Modified genetic algorithms to model atomic cluster structures: CuSi clusters

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Abstract

This paper presents the results obtained using a genetic algorithm (GA) to search for stable structures of Cu−silicon clusters. In this work the GA uses a semiempirical energy function to find the best cluster structures, which are further optimized using density functional theory. For small clusters our results agree well with previously reported structures, but for larger ones new structures appear in addition to those previously found using limited local searches on common structural motifs. This demonstrates the need for global optimization schemes when searching for stable structures of medium size Cu−silicon clusters.

Keywords: Genetic algorithms; Atomic cluster structure

1. Introduction

The study of the structure and physical properties of atomic and molecular clusters is an extremely active area of research due to their importance, both in fundamental science and in applied fields like microelectronics [1].

Existing experimental methods for structural determination seldom can obtain the structure of atomic clusters directly. Therefore the calculation, using theoretical structures and comparison with experimental values of their physical and optical properties is the most common way to obtain structural information of atomic clusters.

The determination and understanding of the factors governing the structure of medium size metal-doped silicon clusters is important because these structures are relevant to the design and fabrication of microelectronic devices. There is consensus that the effects of metal impurities in silicon can be more easily studied in medium size clusters than in extended systems, where the properties of the bulk dominate.

For instance, motivated by the extensive knowledge of metal-doped fullerene species, such as $La@C_n$ ($n = 60$, 74 and 82) [2], Jackson [3] suggested that an impurity in Si_n clusters would produce cage-like structures of metal−Si_n clusters with surprising stability. Beck [4,5] has observed small-mixed transition-metal (TM)−Si_n clusters with TM = Cr, Mo, W; $n = 16$–18. $CuSi_n$ clusters, for up to $n = 10$, have been observed by Scherer et al. [6] and a small series of Cu_mSi_n clusters have been identified using a pulsed UV laser vaporization plasma reactor and time-of-flight mass spectrometry. Hiura et al. [7] have reported the observation of MSi_nH_x (M = Hf, Te, W, Re, I; $n = 9$–14) clusters using an ion trap.

The geometry and electronic properties of $CuSi_n$ ($n = 4$, 6, 8, 10 and 12) clusters have been reported in several recent publications [8–12]. These studies used locally optimized structures based on those that can be constructed by the adsorption of a Cu atom into a Si_n atomic cluster or by substitution of a Si atom by a Cu atom in a Si_{n+1} cluster. The final structures were locally optimized using the B3LYP/6-311 + G(d) density functional method [13]. This approach produces numerous stable structures of $CuSi_n$ clusters, but leaves open the question of the existence of

unrelated stable structures which cannot be derived from the motifs present in the model structures used as starting ones in the local optimizations. Systematic, global geometry optimizations of atomic clusters is complex and time-consuming due to the large number of possible structures [14], the time required for the calculation of their total energy and the lack of effective methods to perform global searches. Nonetheless the need for global searches of atomic cluster structures has been recently demonstrated by our previous work on medium size silicon clusters [15].

In this paper, we demonstrate the use of a Parallel Genetic Algorithm (PGA) to address the problem of the structure prediction of $CuSi_n$ atomic clusters. This method was chosen because in conjunction with Basin Hopping Monte Carlo [16,17], and simulated annealing [18], is one of the best approaches to find global and secondary minima of complex energy potential surfaces (PES) [16]. Moreover, our recent research efforts have demonstrated the success of using PGAs to predict crystalline [19–21] and cluster structures [15,22].

Genetic algorithms (GAs) are a family of search techniques rooted on the ideas of Darwinian biological evolution [23,24]. The introductory sections of Refs. [25,26] offer a very detailed description of the progress in the development of GA strategies to perform optimizations of atomic cluster structures in the last 7 years. The GAs are based in the principle of survival of the fittest, considering that each string or *genome* represents a trial solution candidate of the problem, and that at any generation the genomes or 'individuals' compete with each other in the population for survival, producing off-springs for the next generation by prescribed propagation rules. Operators analogues to crossover, mutation and natural selection are employed to perform a search able to explore and learn the multidimensional parameter space and determine which regions of that space provide good solutions to the problem. One of the advantages of genetic algorithms is that they can provide not only global minima, but also information on other states with energies close to the minimum, an important property when analyzing atomic clusters.

