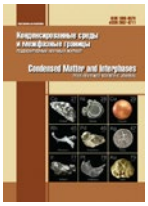

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Search strategy for stable isomers of silicon clusters encapsulating certain fourth-period transition metals

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Abstract

Objectives: A modification of the Wade-Mingos rule is proposed to predict the stable isomers of silicon-metal clusters. According to this modification, stable isomers composed of n silicon atoms with 4n+4 and 4n+6 valence electrons are formed by removing one or two vertices, respectively, from the structures of stable isomers with 4n+2 valence electrons.

Computational method: To demonstrate the modified rule, the atomic structures and electronic spectra of $MeSi_{15}^-$ (Me = Sc, V) clusters calculated using four different DFT functionals are presented. The atomic structures of the most stable isomers are described. The influence of the choice of functional on the cluster geometry optimization results is investigated.

Conclusions: A comparison of the calculated electronic spectra of the stable isomers with the experimental photoelectron spectrum allowed for the determination of which isomers can be obtained experimentally.

Keywords: Atomic clusters, Silicon clusters, Density functional theory, Electronic spectrum

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Оригинальные статьи

Научная статья
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Стратегия поиска стабильных изомеров кремниевых кластеров с инкапсулированными атомами некоторых переходных металлов четвертого периода

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Аннотация

Цель статьи: Предложена модификация правила Уэйда-Мингоса для предсказания стабильных изомеров кремний-металлических кластеров. Согласно этой модификации, стабильные изомеры из n атомов кремния с $4n+4$ и $4n+6$ валентными электронами образуются удалением одной или двух вершин соответственно из структур стабильных изомеров с $4n+2$ валентными электронами.

Метод расчета: Для демонстрации модифицированного правила представлены результаты расчета атомной структуры и электронного спектра кластеров $MeSi_{15}^-$ (Me = Sc, V) с использованием четырех различных DFT-функционалов. Описаны атомные структуры наиболее стабильных изомеров. Исследовано влияние выбора функционала на результаты оптимизации геометрии кластеров.

Выводы: Сравнение рассчитанных электронных спектров стабильных изомеров с экспериментальным фотоэлектронным спектром позволило определить, какие изомеры могут быть получены экспериментально.

Ключевые слова: атомные кластеры, кремниевые кластеры, теория функционала плотности, электронный спектр

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1. Introduction

Silicon clusters are nanostructures of the smallest possible dimensionality, zero-dimensional nanostructures. They are of interest both for studying effects related to low dimensionality and as units for assembling larger nanoforms. Silicon clusters attracted close attention from researchers after the discovery of fullerene in 1985 [1]. That sparked the search for similar structures based on other Group IV elements, especially silicon, since it was and still is the primary material of electronics. However, silicon, unlike carbon, was shown not to be able to form regular spheroidal structures. Calculations [2–4] demonstrated that pure silicon clusters have an irregular geometric shape, while photoelectron spectroscopy experiments [5] revealed that their band gap is smaller than that of crystalline silicon. In 2001, a report was published on the possibility of stabilizing a regular closed structure, a regular hexagonal prism with silicon atoms at its vertices, by a tungsten atom [6]. This was followed by numerous theoretical [7–12] and experimental [13–17] studies of the atomic and electronic structure of silicon–metal clusters and of the feasibility of obtaining regular endohedral structures based on silicon.

Experimental determination of the atomic structure of silicon and silicon-metal clusters is currently difficult; therefore, the primary information regarding the geometric structure of clusters and the patterns of their formation can only be obtained through computer simulation methods. The following algorithm is frequently used for computer experiments aimed at searching for stable isomers of atomic clusters. First, a global search for all possible stable configurations of a given composition and number of atoms is conducted. This search is a resource-intensive

task that requires significant computational power and time expenditures; thus, to save time and computational resources, minimal basis sets are often used for the global search [18–20], which can affect the quality of the results. As a result, several hundred potential isomers may be obtained, from which a few of the most stable ones are selected. These structures are then re-optimized using more advanced basis sets. Establishing the patterns that describe their formation can significantly simplify the task of searching for stable isomers. Such patterns have been formulated, for instance, by Wade and Mingos for boranes and carboranes [21–23].

In this work, using the example of $MeSi_{15}^-$ clusters (Me = Sc, V), we propose a strategy for searching for stable isomers of silicon-metal clusters based on a modification of the Wade–Mingos rules. We present the results of computer simulations, within the framework of density functional theory, of the atomic structure of silicon-metal anionic clusters $MeSi_{15}^-$ (Me = Sc, V) and cationic clusters $ScSi_{16}^+$ and $VSi16^{3+}$. Four different DFT functionals were used for geometry optimization calculations. A comparison of the calculated data with experimental results allows for the selection of a functional whose usage yields results that best agree with the experiment.

