Application of computer simulation for research of spatial structure, growth, and electronic properties of zero-dimensional structures on example of silicon-niobium anionic clusters

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Abstract. The results of geometric structure optimization and calculated electron spectra of anion clusters NbSi\textsubscript{n}– (n = 6 – 18) are presented. The calculations were carried out in the terms of density functional theory. Real geometric structures of NbSi\textsubscript{n}– clusters were established by the comparison of calculated and known experimental data. On the basis of the optimized geometries, energetic properties are calculated for the most stable isomers of clusters, including the average binding energy, fragmentation energy, and the second-order difference of energy. The mechanism of cluster formation is considered.

1. Introduction
Metal-silicon clusters are of great interest as the basis of new materials for nanoelectronics, optoelectronics, high-speed electronics. The clusters with a cage structure are considered as building blocks for the design of cluster-assembled materials. About thirty years ago, after the synthesis of fullerene [1], it was suggested that silicon, an isoelectronic element, can form similar structures [2, 3]. However, the first report about the possibility of obtaining silicon clusters with a cage structure appeared only in 2001 [4]. Further studies showed that the metal atom stabilizes confined silicon structures as prism, antiprism, and fullerene-like clusters [5-7]. According to many calculations, the atomic structure and electronic properties of these clusters are depend upon the sort of the metal atom and the cluster size [8-10]. This allows us to consider them to be the elements for the construction of new functional materials of reduced dimension with variable characteristics [11-13].

Since it is extremely difficult to determine the space structure of atomic clusters by experimental methods, the main method of research is the computer simulation. A lot of works devoted to the theoretical study of the space structure of silicon and metal-doped silicon clusters by various methods are known [8-10, 14-19]. However, the adequacy of the results of computer simulation can not be confirmed due to the absence or lack of the relevant experimental data. In addition, for clusters of the same atomic composition the calculation usually results in several stable isomers, often with close energies. Therefore it is difficult to determine uniquely which isomer is most likely obtained in the experiment.
To solve this problem, the most successful method is to combine the results of calculation of the electron spectra of each stable isomer with the known data on the photoelectron spectroscopy of metal-doped silicon anion clusters [10, 20-26]. Since the profile of the density of electronic states radically depends on the specific features of the space structure of the cluster, it is possible to identify isomers actually detected in the experiment due to the comparison.

This paper presents the results of optimizing of the space structure of some anion clusters $\text{NbSi}_n^-$ ($n = 6 – 18$) and their calculated electron-energy spectra. The mechanism of cluster formation is considered and the regularities explaining the increased stability of «magic» clusters are established. Calculated total density of states were compared with the experimental photoelectron spectra [27], it made possible to determine the structure of clusters detected in the experiment.

2. Computational method
Calculations were carried out within the density functional theory (DFT) framework where the Becke’s three-parameter and Lee-Yang-Parr’s gradient-corrected correlation hybrid functional (B3LYP [28, 29]) and 6-311+G(d) basis sets [30] for silicon atoms and DGDZVP [31] for niobium atom were used for a structural optimization as implemented in GAUSSIAN 09 (G09) [32]. The geometric structure visualization was made using GaussView program [32]. The calculation resulted in the energy eigenvalues of each molecular orbital, i.e., energy spectrum, in which each of the molecular orbital corresponds to an energy level. Theoretical spectra were obtained by replacing each energy level with a 0.15 eV wide Gaussian distribution and summing intensity of all distributions at each energy value together. Calculated and experimental spectra were aligned along the energy scale according to the location of the highest occupied molecular orbital.

The average binding energy $E_b$ was calculated by the formula:

$$E_b = \frac{nE(Si) + E(Nb^-) - E(NbSi_n^-)}{n + 1},$$

$E(Si)$ and $E(Nb^-)$ – total energy of free silicon atom and niobium anion, respectively, $E(NbSi_n^-)$ – total energy of the $\text{NbSi}_n^-$ cluster, $n$ – the number of silicon atoms in the cluster.

Fragmentation energy $D(n, n-1)$, which characterizes the relative stability of the cluster, was calculated by the formula:

$$D(n, n-1) = E(NbSi_{n-1}^-) + E(Si) - E(NbSi_n^-),$$

$E(NbSi_{n-1}^-)$ – total energy of the $\text{NbSi}_{n-1}^-$ cluster.