A significant source of difficulties when studying the structures of metal/Si clusters is that the bonding charac-teristics in silicon metal clusters is quite different than those observed in more common organic compounds. Hence, it is very difficult to obtain accurate but simplified empirical potentials to reproduce the interatomic interactions, forcing the use of more computational demanding quantum mechanical approaches. As discussed above, for medium to large size clusters the option of using ab initio or density functional theory (DFT) methods to calculate the energies has been limited to the study of a few plausible configurations [12]. In this paper we have adopted a compromise by using a semiempirical molecular orbital program, MSINDO [27–29], to evaluate the energy of the clusters in the global GA search, while using a DFT method to further refine the more promising structures.

Among several semiempirical methods the MSINDO was selected because it includes parameters to represent transition metals.

Here we present results on a series of $CuSi_n$ ($n = 4, 6, 8, 10$ and 12), chosen as test cases to check our strategy and analyze its advantages and difficulties.

2. Methodology

Genetic coding of the cluster structures. In any GA implementation it is necessary to define a genome with enough information to calculate the associated fitness function. For the case of atomic clusters, the genome is quite simple because there are no symmetry or periodicity relationships that constrain the parameters in the genome. The genome is just given as an array containing the coordinates of the atoms. This array has dimension $3N$, were N is the number of atoms in the cluster. Moreover, any genetic operator, mating, crossover, mutation, etc. applied to this genome produces a valid individual, i.e. a possible structure for the desired cluster size.

The first population, of size N_{pop}, is constructed by generating a set of atomic coordinates using random numbers. These random numbers, used to define the atomic positions in the cluster, belong to specific intervals selected according to the expected dimensions of the cluster; these restrictions have been included to avoid sampling non-physical configurations. Additionally, the distances between all atom pairs are calculated and compared with a set of rules, which guarantees that they are within the acceptable values for interatomic distances, otherwise the structure is rejected. This set of rules is designated to eliminate from the initial population all those structures that are evidently unphysical. There are basically two rules, the first states that if any pair of atoms is closer than a minimal distance (r_1) the structure will be rejected, the second rule states that if any atom is at a distance larger than r_2 to any other atom in the cluster the structure also will be rejected.

The GA operations of mating, mutation and selection are used to evolve one generation into the next. The population replacement is done through the steady-state genetic algorithm, which typically replaces only a portion of individulas in each generation [30–32]. This technique is also known as elitism because the best individuals among the population, 50% in our case, are copied directly into the next generation. The criteria for fitness probability, selec-tion of the individuals and mutation are discussed in detail in Ref. [20].

The MGAC package has been implemented in C++ language using parallel techniques (MPI), making it very portable as well as easy to maintain and upgrade. Our parallel MGAC implementation of the GA (PGA) is particularly efficient [33].

Using the information contained in the genomes, the energy of each individual was evaluated and its structure

relaxed to the local minimum. All the energy calculations for the GA optimizations were done using the MSINDO code [27]. The GA procedure was repeated several times employing different initial populations to confirm that the final selection of isomers was independent of the initial population. Populations were considered converged when the standard deviation of the energies in the population reaches 0.1 eV. The structures in the final population were manually classified selecting a set of structures with significant diversity for further refinement. The geometry of these isomers was locally optimized using density functional methods with the B3PW91 exchange correlation functional. Following the observations of Xiao et al. [12], that extended basis set have only a slight effect on the cluster geometries, we have used the 6-311G(d) basis for these calculations. All the geometry optimizations were run until the forces on the atoms are less than 0.0002 a.u./Å. The vibrational frequencies were calculated for the optimized structures to check that no imaginary frequencies are present, confirming that the isomers presented here correspond to true minima of the potential energy. All the DFT calculations were done using the GAUSSIAN suite of programs [34].