2. Computational method

Calculations were performed within the framework of density functional theory using four exchange-correlation functionals: B3LYP [24–27], B3PW91 [28, 29], BP86 [30], and PBE [31, 32] in combination with the def2-TZVPD basis set [33, 34]. The Gaussian 09 software package was utilized [35]. Since the def2-TZVPD basis set is not built into the Gaussian 09 software package, it was imported from the open-source Basis Set Exchange repository [36–38].

The calculation of the electronic spectrum yielded the energy eigenvalues for each molecular orbital. The resulting energy spectrum represented a set of energy levels. To construct the theoretical electronic spectrum, each energy level was replaced by a Gaussian distribution with a half-width of 0.12 eV, and then the intensities of all distributions were summed for each energy value.

The average binding energy was calculated using the formula:

$$E_b = \frac{nE(\mathrm{Si}) + E\left(\mathrm{Me}^q\right) - E\left(\mathrm{MeSi}_n^q\right)}{n+1},$$

where E(Si) and $E(\mathrm{Me}^q)$ are the total energies of a free silicon atom and a metal ion with a charge q, respectively; $E(\mathrm{MeSi}_n^q)$ is the total energy of the cluster in the charge state with a charge q; and n is the number of silicon atoms in the cluster.

3. Results and discussion

3.1. Modification of the Wade–Mingos rule for silicon-metal clusters

The formation of stable isomers of silicon clusters with encapsulated metal atoms is proposed to be considered based on a rule analogous to the Wade–Mingos rule for boranes and carboranes [21–23]. According to this rule, stable cluster structures of atoms with four valence electrons correspond to *closo*-, *nido*-, *arachno*-, and other polyhedron types. *Closo*-polyhedra with n vertices contain $4n$+2 valence electrons, *nido*-polyhedra contain $4n$+4 electrons, and *arachno*-polyhedra contain $4n$+6 electrons. *Nido*- and *arachno*-polyhedra are formed from *closo*-structures: removing one vertex yields a *nido*-structure, while removing two yields an *arachno*-structure.

Monoanionic $ScSi_n^-$ clusters contain $4n$+4 valence electrons ($4n$ from silicon atoms ($3s^23p^2$), three from scandium ($3d^14s^2$), and one electron due to the negative charge of the cluster). According to the Wade–Mingos rule [21–23], such clusters should exhibit a *nido*-structure derived from a *closo*-polyhedron by removing one vertex. VSi_n^- clusters have 4n+6 valence electrons (4n electrons from silicon atoms, five electrons from the vanadium atom with a $3d^34s^2$ valence shell, and one more electron since the cluster is monoanionic), meaning they should possess the structure of *arachno*-polyhedra (derived by removing two vertices). For silicon-scandium clusters, the structures of monocationic $ScSi_n^+$ clusters will serve as the *closo*-structures, whereas for silicon-vanadium clusters, the structures of tricationic VSi_n^{3+} clusters play this role. Therefore, to verify the validity of the Wade–Mingos rule for the $ScSi_{15}^-$ and VSi_{15}^- clusters, the structures of stable isomers of the $ScSi_{16}^+$ and VSi_{17}^{3+} clusters were optimized.

Seven stable isomers of the $ScSi_{16}^+$ cluster are shown in Fig. 1a. The structures of all isomers are endohedral; they represent a closed polyhedron

