isomer with triplet spin configuration is the most stable isomer.

The NiSi<sub>4</sub> cluster with  $C_2v(d)$  symmetry is considered, the geometry can be seen as Ni atom being doped in the center site of the Si frame with nonequivalent Ni–Si bond lengths. Theoretical result shows that the singlet spin configuration is a stable structure. On the ground of the total energies of the NiSi<sub>4</sub> isomers with Td and  $C_2v(d)$ symmetries, we find that the difference between the two isomers is very small. In other words, the  $C_2v(d)$  isomer is a degenerated structure of the Td isomer. Furthermore, the Td isomer is more stable than the  $C_2v(d)$  isomer with singlet spin configuration.

The new isomer with *Cs* symmetry is yielded after one silicon atom is capped the side of the NiSi<sub>3</sub> isomer. As seen from the equilibrium geometries and total energies of the Cs isomer considering the spin configurations, which is summarized at Table 1, theoretical results indicate that the Ni–Si (R1) and Si–Si(R2) bond lengths, SiNiSi bond angle ( $\alpha$ ) as well as total energies correlate with spin of these species. In other words, the Ni–Si and Si–Si bond lengths of the Cs NiSi<sub>4</sub> isomer increase, while the SiNiSi bond angle and total energies decrease, together with the drops of the stability, as the spin S goes from singlet spin configuration to quintet spin configuration. Thus, the Cs isomer with singlet spin configuration is the most stable structure.

According to the total energies of the NiSi<sub>4</sub> isomers which are discussed above, one finds that the  $C_2v(b)$  isomer with singlet spin configuration is the lowest-energy structure, reflecting that the  $C_2v(b)$  is the most stable isomer, and is selected as the ground state. 3.1.5. NiSi5

The NiSi<sub>5</sub> isomers with  $C_4v$ ,  $C_2v$ ,  $C_2$ ,  $C_5$ , and  $C_1$ symmetries considering spin configurations are carried out at the B3LYP/LanL2DZ level. For the C<sub>4</sub>v isomer, harmonic vibration frequency analysis shows that the C<sub>4</sub>v isomer has an imaginary frequency, which corresponds to a transition state. After the distortion of the  $C_4$ v geometry, the Cs isomer is obtained; geometry optimization on the Cs isomer turns out to reveal that this is a stable structure. Specifically, the geometry can be described as the Ni atom interacting with three Si atoms simultaneously with nonequivalent bond lengths. In light of the geometries and total energies, which are summarized at Table 1, one should notice that Ni-Si bond lengths and total energies depend on the spin these species considered. In other words, Ni-Si bond lengths increase while total energies decease as spin S goes from singlet spin configuration to quintet spin configuration. Consequently, the Cs NiSi<sub>5</sub> isomer with singlet spin configuration is the most stable isomer.

After one Si is caped the bottom of the C<sub>4</sub>v NiSi<sub>4</sub> isomer, the C<sub>2</sub>v NiSi<sub>5</sub> isomer is generated. Specifically, the Ni atom localizes at the top of Si<sub>4</sub> cluster, and interacts with four Si atoms directly. The C2v NiSi5 isomer with quartet spin configuration is not a stable structure. Furthermore, the C<sub>2</sub>v isomers are less stable than those of the Cs isomers with the same spin configurations. After one silicon atom is capped the Td isomer, the new  $C_1(b)$  isomer with singlet spin configuration turns out to reveal that this is a stable structure. According to the calculated total energies of the  $C_1(b)$  and  $C_2(b)$  isomers, one finds that the  $C_1(b)$  and  $C_2(b)$ isomers are higher in total energies than that of the Cs isomer; Therefore, the Cs isomer is more stable than the  $C_1(b)$  and  $C_2(b)$  isomers. In addition, the new stable  $C_3(b)$ isomer, which is generated with respect to the removal of the weakly bound Si atom from the most stable NiSi<sub>6</sub> isomer, is higher in total energy than others, therefore, it is not presented and discussed in this paper.