3. Results and discussion

Table 1 presents the relative energies for the Si_nCu clusters structures found in this paper compared with those obtained by Xiao et al. [12]. In the table, Xiao's structures are labelled according to the original publication, while those obtained here are labelled using roman numerals as depicted in Figs. 1–5. The relative energies have been calculated with respect to the most stable isomer in the respective study and arrows connect isomers found in both studies.

3.1. CuSi$_4$

The MGAC was able to find four distinct isomers searching for a minimum in the MSINDO energy hypersurface, when using 25 individuals and 20 generations. The optimization of these structures by the B3PW91/6-311G(d) methodology produces the relaxed isomers I–III, shown in Fig. 1 as two different structures produced by the MGAC methodology merge into isomer I. The vibrational analysis of the three final structures shows that they are stable configurations.

The relative energies of these species, listed in Table 1, show that the most stable isomer, I, is identical to the one, **4a**, reported by Xiao et al. [12]. Comparison of the interatomic distances and angles show good agreement between both methods. The second structure from our work, **II**, corresponds to Xiao's **4c** and our third structure, resembles quite closely Xiao's **4b**⁻, which may indicate the possibility of a vertical transition in the photoelectron

Table 1
Relative energy (eV) for CuSi$_n$, $n = 4, 6, 8, 10$ and 12, atomic clusters

XHL, Ref. [12]		This Work	
Isomer	Relative Energy B3LYP/6-311G(d)	Relative Energy B3PW91/6-311G(d)	Isomer
		CuSi$_4$	
4a	**0.000**	**0.000**	**I**
4b	0.003	0.164	**II**
4c	**0.086**	0.188	III
		CuSi$_6$	
6a	**0.000**	**0.000**	**I**
6b	0.078	0.574	II
6c	0.913	0.583	III
		0.643	IV
		0.811	V
		CuSi$_8$	
8a	0.000	**0.000**	**I**
8b	**0.008**	0.256	II
8c	0.357	0.503	III
8d	0.949	0.605	IV
		0.676	V
		CuSi$_{10}$	
10a	**0.000**	**0.000**	**I**
10b	**0.006**	**0.064**	**II**
10c	0.049	0.164	III
10d	**0.090**	**0.196**	**IV**
10e	0.091	0.478	V
10f	0.289	0.608	VI
10g	0.392	0.738	VII
10h	0.405	0.783	VIII
10i	0.422	0.903	IX
		0.938	X
		0.978	XI
		CuSi$_{12}$	
12a	0.000	0.000	I
12b	0.275	0.199	II
12c	0.342	0.278	III
12d	0.353	0.542	IV
12e	0.855	2.196	V

spectra. The different energy ordering of the structures found in this work when compared with those of Xiao is attributed to the different exchange correlation functionals used in the two studies. Nonetheless, it is apparent that for this small cluster both approaches produce the same structures with a somehow different ordering of the structures.

3.2. CuSi$_6$

The MGAC algorithm was able to find six isomers in the MSINDO energy hypersurface using 50 individuals and 30 generations. Fig. 2 shows the B3PW91/6-311G(d) optimized structures, ordered by increasing energy. Isomers II and V look very similar. From the comparison of the corresponding bond lengths, bond angles and dihedral angles, one can see that isomer II has a higher symmetry.
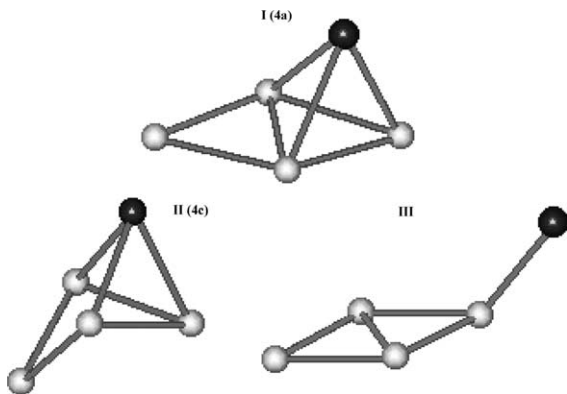
Fig. 1. CuSi$_4$ structures obtained by the MGAC/MSINDO followed by B3PW91/6-311G(d) local optimization. Notation between parenthesis indicates the numbering according to Ref. [12].