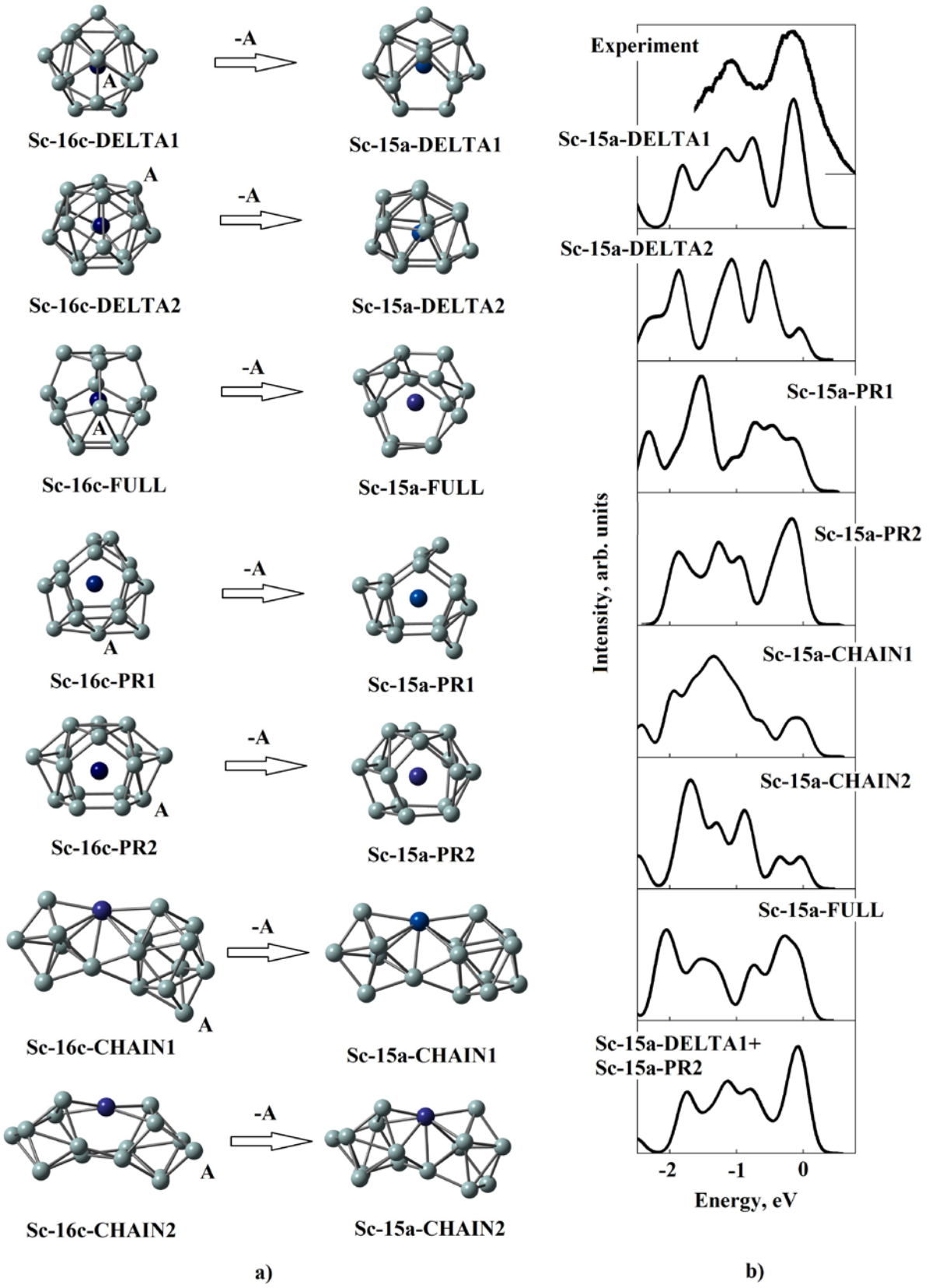

Fig. 1. Spatial structures of the $ScSi_{16}^{+}$ and $ScSi_{15}^{-}$ clusters (a) and comparison of the calculated electronic spectra of the $ScSi_{15}^{-}$ cluster with the experimental photoelectron spectrum [13] (b). Silicon atoms are shown in gray, and scandium atoms are shown in blue. Sc-Si bonds are omitted for clarity

with silicon atoms at the vertices, encapsulating the scandium atom inside. The Sc-16c-DELTA1 isomer belongs to the deltahedral endo-structure type, as it is a polyhedron with predominantly triangular (delta-like) faces. The silicon atoms in the Sc-16c-DELTA1 isomer are coordinated by four or five neighboring silicon atoms, as well as the metal atom. The Sc-16c-DELTA2 isomer is an endocluster in the form of a polyhedron with tetragonal bases and triangular faces. In this isomer, each silicon atom is surrounded by five silicon atoms and also forms a bond with the scandium atom. Three more isomers of the $ScSi_{16}^{+}$ cluster belong to the type of three-connected structures, where the silicon atoms form predominantly three Si-Si bonds each. The Sc-16c-FULL isomer is a fullerene-like polyhedron with tetragonal bases and pentagonal faces. In the Sc-16c-PR1 and Sc-16c-PR2 isomers, a common structural fragment can be identified – a distorted hexagonal prism. The Sc-16c-PR1 isomer is constructed by adding four silicon atoms above one of the prism bases, while the Sc-16c-PR2 isomer is formed by adding three atoms above one base and one atom above the opposite base. The Sc-16c-CHAIN1 and Sc-16c-CHAIN2 isomers exhibit a longitudinal, chain-like structure. In this structure, two units can be distinguished, each representing a small silicon cluster. These units form several Si–Si bonds with each other and with the shared scandium atom.