On the basis of the theoretical analysis above, it obviously shows that the Ni atom in the NiSi<sub>5</sub> isomers is in favorable of the surface site, furthermore, the Cs isomer is selected as the ground state.

# 3.1.6. NiSi<sub>6</sub>

The NiSi<sub>6</sub> clusters are calculated with spin configurations taking into account. For the Cs isomer, one finds that the Cs isomer with singlet spin configuration is a stable isomer. Specifically, the geometry can be described as one silicon atom being capped the side of the Cs NiSi<sub>5</sub> isomer. After the relaxation of the Cs NiSi<sub>6</sub> geometry, the new stable C<sub>1</sub> isomer is yielded. According to the total energies of the C<sub>1</sub> isomers, it obviously indicates that the C<sub>1</sub> isomer with singlet spin configuration is lower in total energy than those with spin triplet and quintet configurations. Furthermore, the C<sub>1</sub> isomer with singlet spin configuration is more stable than the Cs isomer with spin singlet configuration, and the Cs isomer with singlet spin configurations can be seen

a the degenerate structure of the  $C_1$  isomer with singlet spin configuration; consequently, the  $C_1$  isomer with singlet spin configuration is the most stable isomer.

In light of the ReSi<sub>6</sub> isomer, a new NiSi<sub>6</sub> isomer with Cs(b) symmetry is considered. Specifically, this isomer can be seen as the Ni atom being capped the surface of the distorted D<sub>3</sub>d Si<sub>6</sub> isomer. On the basis of the calculated total energies of different spin configurations, it apparently reveals that the Cs(b) isomer with triplet spin configuration is lower in total energy than those of the Cs(b) isomer with triplet and quintet spin configurations. In other words, the Cs(b) isomer with spin singlet configurations. The new Cs(c) isomer is considered and calculated, however, it is less stable than the Cs(b) isomer.

The stable  $C_2$  isomer is calculated, theoretical results show that the total energies of the  $C_2$  isomer are associated with spin of these species considered. In other words, the stability of the  $C_2$  isomer drops as spin S goes from singlet spin configuration to quintet spin configuration. Therefore, the spin singlet configuration is the most stable geometry; the corresponding electron state is  ${}^1A_1$ .

The  $C_1(b)$  isomer with Ni atom replacing one Si atom of the  $D_5h$  Si<sub>7</sub> cluster is considered. According to the total energies of the NiSi<sub>6</sub> isomers, one can notice that the  $C_1(b)$ isomer with singlet spin configuration is a lowest-energy structure, and is selected as the ground state. Theoretical results show that the Ni atom in the NiSi<sub>6</sub> isomers prefers absorbing on the surface site of the Si<sub>6</sub> cluster to the center site of the Si frame.

# 3.1.7. NiSi<sub>7</sub>

Guided by previous theoretical results of the  $\text{CuSi}_x$  and  $\text{ReSi}_7$  clusters [14,27], the initial geometry of the  $\text{NiSi}_7$  cluster is generated by replacing one Si of the D<sub>4</sub>h Si<sub>8</sub> cluster or by relaxing the geometry of the D<sub>4</sub>h Si<sub>8</sub> cluster with respect to the removal of one Si atom. Specifically, this *Cs* geometry can be seen as one of the Si atoms being capped the bottom of the Cs  $\text{ReSi}_6$  cluster with Ni atom interacting with 6 atoms directly. Harmonic vibrational frequencies analysis shows that the Cs isomer with quintet spin configuration is a stable structure; furthermore, the Cs isomer with triplet spin configuration. Thus, the Cs isomer with singlet spin configuration. Thus, the Cs isomer with singlet spin configuration is the most stable isomer. In addition, theoretical results show that the Ni atom in the Cs isomer prefers the surface site of the Si frame.

The new  $C_3v$  geometry is considered, theoretical result shows that the  $C_3v$  isomer is not a stable structure. After the distortion of the  $C_3v$  isomer, the new Cs(b) isomer is generated. The Ni atom in the Cs(b) isomer moves to the center site of the Si frame and interacts with six Si atoms simultaneously with nonequivalent bond lengths. The NiSi<sub>7</sub> isomer with singlet spin configuration is a stable isomer.