The second-order difference of energies $\Delta_2 E$ was calculated by the formula:

$$\Delta_2 E = E(NbSi_{n-1}^-) + E(NbSi_{n+1}^-) - 2E(NbSi_n^-).$$

$E(NbSi_{n+1}^-)$ – total energy of the $\text{NbSi}_{n+1}^-$ cluster.

$\Delta_2 E$ shows how much more energetically profitable (or not more profitable if $\Delta_2 E < 0$) the formation of clusters with $n$ silicon atoms compared to the formation of two clusters, containing $n+1$ and $n-1$ silicon atom.

For each isomer, the structure was optimized in the three multiplet states – singlet (2S+1=1), triplet (2S+1=3), and quintet (2S+1=5).
3. Results and discussion

The major cluster isomers are indicated by the letter A, the secondary ones by letters B and C. The structures of all isomers described are shown in figure 1.

The 6A isomer is a pentagonal bipyramid with a niobium atom at one of the tops. The niobium atom is displaced from the central axe of the bipyramid. The 6B isomer is a quadrangular bipyramid with a distorted base and the additional silicon atom. The niobium atom is one of the bipyramid tops and forms four Nb-Si bonds. The additional silicon atom forms three Si-Si bonds. The 6C isomer has a longitudinal structure made of two diamond-shaped segments with a shared niobium atom at one top of each segment.

Cluster 7A has the shape of a pentagonal bipyramid with an additional atom of silicon, which forms bonds with two silicon atoms at the base of the bipyramid and with a niobium atom. The bipyramid is distorted so that the bond of one of the silicon atoms in its basis with the niobium atom is weaker than for the others. The 7B isomer is also constructed by adding the additional silicon atom to the pentagonal bipyramid. However, in contrast to the major isomer, the additional atom now forms only three bonds with the silicon atoms: two with atoms from the base of the bipyramid and one with the top atom. The niobium atom forms six Nb-Si bonds with all silicon atoms except the additional one. The 7C isomer was constructed from two segments. One of them is a triangular bipyramid, the second is a triangular pyramid. The niobium atom is shared to them.

The major isomer 8A is constructed by adding two silicon atoms to the pentagonal bipyramid. Additional silicon atoms are located on the adjacent edges of the bipyramid base. The 8B isomer is also constructed by adding two additional silicon atoms in a pentagonal bipyramid, but now the additional atoms are located on the opposite edges of the bipyramid base. Each of them forms two Si-Si bonds. The 8C isomer is constructed of two triangular bipyramids with the shared atom of niobium in one of the tops. This isomer is similar to cluster 7C and is derived from it by adding a silicon atom.

The structure of the 9A isomer is a distorted pentagonal bipyramid with free additional silicon atoms. The niobium atom on one of the bipyramid tops and forms bonds with all silicon atoms. The 9B isomer has a pentagonal bipyramid in the base of its structure like the major isomer. Additional silicon atoms are arranged in such a way that they form bonds mainly with each other and with the niobium atom. The bipyramid is deformed in such a way that one of the silicon atoms in its basis is at a greater distance from the niobium atom than the others. The minimal Si-Si interatomic distance in this cluster is between additional silicon atoms. The 9C isomer structure is similar to the structure of 7C and 8C cluster. This isomer is constructed from two triangular bipyramids with the shared niobium atom in the bases. Another silicon atom forms bonds with the tops of the bipyramids.

The structure of the major isomer 10A is a pentagonal bipyramid with four additional silicon atoms. The 10B isomer has a ring structure in which silicon atoms surround the niobium atom. The 10C isomer is constructed from two segments in the form of a quadrangular bipyramid with the niobium atom in its base.