The relative stabilities of the isomers depend on the functional used in the geometry optimization calculations (see Table 1). In the calculation utilizing the B3LYP functional, the highest average binding energy corresponds to the fullerene-like isomer Sc-16c-FULL. Its energy difference from the remaining isomers is significant, leading to the conclusion that this is the only experimentally accessible structure

Table 1. Differences in the average binding energies (eV/atom) between the ground-state isomer and the remaining ones calculated using various functionals. The zero value corresponds to the

Cluster	Isomer	Functional			
		B3LYP	B3PW91	BP86	PBE
$ScSi_{16}^{+}$	Sc-16c-DELTA1	0.0422	0.0014	0.0014	**0.0000**
	Sc-16c-DELTA2	0.0561	0.0138	0.0116	0.0084
	Sc-16c-CHAIN1	0.0151	0.0172	0.0349	0.0443
	Sc-16c-CHAIN2	0.0258	0.0228	0.0406	0.0538
	Sc-16c-FULL	**0.0000**	0.0034	0.0040	0.0276
	Sc-16c-PR1	0.0136	**0.0000**	**0.0000**	0.0101
	Sc-16c-PR2	0.0361	0.0163	0.0176	0.0264
VSi_{17}^{3+}	V-17c-DELTA	0.0745	0.0119	**0.0000**	**0.0000**
	V-17c-FULL	**0.0000**	**0.0000**	0.0010	0.0313
	V-17c-PR	0.0652	0.0427	0.0249	0.0431
$ScSi_{15}^{-}$	Sc-15a-DELTA1	0.0326	**0.0000**	**0.0000**	**0.0000**
	Sc-15a-DELTA2	0.0420	0.0141	0.0131	0.0147
	Sc-15a-CHAIN1	0.0256	0.0100	0.0267	0.0328
	Sc-15a-CHAIN2	0.0751	0.0677	0.0890	0.1030
	Sc-15a-FULL	0.0400	0.0405	0.0355	0.0515
	Sc-15a-PR1	**0.0000**	0.0086	0.0064	0.0251
	Sc-15a-PR2	0.0336	0.0101	0.0066	0.0111
VSi_{15}^{-}	V-15a-DELTA1	0.0179	0.0023	0.0019	0.0013
	V-15a-DELTA2	0.0194	0.0020	0.0037	0.0023
	V-15a-DELTA3	0.0141	**0.0000**	**0.0000**	**0.0000**
	V-15a-DELTA4	0.0138	0.0002	**0.0000**	0.0001
	V-15a-PR1	**0.0000**	0.0349	0.0418	0.0665
	V-15a-PR2	0.0114	0.0207	0.0181	0.0434
	V-15a-FULL	0.0403	–	–	–

for the $ScSi_{16}^{+}$ cluster that can be synthesized experimentally. Using the PBE functional for geometric structure optimization yielded a result where the highest average binding energy corresponds to the deltahedral isomer Sc-16c-DELTA1. At the same time, another deltahedral isomer, Sc-16c-DELTA2, was found to have only a slightly lower average binding energy. Thus, both isomers can be considered the lowest-energy isomers of the $ScSi_{16}^{+}$ cluster. Calculations using the B3PW91 and BP86 functionals showed that the prismatic isomer Sc-16c-PR1 possesses the highest average binding energy, but its energy separation from the Sc-16c-DELTA1 isomer is so small that both structures can be regarded as the most stable isomers of the $ScSi_{16}^{+}$ cluster based on these calculation results. The longitudinal isomers Sc-16c-CHAIN1 and Sc-16c-CHAIN2 proved to be the least stable according to the results of all four calculations.

For the VSi_{17}^{3+} cluster, three stable isomers are presented in Fig. 2a. Similarly to the $ScSi_{16}^{+}$ cluster isomers, they can be divided into deltahedral and three-coordinate structures. The V-17c-DELTA isomer belongs to the deltahedral structures – it is a polyhedron in which most faces are delta-like, and the vanadium atom is encapsulated inside this silicon cage. As can also be seen in Fig. 2a, this structure can be viewed as a sixteen-vertex deltahedral polyhedron (similar to Frank–Kasper polyhedra) with an additional silicon atom. The core of the V-17c-PR isomer features an irregular, highly distorted hexagonal prism. Five more silicon atoms form bonds with the atoms at the vertices of this prism. The V-17c-FULL isomer belongs to the three-connected type of structure; it is a sixteen-vertex fullerene-like polyhedron, with the seventeenth silicon atom bonded to two atoms on the surface of the polyhedron. The structures of all three isomers of the VSi_{17}^{3+} cluster can be described as quasi-endohedral. Specifically, the V-17c-DELTA and V-17c-FULL isomers are endoclusters of sixteen silicon atoms encapsulating a vanadium atom, while the bond between the additional silicon atom and the vanadium atom is significantly weakened. In the V-17c-PR isomer, the bond of the additional silicon atoms to the vanadium atom is also weakened.