On the basis of calculated total energies of the  $NiSi_7$  isomers, it indicates that the  $NiSi_7$  isomer with Cs(b)

symmetry is 0.67 eV higher in total energy than that with Cs symmetry, it apparently shows that the Cs NiSi<sub>7</sub> isomer is more stable than that of the Cs(b) isomer. Therefore, the Cs isomer is selected as the ground state. In other words, the Ni atom in the NiSi<sub>7</sub> isomer prefers the surface site of the Si frame to the center site of the Si frame.

#### 3.1.8. NiSi8

Initial geometries of the Si<sub>8</sub>Ni clusters, maintaining  $D_4h$ and  $D_4d$  symmetries, are considered as the possible candidates of the ground state structure. The harmonic vibrational frequency analyses reveal that the Si<sub>8</sub>Ni clusters with  $D_4h$  and  $D_4d$  symmetries are not the thermodynamically stable structures. After the distortion of the geometry according to the imaginary coordinate, the Cs Si<sub>8</sub>Ni cluster is yielded after the distortion of the D<sub>4</sub>h isomer. The final equilibrium geometry shows that the Ni atom in the Cs isomer is encapsulated into the center site of the Si<sub>8</sub> frame and interacts with all atoms simultaneously with nonequivalent bond lengths. According to the calculated total energies, which are shown in Table 1, it obviously indicates that the Cs isomer with spin singlet configuration is the most stable structure.

The new Cs(b) isomer is taken into account. However, the Cs(b) isomer with quintet spin configuration is not a stable structure. Specifically, the Cs(b) isomer with singlet spin configuration can be seen as the Ni atom being capped the Si8 frame and Ni interacting with four Si atoms simultaneously. For the Cs(b) isomer with quintet spin configuration, the Ni atom in the Cs(b) isomer tends to move from the surface site of the Si frame to the center site of the Si frame and interacts with all silicon atoms simultaneously with nonequivalent bond lengths. Furthermore, the chargetransfer among the Ni and Si atoms reduces the repulsion of Si frames and the electrostatic attractive interactions among the Ni and Si atoms enhance the stability of the NiSi8 cluster simultaneously. The calculated total energy shows that the Cs(b) isomer with singlet spin configuration is the most stable structure.

According to the calculated total energies of the Cs and  $C_{s}(b)$  isomers, one finds that the  $C_{s}(b)$  isomer is about 1.53 eV higher in total energy than the Cs isomer. The theoretical result shows that the Ni atom in the NiSi<sub>8</sub> isomer prefers the center site of the Si8 frame. This observation reveals that the Ni atom in NiSi8 isomer prefers to move into the silicon frame and interacts with all silicon atoms, and that the NiSi8 with Ni atom absorbing on the surface of the Si frame is less stable than that with Ni being encapsulated into Si frame. This phenomenon is verified by experimental measurement and theoretical calculations [10,23,24,27,39]. In other words, the threshold number of silicon atoms with Ni being encapsulated into the center site of the silicon frame is eight. It is worth pointing out that the threshold number of Si atoms with transition metal atom moving from the surface site of the Si frame to the center site of the Si frame depends on the type of transition metal atom.

In addition, the behavior at variance to the large number of previous  $Si_n$  cluster studied involving encapsulated transitional metal species is shown on  $MSi_{12}(M=Mo,W, and Re)$  clusters[12,24,27].