The major isomer 11A has a similar to the cluster 10A structure – a pentagonal bipyramid with a niobium atom in one of the tops and with five additional silicon atoms. The 11B isomer has a semi-closed structure with an encapsulated niobium atom. The 11C isomer has a structure which is also based on a pentagonal bipyramid with a niobium atom in one of the tops. The bipyramid is distorted considerably stronger than in the major isomer. The 12A isomer has a hexagonal prism structure centered by the niobium atom. This is the first of the major isomers, which structure can be attributed to the endohedral type. The structure of the 12B isomer is a regular hexagonal antiprism. In the structure of the 12C isomer, the niobium atom forms Nb-Si bonds with all silicon atoms. The three most stable NbSi$_{13}$ cluster isomers have a structure based on a hexagonal prism encapsulated by a niobium atom similar to the major isomer of NbSi$_{13}$ cluster. The major 13A isomer has a structure that can be viewed as a hexagonal prism, between the bases of which an additional silicon atom is placed outside. As a result, the prism bases deform. In the 13B isomer, an additional silicon atom
Figure 1. Geometric structures of $\text{NbSi}_n$ ($n = 6 \rightarrow 18$) clusters. Black ball – niobium atom, grey balls – silicon atoms. Numbers indicate the difference between the average building energies of an isomers B and C from the isomer A (in eV/atom).
forms two bonds with the atoms of one of the prism edge. In the 13C isomer, an additional silicon atom forms three Si-Si bonds, the prism is strongly deformed. The bond between the niobium atom and the additional silicon atom is weakened.

The structure of 14A isomer is a polyhedron, which can be called fullerene-like. The 14B isomer is constructed by adding two silicon atoms to the hexagonal prism. Additional silicon atoms are located above one of the prism bases. At the same time the prism bases are considerably deformed.

The 14C isomer is also constructed from a hexagonal prism by the addition of two silicon atoms, which form two bonds with the atoms on the opposite edges of the one of the bases. Cluster 15A is derived from a cluster 14C by adding a single silicon atom, so this structure can be seen as a distorted hexagonal prism with three additional silicon atoms. The 15B isomer has a shape of fullerene-like polyhedron with quadrangular and pentagonal faces. The 15C isomer is constructed by adding a silicon atom to the 14C cluster like the major isomer. As well as this structure can be seen as a hexagonal prism with three additional silicon atoms. Two additional silicon atoms form two bonds with the atoms of one base. The third forms bonds with all silicon atoms from the other base of the prism. The niobium atom forms thirteen Nb-Si bonds.

The isomers 16A, 16B and 16C have a fullerene-like structure. In 16A and 16B isomers one of the silicon atoms is located at a much greater distance from the niobium atom than the rest. The 16C isomer has the most proper structure of all these fullerene-like isomers. In the structure of this isomer the Nb-Si distance for two silicon atoms is significantly greater than for the rest. Three most stable isomers of NbSi\textsubscript{17} and NbSi\textsubscript{18} clusters have similar structures constructed by adding the silicon atoms to a fullerene polyhedron similar to cluster 16A.

Analyzing the described structures, it is possible to note that for clusters with \( n = 7 - 11 \) the major structure is the pentagonal bipyramid, similar to the major isomer of the NbSi\textsubscript{6} cluster. Large clusters are sequentially formed by adding the additional silicon atoms to the bipyramid. The existence of endohedral structures in NbSi\textsubscript{n} (\( n = 6 - 18 \)) clusters series becomes possible starting from \( n = 12 \). The stable structure of the prism encapsulated by the niobium atom is formed, which can serve as the elementary block for the construction of larger nanostructures by the type of nanowires. The prism serves as a basis for the formation of the major and secondary clusters isomers with \( n = 13 - 15 \). The fullerene-like NbSi\textsubscript{16} cluster is the base for constructing larger clusters with \( n = 17, 18 \). This suggests that fullerene-like clusters can form one-dimensional structures and nanocrystals with a structure similar to silicon clathrates [33].

The dependence of the average binding energy \( E_b \) in the major isomers of NbSi\textsubscript{n} (\( n = 6 - 18 \)) clusters on the number of silicon atoms is represented in figure 2. In \( n = 6 - 16 \) interval the average binding energy increases smoothly as the cluster increases. The jump-like increase is observed at \( n = 12 \), when there is a transition to endohedral structures. The growth of \( E_b \) is smooth again up to \( n = 16 \), from \( n = 17 \) the decrease of this characteristic begins. Obviously, this is due to the specifics of NbSi\textsubscript{17} and NbSi\textsubscript{18} cluster structure: they are constructed by adding silicon atoms to the NbSi\textsubscript{16} cluster, so the bonds of the additional atoms with the rest are weakened. The decrease of the bonding energy for clusters with \( n = 12, 13 \), constructed by adding the additional silicon atom to NbSi\textsubscript{12} cluster and in the area with \( n = 8, 9 \) is also explained by the similar reasons.