Just as for the $ScSi_{16}^{+}$ cluster, the relative stabilities of the VSi_{17}^{3+} cluster isomers depend on the functional used for the geometric structure optimization calculations (see Table 1). Optimization utilizing the B3LYP functional shows that the highest average binding energy corresponds to the fullerene-like isomer V-17c-FULL. The results of the B3PW91 calculation also indicate the energetic preference of this isomer, though not as significant. Calculations using the PBE functional show that the deltahedral isomer V-17c-DELTA is the most stable, exhibiting a large energy difference from the remaining isomers. According to the BP86 calculation results, the V-17c-FULL and V-17c-DELTA isomers have nearly identical binding energies, and both can be considered the lowest-energy isomers of the VSi_{17}^{3+} cluster.

Although the structures of the $ScSi_{16}^{+}$ and VSi_{17}^{3+} clusters are referred to above as *closo*-structures, this designation is conventional and is not related to their similarity to the *closo*-structures of boranes and carboranes, which received this name due to the geometry of regular *closo*-polyhedra [21–23]. Of all the described structures, only the Sc-16c-DELTA2 isomer is analogous to the sixteen-vertex *closo*-polyhedron described for boranes and carboranes [21–23]. None of the other $ScSi_{16}^{+}$ and VSi_{17}^{3+} cluster isomers described above have such analogues. Furthermore, not all of these structures are closed polyhedra; some of them represent either quasi-endohedral structures, in which the metal atom does not form bonds with all silicon atoms, or longitudinal structures.

3.2. Atomic structure and electronic spectra of stable isomers of monoanionic $MeSi_{15}^{-}$ (Me = Sc, V) clusters

Figure 1a shows the stable isomers of the $ScSi_{15}^{-}$ cluster and the scheme of their formation from the stable isomers of the $ScSi_{16}^{+}$ cluster; Table 1 presents the relative energies of the stable isomers with respect to the lowest-energy isomer. Two isomers, Sc-15a-CHAIN1 and Sc-15a-CHAIN2, possess a longitudinal structure in which two small silicon subclusters are connected by a scandium atom. The initial structures for the optimization of these isomers were obtained by removing one silicon atom from the longitudinal

