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Theoretical study of isoelectronic $\text{Si}_n^M$ clusters ($M=\text{Sc}^-,\text{Ti},\text{V}^+; \ n=14−18$)

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We study, from first-principles quantum mechanical calculations, the structural and electronic properties of several low-lying energy equilibrium structures of isoelectronic $\text{Si}_n^M$ clusters ($M=\text{Sc}^-,\text{Ti},\text{V}^+$) for $n=14−18$. The main result is that those clusters with $n=16$ are more stable than its neighbors, in agreement with recent experimental mass spectra. By analyzing the orbital charge distribution and the partial orbital density of states, that special stability is rationalized as a combination of geometrical (near spherical cage-like structure for $n = 16$) and electronic effects ($l$-selection rule of the spherical potential model). The structures of the two lowest energy isomers of $\text{Si}_{16}^M$ are nearly degenerate, and consist of the Frank-Kasper polyhedron and a distortion of that polyhedron. The first structure is the ground state for $M=\text{V}^+$, and the second is the ground state for Ti and Sc$^-$. For the lowest energy isomers of clusters $\text{Si}_n^M$ with $n=14−18$, we analyze the changes with size $n$, and impurity $M$ of several quantities: binding energy, second difference of total energy, HOMO-LUMO gap, adiabatic electron affinity, addition energy of a Si atom, and addition energy of an $M$ impurity to a pure $\text{Si}_n$ cluster. We obtain good agreement with available measured adiabatic electron affinities for $\text{Si}_n\text{Ti}$.

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I. INTRODUCTION

Promising applications of silicon nanoclusters, both pure and doped with transition-metal atoms, have originated many studies and raised interesting questions about their electronic and structural properties. Pure $\text{Si}_n$ clusters, as inferred from experimental measurements, are prolate for $n < 27$ and become near spherical for $n > 27$, which has been corroborated by computational studies. 12 On the other hand, the growth behavior of transition-metal-doped silicon clusters seems to follow a different pattern than pure Si clusters. There are several calculations of $\text{Si}_n^M$ structures for various cluster sizes and impurity atoms or ions. Kumar and co-workers have found that open basket-like structures are the most favorable for $n=8−12$, while for $n=13−16$ the metal atom is completely surrounded by Si atoms. The optimal cage for many of the metal-encapsulated silicon clusters, occurs at $n=16$. These predictions were later confirmed indirectly by experiments. Thus, experiments on photodissociation of $\text{Si}_{16}^M$ clusters indicate that, for $M=\text{Cr}$, encapsulation of Cr occurs at $n=15−16$. A mass spectrometric stability study of binary $\text{MS}_n$ clusters, with $\text{S}=\text{Si},\text{Ge},\text{Sn},\text{Pb}$, and $M=\text{Cr},\text{Mn},\text{Cu},\text{Zn}$, reveals interesting trends. For example, Cr-doped silicon cationic clusters are peculiarly abundant at sizes $n=15$ and 16, as already obtained by Beck twenty years ago. Other experiments, combining mass spectrometry, a chemical probe method, and photoelectron spectroscopy, revealed that one metal atom ($M=\text{Ti},\text{Hf},\text{Mo},\text{W}$) can be encapsulated inside a $\text{Si}_n$ cage at $n \approx 15$. In recent mass spectrometry experiments, Nakajima and co-workers have shown the size-selective formation of $\text{Si}_{16}^\text{Sc}^-,\text{Si}_{16}^\text{Ti},\text{Si}_{16}^\text{V}^+$ clusters. More details about these experiments, combining mass spectrometry, anion photoelectron spectroscopy, and adsorption reactivity towards $\text{H}_2\text{O}$, have been published very recently. Concerning the special stability of $\text{Si}_{16}^M$ for the type of $M$ impurity involved in the experiments of Nakajima and co-workers, we have found very few works. Kumar and Kawazoe obtained for $\text{Si}_{16}^\text{Ti}$ a truncated tetrahedral structure, called the Frank-Kasper polyhedron. In further studies (see Ref. 2 for a review), Kumar and co-workers explained the special stability of that cluster in terms of the spherical potential model as a combination of geometrical and electronic shell effects. In the work of Reveles and Khana, cationic, neutral, and anionic doped clusters $\text{Si}_n^M$ with $n=15−17$, were optimized. These authors obtained that $\text{Si}_{16}^M$ clusters with $M=\text{Sc}^-,\text{Ti},V^+$, adopt the FK-polyhedron structure in their ground state, having the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap and the atomization energy larger than the same clusters within other charge states, which is a manifestation of stability against changes in the electronic charge. The explanation of this fact was based on a 20 electron rule, assuming that only one electron is contributed by a Si atom to the valence manifold when that Si atom is bonded to the metal atom.