Fragmentation energy \( D(n, n - 1) \) maxima correspond to NbSi\textsubscript{12}, NbSi\textsubscript{14} and NbSi\textsubscript{16} clusters (figure 2). The lowest values of \( D(n, n - 1) \) correspond to clusters that were constructed by adding the silicon atoms to the smaller size clusters. The bonds of the additional atoms with the basic silicon structure and the niobium atom are weaker, than those between the atoms of the silicon structure itself. So their "separation" requires less energy than to separate one silicon atom from
Figure 2. Size dependence of the average binding energy, fragmentation energy and second-order differences energies for the lowest-energy structures of \( \text{NbSi}_n \) \((n = 6 - 18)\) clusters.
clusters with high fragmentation energy. Therefore, it is clear why the lowest values of \( D(n, n-1) \) correspond to \( \text{NbSi}_9 \), \( \text{NbSi}_{13} \), \( \text{NbSi}_{17} \) and \( \text{NbSi}_{18} \) clusters.

The dependence of the second-order difference of energy \( \Delta_2E \) on the number of silicon atoms in the cluster is shown in figure 2. This parameter allows to estimate the stability of this cluster in comparison with the neighboring by the number of silicon atoms. The \( \Delta_2E \) maxima correspond to clusters with \( n = 10, 12, 14 \) and 16, the main maximum falls on the first \( \text{NbSi}_{12} \) endohedral cluster in this series.

The analysis of all the above parameters shows that \( \text{NbSi}_{12} \) cluster is "magic" in \( \text{NbSi}_n \) clusters series. The increased relative stability of this cluster can be explained under the Reveles and Khanna hypotheses [34]. According to this hypothesis, a free electron gas in the clusters is taken into consideration. Each silicon atom gives one valence electron, and the metal atom – all valence electrons, including \( d \)-electrons, into gas. The silicon-metal clusters containing 18 electrons (18-electron rule) or 20 electrons (20-electron rule) are the most stable. The increased stability of \( \text{NbSi}_{12} \) cluster is explained by the 18-electron rule; free electron gas is formed by one electron from each silicon atom, five electrons from the niobium atom and one additional electron, because the cluster is anionic.

To determine the structure of the isomers, detected in the experiment, the electron spectra of each cluster were calculated. The comparison of the calculated and known experimental photoelectron spectra [27] was made (figure 3). As can be seen from figure 3, there is a good agreement between the calculated electron spectra of the major isomers and the experimental data. It indicates that such structures were experimentally detected. In the case of \( \text{NbSi}_9 \) and \( \text{NbSi}_{18} \) clusters, which have two isomers with close average binding energies, it is possible to note good agreement for the spectra of both isomers with the experimental spectrum. This indicates that both isomers could be detected in the experiment.

4. Conclusions

For clusters \( \text{NbSi}_n \) with \( n = 6 - 11 \), the pentagonal bipyramide is the basis of the structure. The existence of endohedral structures in \( \text{NbSi}_n \) clusters series becomes possible starting from \( n = 12 \). The stable structure of the prism, encapsulated by the niobium atom, is formed in this case. It can be used as the elementary block for the construction of larger nanostructures. Clusters with \( n = 13 - 15 \) are formed by adding the silicon atoms to a prism similar to \( \text{NbSi}_{12} \) cluster. \( \text{NbSi}_{16} \) cluster with fullerene-like structure is the basis for constructing the larger clusters with \( n = 17, 18 \). This suggests that \( \text{NbSi}_{16} \) fullerene-like clusters can form one-dimensional structures, as well as nanocrystals with a structure similar to silicon clathrates. \( \text{NbSi}_{12} \) cluster is «magic» in the series of silicon-niobium anion clusters. Its increased stability can be explained in the terms of 18-electron rule.

The calculated electron spectra of the major isomers of all clusters are in a good agreement with experimental photoelectron spectra. It indicates that such structures were detected experimentally.

During the calculations, the computing resources of the Voronezh State University Supercomputer Center were used.
Figure 3. Comparison of the calculated electron spectra of $\text{NbSi}_n^-$ ($n = 6 - 18$) clusters with experimental photoelectron spectra [27]. The location of the higher occupied molecular orbital is taken as the origin of counting.
5. References

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