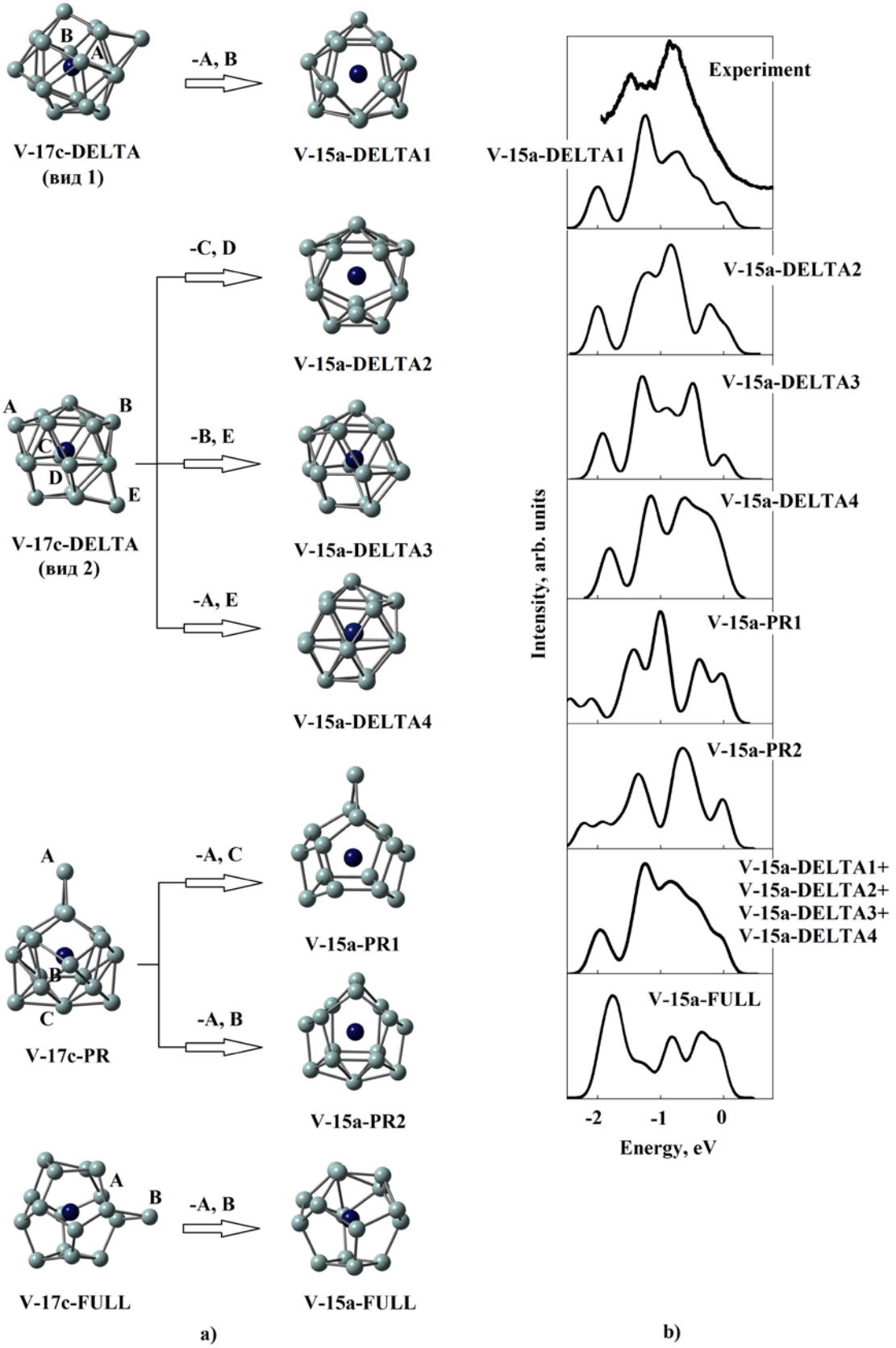

Fig. 2. Spatial structures of the VSi_{17}^{3+} and VSi_{15}^{-} clusters (a) and comparison of the calculated electronic spectra of the VSi_{15}^{-} cluster with the experimental photoelectron spectrum [13] (b). Silicon atoms are shown in gray, and vanadium atoms are shown in blue. V-Si bonds are omitted for clarity

isomers of the $ScSi_{16}^{+}$ cluster – Sc-16c-CHAIN1 and Sc-16c-CHAIN2, respectively. The remaining isomers exhibit an endohedral structure. The endo-structures can be conventionally divided into deltahedral (Sc-15a-DELTA1 and Sc-15a-DELTA2) and prismatic (Sc-15a-PR1 and Sc-15a-PR2) ones. The Sc-15a-DELTA1 isomer is obtained by removing one silicon atom from the Sc-16c-DELTA1 isomer, whereas the Sc-15a-DELTA2 isomer is derived from the Sc-16c-DELTA2 isomer.

The prismatic isomers Sc-15a-PR1 and Sc-15a-PR2 are based on a distorted hexagonal prism with additional silicon atoms. In the Sc-15a-PR1 isomer, all three additional silicon atoms are located above one of the prism bases, while in the Sc-15a-PR2 isomer, two atoms are situated above one of the bases and another one is above the opposite base. The Sc-15a-PR1 isomer is obtained by removing one silicon atom from the Sc-16c-PR1 isomer, and the Sc-15a-PR2 isomer is formed from the Sc-16c-PR2 isomer. The Sc-15a-FULL isomer was obtained after optimizing an initial structure formed from the Sc-16c-FULL isomer by removing one of the vertices at the base of the fullerene-like polyhedron. As a result, the optimized structure became highly distorted. According to the results of all calculations, this isomer is one of the least stable.

The relative stabilities of the various $ScSi_{15}^{-}$ cluster isomers depend on the method used for their optimization. Calculations with the B3LYP functional point to Sc-15a-PR1 as the lowest-energy isomer with a significant energetic advantage. Such a large gap may lead to the conclusion that predominantly or only such structures can be obtained experimentally. In the remaining calculations, the highest average binding energy corresponds to the Sc-15a-DELTA1 isomer. In the calculation utilizing the PBE functional, this isomer has a substantial energy difference from the others and can be considered the most likely to be detected experimentally. Calculations with the B3PW91 and BP86 functionals show a negligible difference in the binding energies of the prismatic Sc-15a-PR1 and Sc-15a-PR2 isomers, suggesting that all three isomers – Sc-15a-DELTA1, Sc-15a-PR1, and Sc-15a-PR2 – could coexist experimentally.