We have studied recently $\text{Si}_n^\text{Sc}^-$ clusters in the range $n=14−18$, resulting at $n=16$ a positive peak for the second difference in the total energy [see Eq. (4)], which is related directly to the higher abundance of that cluster in the mass spectrometry experiment. In order to explain these experiments for $M=\text{Ti}$ and $V^+$, and to reveal the roll of the impurity, we have performed in the present work systematic stud-
ies of the relative stability of Si$_n$ and Si$_nM$ for $n=14–18$ and $M=\text{Sc}^-,\text{Ti}$, and V$^+$. We find that for $n=16$ these doped clusters are more stable than its neighbors clusters, in agreement with the experiments. In the course of searching for equilibrium geometries we have found a new lowest energy isomer of Si$_{16}\text{Sc}^-$ which is nearly degenerate with the one reported in our preliminary work.

In addition to geometries and stability, we have studied other properties of Si$_nM$ clusters. For these doped clusters, we will compare the binding (atomization) energy per atom,

$$E_b(Si_nM) = (E(M) + nE(Si) - E_i(Si_nM))/(n+1),$$

the addition energy of an M impurity to a Si$_n$ cluster,

$$E_{ad}^{M}(Si_nM) = E(Si_n) + E(M) - E_i(Si_nM),$$

the addition energy of a Si atom to a Si$_{n-1}$M cluster,

$$E_{ad}^{Si}(Si_{n-1}M) = E(Si) - E_i(Si_{n-1}M),$$

and the energy difference between the eigenvalues of the lowest unoccupied (LUMO) and the highest occupied (HOMO) molecular orbital, $\Delta_{n}^{\text{opt}}$. In the expressions above $E(X)$ is the total energy of system X. The second difference energy $\Delta_2E_n$ is equivalent to $E_{ad}^{Si}(Si_{n+1}M) - E_{ad}^{Si}(Si_{n+1}M)$. This second difference is proportional to log($I_n/I_{n+1}$), where $I_n$ is the intensity of the Si$_nM$ signal in the experimental mass spectra. In order to compare with existing experimental values, we calculated the adiabatic electron affinity of neutral Si$_n\text{Sc}$, Si$_n\text{Ti}$, and Si$_n\text{V}$. To do that, we have also optimized the structures of Si$_n\text{Sc}$, Si$_n\text{Ti}^-$, Si$_n\text{V}^-$, and Si$_n\text{V}^+$ starting with several low-lying energy isomers of conveniently charged Si$_nM$ clusters.

In Sec. II we outline briefly the computational method. In Sec. III we present and discuss the results. Firstly, in Sec. III A we present the geometrical structures of several low-lying isomers, which are compared to previous results. In Sec. III B we discuss the electronic energy trends of the lowest energy isomer of Si$_n\text{Sc}^-$, Si$_n\text{Ti}$, and Si$_n\text{V}^+$ clusters. Conclusions of this study are given in Sec. IV.

### II. COMPUTATIONAL PROCEDURE

We have used the density functional theory (DFT) code SIESTA within the generalized gradient approximation as parametrized by Perdew, Burke, and Ernzerhof for the exchange-correlation effects. Details about the pseudopotentials and basis sets are the same as in our previous work. Specifically, we used norm conserving scalar relativistic pseudopotentials in their fully nonlocal form, generated from the atomic valence configuration $3s^23p^2$ for Si (with core radii 1.9 a.u. for $s$ and $p$ orbitals), and the semicore valence configuration $4s^23p^23d^6$ for Sc ($n=1$), Ti ($n=2$), and V ($n=3$) (all of them with core radii, in a.u., 2.57, 1.08, and 1.37 for $s$, $p$, and $d$ orbitals, respectively). In the present calculations we used a double-$\zeta$ basis $s,p$ (for Si) and $s,p,d$ (for $M$), with single polarization $d$ (for Si) and $p$ for $M$, having maximum cutoff radius, in a.u., 7.47 (Si), 8.85 (Sc), 8.45 (Ti), and 8.08 (V). The basis set and pseudopotentials of $M$ atoms were used and tested before in Refs. 44 and 45. The grid fineness is controlled by the energy cutoff of the plane waves that can be represented in it without aliasing (120 Ry in this work).