There is a reflection plane formed by four silicon atoms and the copper atom. Instead, for isomer V the dihedral angle between the silicon atoms and the copper atom is 174°. The Cu–Si bond length is 2.13 Å for isomer II and 2.32 Å for isomer V. Both isomers are stable and the vibrational spectra show that they correspond to different local minima in the energy hypersurface.

From Table 1 it is apparent that our method is able to find the same lowest energy isomer than Xiao et al. [12]. The MGAC method finds several new isomers not present in Xiao's study with energies lower than the highest energy isomer, **6c**, in Xiao's study, but it misses the second isomer, **6b**, from Xiao's paper. When comparing the relative
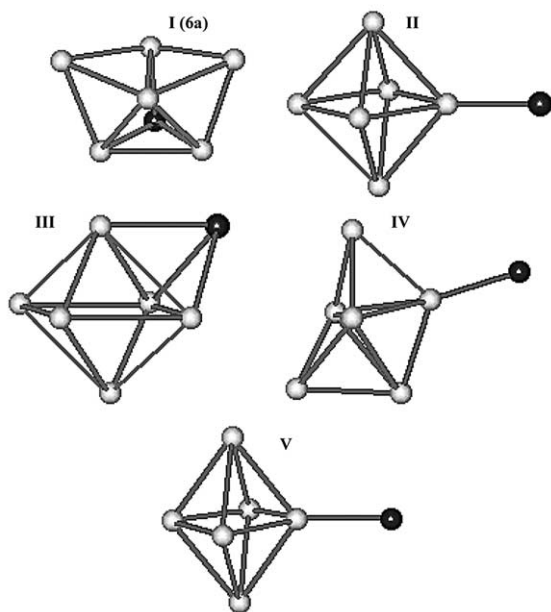

Fig. 2. CuSi$_6$ structures obtained by the MGAC/MSINDO followed by B3PW91/6-311G(d) local optimization. Notation between parenthesis indicates the numbering according to Ref. [12].
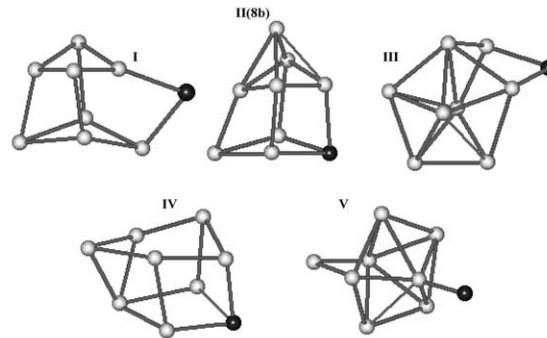

Fig. 3. CuSi$_8$ structures obtained by the MGAC/MSINDO followed by B3PW91/6-311G(d) local optimization. Notation between parenthesis indicates the numbering according to Ref. [12].

energies of isomers **6a** and **6b**, the latter is less stable by only 0.078 eV for the DFT method [12] but 0.944 eV for the MSINDO, so it is readily eliminated from population in the GA. As it will be shown later this is not an isolated case, isomer **6b** presents a tetra-coordinated Cu and the MSINDO calculations consistently underestimate the binding energies of Cu with coordination numbers larger than three, leading to the elimination of any isomer with this type of bonding from the GA population. Nevertheless, these results show that the MGAC approach is able to find several new isomers of CuSi$_6$ with coordination numbers lower than four.

3.3. CuSi$_8$

The MGAC approach found seven candidates for the structures of the CuSi$_8$ isomers using 25 individuals and 20 generations. The search was repeated four times with different initial populations to confirm the selection of candidates. Fig. 3 shows the five more stable B3PW91/6-311G(d) structures ordered by their increasing energy. The bond lengths are between 2.3 and 2.5 Å for the Si–Si bonds and between 2.21 and 2.33 Å for the Si–Cu, which agrees well with those reported in the literature: 2.35–2.68 Å for Si–Si, and 2.36–2.47 Å for Cu–Si bonds [12].