To verify the accuracy of the anionic cluster calculations, the calculated electronic spectra (total densities of electronic states) of each $ScSi_{15}^{-}$ cluster isomer can be compared with the experimental photoelectron spectrum [13] (see Fig. 1b). The calculations showed that the electronic spectrum profile changes insignificantly depending on the functional used; therefore, the figure presents only the spectra obtained using the B3PW91 functional.

A comparison of the calculated and experimental electronic spectra demonstrates good agreement for the Sc-15a-DELTA1 and Sc-15a-PR2 isomers. The positions of the main peaks and their intensity ratios in the calculated spectra of these isomers are consistent with the experimental photoelectron spectrum. The spectra of the remaining isomers differ significantly from the experimental one. For instance, the spectrum of the Sc-15a-DELTA2 isomer features a small maximum near the top of the valence band, which shifts the main maximum toward lower energies. In the spectra of the Sc-15a-PR1 isomer and the longitudinal Sc-15a-CHAIN isomer, which are the most stable according to the B3LYP calculation results, the intensity ratio between the high-energy and low-energy maxima differs greatly compared to the experimental spectrum.

Thus, using the B3LYP functional to optimize the stable isomers of the $ScSi_{15}^{-}$ cluster led to an erroneous overestimation of the average binding energy in the prismatic Sc-15a-PR1 isomer – according to the binding energy ratio of the isomers shown by the B3LYP calculation, the probability of observing the Sc-15a-PR1 isomer in the experiment is the highest. However, the calculated electronic spectrum of Sc-15a-PR1 does not match the experimental photoelectron spectrum [13], which casts doubt on the B3LYP calculation results. The calculation utilizing the PBE functional demonstrated good agreement with the experimental data – the calculated spectrum of the Sc-15a-DELTA1 isomer is in good agreement with the photoelectron one [13]. Nevertheless, by restricting oneself solely to the PBE calculation, one might overlook the Sc-15a-PR2 isomer, whose spectrum also agrees well with the experimental one, providing grounds to suggest the possibility of its experimental realization. Consequently, using the PBE functional to calculate relative binding energies

may lead to an overestimation of the binding energies of deltahedral structures compared to prismatic ones.

In summary, it can be concluded that both isomers of the $ScSi_{15}^-$ cluster (Sc-15a-DELTA1 and Sc-15a-PR2) could be detected experimentally. Figure 1b also shows the cumulative electronic spectrum of these two isomers. As seen in the figure, the cumulative spectrum practically coincides with the experimental photoelectron spectrum [13] in terms of the energy position and relative intensities of both the main maxima and minor features.

For the VSi_{15}^- cluster, seven stable isomers were obtained (Fig. 2a). The isomers having the form of polyhedra with predominantly triangular faces are designated as V-15a-DELTA1, V-15a-DELTA2, V-15a-DELTA3, and V-15a-DELTA4 and can be classified as deltahedral structures. These isomers were produced by optimizing initial structures derived from the deltahedral V-17c-DELTA isomer of the VSi_{17}^{3+} cluster by removing two silicon atoms (see Fig. 2a). During the optimization process, the initial structures changed only slightly. The V-15a-PR1 and V-15a-PR2 isomers can be referred to as prismatic isomers. Their structures are based on a hexagonal prism encapsulating a vanadium atom. These structures were obtained after optimizing an initial structure derived from the V-17c-PR isomer. The V-15a-FULL isomer is a fullerene-like polyhedron. It was formed during the optimization of the initial V-17c-FULL structure lacking two silicon atoms.

According to the B3LYP calculation results, the prismatic isomer V-15a-PR1 is the ground state. The second energetically favorable structure is also prismatic – the V-15a-PR2 isomer. However, the difference in the average binding energies between these structures is quite significant, so based on this calculation, it can be concluded that predominantly V-15a-PR1 isomers can be obtained experimentally. Isomers with deltahedral structures have significantly lower binding energies than the V-15a-PR1 isomer. Calculations using the B3PW91, BP86, or PBE functionals yield results similar to each other and show that the V-15a-DELTA1, V-15a-DELTA2, V-15a-DELTA3, and V-15a-DELTA4 isomers are the most stable structures, while the remaining structures possess radically lower average binding energies. At the same time, the energies of the deltahedral structures V-15a-DELTA1, V-15a-DELTA2, V-15a-DELTA3, and V-15a-DELTA4 are practically identical, which may imply equally probable chances of obtaining them experimentally. The fullerene-like isomer V-15a-FULL transformed into the V-15a-DELTA2 structure during optimization utilizing the B3PW91, BP86, or PBE functionals. This isomer was found to be stable only according to the B3LYP calculation results. The average binding energy in the V-15a-FULL isomer is substantially lower than in the remaining isomers, so the formation of this structure in the experiment can be considered unlikely.