#### 3.2. Population analyses

Natural populations and natural electron configurations of the most stable NiSi<sub>n</sub> (n=1-8) clusters are calculated, which are included at Table 2. Theoretical results show that the net populations of Ni atoms in the most stable  $NiSi_n$  (n =1-7) clusters are positive, indicating that charges in the most stable NiSi<sub>n</sub> (n=1-7) clusters transfer from the Ni atom to the Si atoms. According to natural electron configurations, it indicates that the charge in the most stable NiSi<sub>n</sub> (n=1-7) clusters with Ni atom absorbing on the surface site of the Si frame transfers from 4s of the Ni atom to the Si atoms and 4d subshells of the Ni atom. On the contrary, it is worthwhile pointing out that the natural population of the Ni atom in the most stable NiSi8 cluster with the Ni atom being encapsulated into the center of the Si frame is negative, reflecting that charges in the most stable NiSi<sub>8</sub> transfer from the Si atoms and the 4s shells of Ni atom to the 4d subshells of the Ni atom and the electrostatic interactions among the Ni and Si atoms contribute to the stability of the NiSi8 cluster. This finding on charge-transfer is similar to the MSi<sub>n</sub> (n=1-12) (M=Ta,Re) and CuSi<sub>n</sub> clusters [27,40-42].

## 3.3. Relative stability

A systematic investigation of relative stabilities of the  $Si_nCu$  and  $ReSi_n$  (n=1-12) clusters with respect to the removal one silicon atom from the  $MSi_n$  clusters has been done theoretically [14,27]. In a further series of investigations, we evaluated the  $NiSi_n$  (n=1-8) fragmentation energies with respect to the removal of one silicon atom according to the formulae.

$$D(n, n-1) = E_{b}(Si) + E_{b}(NiSi_{n-1}) - E_{b}(NiSi_{n}),$$

$$A(n, n-1) = E_{b}(Si) + E_{b}(NiSi_{n-1}^{*}) - E_{b}(NiSi_{n})$$

Where  $E_b(\text{NiSi}_{n-1})$ ,  $E_b(\text{Si})$ , and  $E_b(\text{NiSi}_n)$  are the total energies of the most stable  $\text{NiSi}_{n-1}$ , Si, and  $\text{NiSi}_n$  clusters, respectively. However, the  $\text{Eb}(\text{NiSi}_{n-1}^*)$  represents the total energy of the  $\text{NiSi}_{n-1}^*$ , which is defined as the isomer that arises from relaxation of the  $\text{NiSi}_n$  after removal of the most weakly bound Si atom. The total energies of Si atom with singlet, triplet and quintet spin configurations are -3.7193, -3.7635 and -3.6182 hartrees, respectively. As the change in total energy upon removal of one Si atom from the cluster, where in each case the most stable  $\text{MSi}_n$ structures are compared. Our findings are 2.144, 3.461, 2.967, 2.820, 3.079, 2.994,3.147, and 3.544 eV for D(1,0), D(2,1), D(3,2), D(4,3), D(5,4), D(6,5), D(7,6), and D(8,7), respectively, at the B3LYP/LanL2DZ level. Our results indicate that D(8,7) and D(2,1) are bigger than others, in other words, the NiSi<sub>8</sub> and NiSi<sub>2</sub> clusters are more stable than the NiSi<sub>n</sub> (n=1,3-7) clusters with respect to the removal of one silicon atom. After the Ni atom is doped into the Si<sub>8</sub> frame, the Ni atom enhances the stability of the NiSi<sub>8</sub> cluster; therefore, the relative stability of the NiSi<sub>8</sub> cluster is the biggest one. According to our calculated total energies  $(E_b)$  of the NiSi<sub>n</sub> (n=1-8) clusters (Table 2), a general trend of stability for the NiSi<sub>n</sub> (n=1-8) clusters is found. This finding is in good agreement with the theoretical and experimental observations of the MSi<sub>n</sub> (M=Re,Ta,Tb; n=1-8) clusters [27,41,43].

For the A(n,n-1), our calculated results for A(1,0), A(2,1), A(3,2), A(4,3), A(5,4), A(6,5), A(7,6), and A(8,7) are 2.144, 3.461, 2.967, 3.433, 3.135, 3.354, 3.140, and 3.544 eV, respectively. It apparently indicates that the general trend of A(n,n-1) is different from that of D(n,n-1). The remarkable A(2,1) and A(8,7) results are found, showing that the NiSi<sub>8</sub> and NiSi<sub>2</sub> clusters are more stable than others. Furthermore, the NiSi<sub>8</sub> is the most stable structure. This finding is in good agreement with that of the fragmentation energy calculation with respect to the removal of one Si atom discussed above.