Isomer **I** matches isomer **8b** from Xiao et al. [12], while isomers II–V are new stable states that have not been previously reported. Isomer V presents an interesting geometry, a cage like structure with a Cu atom attached to only one silicon atom with a bond length of 2.14 Å. The other silicon atoms are more than 3 Å away from the copper atom. This type of structure appears also in CuSi$_{10}$ and CuSi$_{12}$. Xiao et al. [12] documented that cage like structures with Cu at the center site are unfavorable, both for CuSi$_6$ and CuSi$_8$, indicating that they are unstable and that the Cu atom tends to move to the surface of the cluster while the framework of Si$_n$ relaxes to a non-cage like structure. The MGAC/MSINDO fails to find isomers 8a, 8c and 8d. All these structures present a Cu atom with a coordination number higher than three; therefore they are eliminated very early from the population by the GA due to the under-estimation of the binding energy of highly coordinated Cu
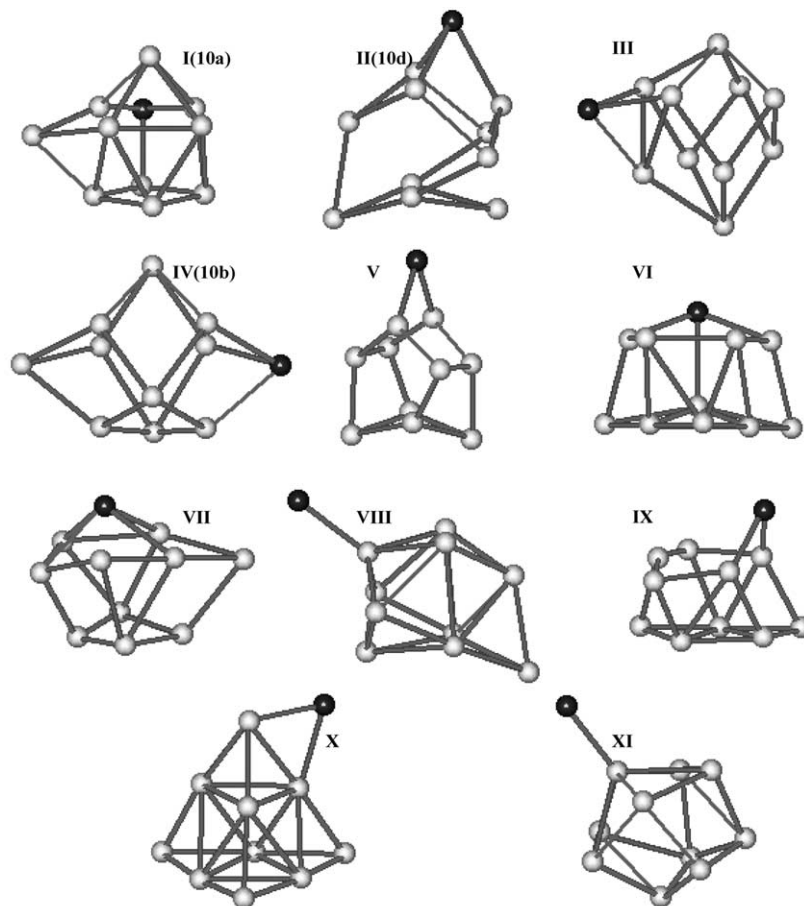
Fig. 4. CuSi$_{10}$ structures obtained by the MGAC/MSINDO followed by B3PW91/6-311G(d) local optimization. Notation between parenthesis indicates the numbering according to Ref. [12].

by the MSINDO method. For instance, the MSINDO predicts that 8a is less stable than 8b by 2.028 eV, while the DFT method [12] predicts the reverse trend with **8a** more stable by 0.008 eV.