Figure 2b shows the calculated electronic spectra of all isomers and the experimental photoelectron spectrum. As with the $ScSi_{15}^-$ cluster, the electronic spectra obtained from the calculation using the B3PW91 functional are presented. The only exception is the spectrum of the fullerene-like V-15a-FULL isomer. Since this isomer proved to be stable only in the B3LYP calculation, its electronic spectrum was constructed based on the results of that calculation. A comparison of the calculated electronic spectra of the presented isomers with the experimental photoelectron spectrum demonstrates a mismatch between the profiles of the calculated electronic spectrum of the V-15a-PR1 isomer and the photoelectron spectrum. Neither the energy positions of the main maxima nor their relative intensities coincide. This means that the calculation results obtained using the B3LYP functional are not confirmed by the experimental data. Among the spectra of the isomers with a deltahedral structure (V-15a-DELTA1, V-15a-DELTA2, V-15a-DELTA3, and V-15a-DELTA4), the spectrum of the V-15a-DELTA4 isomer shows the best agreement with the photoelectron spectrum – both the energies of the main features of the electronic spectrum and their relative intensities match well. The spectrum of the V-15a-DELTA1 isomer coincides with the experimental one in terms of the energies of the main features but differs in the intensity ratio between them. The spectra of the remaining deltahedral isomers show significantly poorer agreement with the experiment.

Since the calculations showed that the average binding energies of the four isomers (V-15a-DELTA1, V-15a-DELTA2, V-15a-DELTA3, and V-15a-DELTA4) are nearly identical. Their combined spectrum should be compared with the experimental one to evaluate the validity of these results, as all these structures could coexist in the experiment. Figure 2b illustrates this combined spectrum. The computational results provide no grounds to assume that any single isomer has a higher relative abundance than the others; thus, the contributions of all four isomers to the total spectrum were assumed to be equal. As shown in the figure, the total spectrum of the deltahedral isomers (V-15a-DELTA1 to V-15a-DELTA4) matches the experimental photoelectron spectrum [13] regarding the positions of the main spectral features, although some discrepancies in their intensity ratios are observed. This may stem from the probabilistic nature of isomer formation during the experiment. Specifically, the higher the relative abundance of the V-15a-DELTA4 isomer among the synthesized clusters, the closer the calculated intensity ratio will be to the experimental one.

4. Conclusions

Using the $ScSi_{15}^-$ and VSi_{15}^- clusters as examples, we have demonstrated the effectiveness of an algorithm based on the modified Wade–Mingos rule in searching for stable isomers of silicon clusters with encapsulated metal atoms. The algorithm begins with calculating the geometry of the stable isomers of the $ScSi_{16}^+$ and VSi_{17}^{3+} clusters (analogues of *closo*-structures in the Wade–Mingos rule). The initial structures for optimizing the geometry of the $ScSi_{15}^-$ cluster are obtained by removing one silicon atom from the $ScSi_{16}^+$ cluster isomers, while for the VSi_{15}^- cluster, they are derived by removing two silicon atoms from the VSi_{17}^{3+} cluster isomers. During the optimization process, the initial structures change only slightly, which significantly reduces the time required for geometry optimization. As a result of the optimization, stable cluster isomers are obtained, which are analogues of the *nido*- or *arachno*-structures of boranes and carboranes. It is proposed to use several DFT functionals, such as B3LYP, B3PW91, BP86, and PBE, for these calculations.

The second step of the algorithm for searching for stable isomers of silicon-metal clusters is the selection of the most stable cluster isomers. For a reliable selection, the specific features of each of the aforementioned functionals should be taken into account. The use of the B3LYP functional can lead to an overestimation of the relative average binding energies in three-connected structures (e.g., prismatic or fullerene-like ones), whereas in calculations with the PBE functional, they may, conversely, be underestimated. A comparison of the calculated electronic spectra of the $ScSi_{15}^-$ and VSi_{15}^- cluster isomers with experimental photoelectron spectra shows the best agreement for the results obtained in calculations using the B3PW91 and BP86 functionals. Therefore, the choice of these functionals appears to be optimal for calculating the geometric structures of stable cluster isomers and their relative average binding energies.

Conflict of interests

The author declares that he has no known financial conflicts of interest or personal relationships that could have influenced the work presented in this article.

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