#### 4. Summary and conclusion

Geometry optimizations of the NiSi<sub>n</sub> (n=1-8) units are carried out under constraint of well- defined symmetries at the B3LYP/LanL2DZ level. Consequently, the resulting total energies, fragmentation energies and equilibrium geometries of the NiSi<sub>n</sub> (n=1-8) clusters, together with natural populations and natural electron configurations, are presented and discussed. Theoretical results reveal that the Ni atom at small clusters absorbs on the surface site and the Ni atom of the NiSi<sub>8</sub> cluster prefers the center site of the Si frame, the threshold number of the Si atoms in  $Si_n$  frame with the Ni atom moving into the  $Si_n$  clusters is 8, this observation is in good agreement with experimental measurement on the  $\text{TbSi}_n^-$  clusters. According to the calculated total energies, the stability is discussed, theoretical result indicates that the most stable NiSi cluster corresponds to spin triplet configuration. The most stable NiSi<sub>2</sub> is the triplet spin configuration also, which is different from previous  $MSi_n$  (M=Cr, Mo, W, Re and Cu) clusters; and the most stable NiSi<sub>n</sub> (n=3-8) clusters correspond to the spin singlet configuration. Charge-transfer mechanism and relative stability of the NiSi<sub>n</sub> clusters are discussed, the calculated results show that charges in the NiSi<sub>n</sub> (n=1-7)atoms with Ni absorbing on the surface site are transferred from the Si atoms to the Ni atoms, on the contrary, charges in the NiSi<sub>8</sub> cluster with Ni localized at the center site of the Si frame are transferred from the Si atoms to the Ni atom, the electrostatic interactions among the Ni and Si<sub>8</sub> resulted from charge-transfer contribute the stability of the NiSi8 cluster. On the basis of the fragmentation energies with respect to the removal one of the Si atoms from the NiSi<sub>n</sub> clusters, the relative stabilities are calculated; the theoretical results show that the NiSi<sub>2</sub> and NiSi<sub>8</sub> clusters are the most stable structures, and correspond to the enhanced abundances in mass spectroscopy.

#### Acknowledgements

This work is supported by Chinese National Science foundation (20173055); National Natural Science Foundation of China (cooperation item of west and east, 10247007); Natural Science Foundation of ShaanXi province(2002A09); Special Item Foundation of Educational Committee of ShaanXi province(02JK050).

#### References

- [1] M. Seel, P.S. Bagus, Phys. Rev. B 28 (1983) 2032.
- [2] G. Abbate, V. Barone, F. Lelj, E. Iaconis, N. Russo, Surf. Sci. 152/153 (1985) 690.
- [3] I. Hellmann, J. Chem. Phys. 1935; 361.
- [4] P. Gombas, Z. Phys. 94 (1935) 473.
- [5] J. Andzelm, N. Russo, D.R. Salahub, J. Chem. Phys. 87 (1987) 6562.
- [6] J.G. Han, Chem. Phys. Lett. 324 (2000) 143.
  [7] K.A. Gingerich, in: E. Kaldis (Ed.). In current topics in
- [7] K.A. Gingerich, in: E. Kaldis (Ed.), In current topics in material science, North-Holland, Amsterdam, 1980.
- [8] K. Hilpert, Struct. Bonding (Berlin) 73 (1990) 97.
- [9] S.M. Beck, J. Chem. Phys. 90 (1989) 6306.
- [10] J.G. Han, Y.Y. Shi, Chem. Phys. 266 (2001) 33.
- [11] J.G. Han, F. Hagelberg, J. Mol. Struct. (Theochem) 549 (2001) 165.
- [12] J.G. Han, C. Xiao, F. Hagelberg, Struct. Chem. 13 (2002) 173.
- [13] J.G. Han, Chem. Phys. 28 (2003) 181.
- [14] C. Xiao, F. Hagelberg, J. Mol. Struct. (Theochem) 549 (2001) 181.
- [15] J.G. Han, F. Hagelberg, Chem. Phys. 263 (2001) 255.
- [16] J.J. Scherer, J.B. Paul, C.P. Collier, A. O'Keefe, R.J. Saykally, J. Chem. Phys. 103 (1995) 9187.