3.4. CuSi$_{10}$

CuSi$_{10}$ appears with the highest abundance in the mass spectrum [4], indicating that it has an enhanced stability and that it most likely exhibits a large number of nearly iso-energetic low-lying isomers. For CuSi$_{10}$ we employed a population of 50 individuals that converged after 23 generations. The procedure was repeated five times with different initial populations. This significant enlargement of the population, with respect to the one used for the CuSi$_8$ search, allows more diversity in the final sample a desired feature due to the known existence of the higher number of isomers of CuSi$_{10}$. MGAC found 15 structures that were relaxed locally employing the B3PW91/6-311G(d) pro-cedure, leading to 11 distinct ones. The schemes of these final structures are shown in Fig. 4, ordered by their increasing energy. The lowest energy isomer, **I**, is

the same that the lowest energy isomer, **10a**, found by Xiao et al. [12] while isomers **II** and **IV** corresponds to **10d** and **10b**, respectively. Isomers III and V–XI have not been previously reported. Isomers VII–IX seem to be originated from a common silicon cluster that relaxes to different conformations by different insertions of a Cu atom. Structure XI is very similar to structure V of CuSi$_8$.
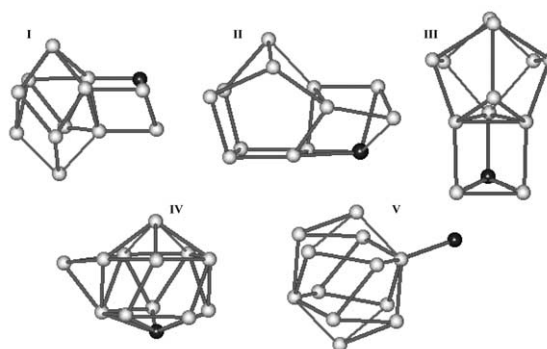

Fig. 5. CuSi$_{12}$ structures obtained by the MGAC/MSINDO followed by B3PW91/6-311G(d) local optimization.

The MGAC/MSINDO method does not find numerous isomers presented by Xiao et al. [12], this can again be attributed to the fact that all the missed ones show a highly coordinated Cu atom. For instance the MSINDO predicts that the isomer 10c is 1.37 eV less stable than 10a, while the DFT theory predicts only 0.049 eV [12].

3.5. CuSi$_{12}$

For the GA optimizations of CuSi$_{12}$ we used a population made of 50 individuals, which needed 125 generations to reach convergence. The procedure was repeated four times to confirm the candidates' selection. The MGAC selected isomers, six, have been further relaxed employing the B3PW91/6-311G(d) procedure, leading to five unique ones that are presented in Fig. 5 labelled by increasing energy. The bond distances Cu–Si are in the order of 2.3 Å (I–III), and 2.4 Å (IV and V). The average Si–Si bond is of 2.55 Å.

The clusters produced by the MGAC methodology do not correspond to any of those proposed in Ref. [12], this can be attributed to the already mentioned failure of the MSINDO methodology to describe correctly clusters with copper coordination number higher than three. All the structures in Ref. [12] show the Cu atom with this type of bonding. Because the DFT calculations in this paper have been done using a different exchange correlation functional and basis set it is difficult to compare the energies of the isomers found here with those in the literature [12]. The calculated energy of isomer 12a (locally optimized using the B3PW91/6-311G(d) procedure) is 0.283 eV lower than our best isomer, I. The MGAC/MSINDO method fails to found the lowest energy isomer for CuSi$_{12}$, it is able to find several new isomers, I–IV that appear to have energies within the range of those of Xiao et al. [12].

4. Concluding remarks

This paper presents a new strategy to perform global searches of low energy isomers for CuSi$_n$ clusters. The results show that local optimizations of potential structures derived from known structural motifs do not produce a comprehensive set of possible structures, leaving out stable isomers that cannot be derived from previously built models. The MGAC/MSINDO method presented here, because it does not use neither symmetry constraints nor techniques based on combination of subunits to propose a starting geometry, is able to find numerous new isomers that were not discover before. Unfortunately, the results on CuSi$_n$ clusters are not as encouraging as those obtained for the pure silicon clusters [15] due to the underestimation of the bonding energy of Cu with coordination number larger than three by the MSINDO method. This large underestimation of the binding energy leads to the rapid elimination from the GA population of

any isomer with Cu atoms with high coordination number, in spite of their lower energy when using DFT methods. It appears that to provide a comprehensive list of stable medium size isomers of CuSi$_n$, it is unavoidable to use the MGAC coupled directly with the DFT method. While this will increase considerably the computational resources needed, the high degree of parallelization available in the MGAC approach [33] will make this possible in the near future.

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