- [17] J. Budinavicius, L. Pranevicoius, S. Tamulevicius, Phys. Status. Solidi. A 114 (1989) K25.
- [18] J.E. Kingcade Jr., K.A. Gringerick, J. Chem. Soc. Faraday Trans. 285 (1989) 195.
- [19] K.A. Gringerick, J. Chem. Phys. 505 (1969) 426.
- [20] Y.M. Harrick, W. Weltner Jr., J. Chem. Phys. 943 (1991) 371.
- [21] G. Riecker, P. Lamparter, S. Steeb, Z. Metall. 72 (1981) 765.
- [22] P.F. Zhang, J.G Han, Q.R. Pu, J. Mol. Struct. (Theochem) 635 (2003) 25.
- [23] F. Hagelberg, et al., J. Mol. Struct. (Theochem) 487 (1999) 183.
- [24] F. Hagelberg, C. Xiao, W.A. Lester Jr., Phys. Rev. B 67 (2003) 35426.
   [25] C. Xiao, A. Abraham, R. Quinn, et al., J. Phys. Chem. A 106 (2002)
- [25] C. Alao, A. Abraham, K. Quini, et al., J. Phys. Chem. A 100 (2002) 1380.
- [26] J.G. Han, M.J. Huang, to be submitted.
- [27] J.G. Han, Z.Y. Ren, B.Z. Lu, J. Phys. Chem. A 108 (2004) 5100.
- [28] A.N. Andriotis, M. Menon, Phys. Rev. B 57 (1998) 10069.
- [29] G.P. Das, P. Blochl, O.K. Anderson, N.E. Christensen, O. Gunnarsson, Phys. Rev. Lett. 63 (1989) 1168.
- [30] B. Voigtlander, V. Scheuch, H.P. Bonzel, S. Heinze, S. Blugel, Phys. Rev. B 55 (1997) R13444.
- [31] J. Robertson, J. Phys. C: Solid State Phys. 18 (1985) 947.
- [32] P.J. Hoek, W. Ravenek, E.J. Baerends, Phys. Rev. Lett. 60 (1988) 1743.
- [33] N.N. Lathiotakis, A.N. Andriotis, M. Menon, J. Connolly, J. Chem. Phys. 104 (1996) 992.
- [34] S. Caratzoulas, P.J. Knowles, Mol. Phys. 98 (2000) 1811.
- [35] M.J. Frisch, et al., Gaussian, Gaussian Inc, Pittsburgh, PA, 1998.
- [36] K. Raghavachari, J. Chem. Phys. 84 (1986) 5672.
- [37] P.J. Bruna, S.D. Peyerimhoff, R.J. Buenker, J. Chem. Phys. 72 (1980) 5437.
- [38] A.N. Andriotis, M. Menon, G.E. Froudakis, Z. Fthenahis, J.E. Lowther, Chem. Phys. Lett. 292 (1998) 487.
- [39] M. Ohara, K. Miyajima, A. Pramann, A. Nakajima, K. Kaya, J. Phys. Chem. A 106 (2002) 3702.
- [40] Z.S. Yuan, L.F. Zhu, X. Tong, J. Mol, et al., Struct. (Theochem) 589 (2002) 229.
- [41] P. Guo, Z.Y. Ren, F. Wang, J.G. Han, G.H. Wang, J. Chem. Phys. 121 (2004) 12265.
- [42] C. Xiao, F. Hagelberg, J. Mol. Struct. (Theochem) 529 (2000) 241.
- [43] H. Hiura, T. Miyazaki, T. Kanayama, Phys. Rev. Lett. 86 (2001) 1733.