As a further test of the pseudopotentials, basis sets, and cutoff energy, we have calculated the relative stability, bond distance, and dipole moment of different spin states of Si$^nM^+$ monosilicides ($M=\text{Sc}^-,\text{Ti},\text{V}^+$; $\nu=\pm1,0$), and compared these values with those calculated recently by Wu and Su using a standard all-electron density functional method. In all cases the spin multiplicity of the lower energy state is the same as in the Wu and Su calculations. Specifically, we obtained a triplet state for Si$\text{Sc}^-$ and a quintuplet for Si$\text{Ti}$ and Si$\text{V}^+$, with bond distances 2.50, 2.51, and 2.51 Å, respectively, to be compared with the values 2.43, 2.45, and 2.50 Å, respectively, obtained by Wu and Su. The calculated electric dipole moments for the neutral species are, in Debye, 3.17 D (Si$\text{Sc}$ quadruplet), 3.36 D (Si$\text{Ti}$ quintuplet), and 3.13 D (Si$\text{V}$ sextuplet), to be compared with the values 3.62, 3.58, and 3.20 D, respectively, reported by Wu and Su.

The equilibrium geometries result from an unconstrained conjugate-gradient structural relaxation using the DFT forces. We try out several initial structures for each cluster (typically more than twenty) until the force on each atom was smaller than 0.010 eVÅ. These initial geometries were constructed from previous works, from our optimized geometries of neutral Si$_n$ with a Sc$^-$, Ti, or V$^+$ atom added at different sites, and from many other configurations that we have invented.

In order to identify the isomers of a particular Si$_nM$ cluster, we have ordered the isomers according to their energy difference with the lowest energy one and labeled clusters 1, 2, 3,...starting with the ground state. This number we refer to as the ordinal number of the isomer.

### III. RESULTS AND DISCUSSIONS

#### A. Geometry of Si$_nM$ doped clusters ($M=\text{Sc}^-,\text{Ti},\text{V}^+$; $n=14–18$)

The equilibrium geometry of a few low-lying energy isomers of isoelectronic Si$_nM$ doped clusters ($M=\text{Sc}^-,\text{Ti},\text{V}^+$) is represented in Figs. 1–5 for the sizes $n=14–18$, respectively. In all these structures the M impurity is surrounded by Si atoms. For each structure and type of impurity ($M$) are given the total energy difference with respect to the lowest energy isomer, the HOMO-LUMO gap, and the ordinal number for that isomer, which was described earlier in Sec. II. Most structures are common to the three types of impurity, but the ordinal of the isomer changes in several cases from an impurity to the other. Specifically, the structure of the first isomer is the same for all Si$_nM$ clusters, except for Si$_nV^+$ with $n=16–18$. The first isomer of Si$_nV^+$, for $n=16,17$, is the second isomer of Si$_nM$ ($M=\text{Sc}^-,\text{Ti}$). In general, the structure of the third, and higher, isomers of Si$_nV^+$ and Si$_nTi$ depart from the sequence for SiSc. On the other hand, there is no relation between the structures of Si$_nM$ in Figs. 1–5 and...
those of Si or Si$_{n+1}$ obtained in our previous work.$^{34}$ A common structural motif for the ground state structure of Si$_{nM}$ with $n = 14, 17, 18$, is a distorted hexagonal prism (DHP) of Si atoms surrounding the $M$ impurity, with additional Si atoms and dimers decorating the lateral prism faces.$^{34}$ That DHP motif resembles the structures $C_s$ (ground state) and $C_{2h}$ reported recently for Si$_{12}$Ni.$^{20}$ That structure $C_s$ has been found as the new ground state of Si$_{12}$Ni, instead of the $C_{5v}$ symmetric Frank-Kasper structure, which was believed the lowest energy isomer, but it is unstable.

Similarly to the case of pure Si$_n$ clusters discussed by Hellmann and co-workers$^{13}$ and in previous works,$^9$-$^{11}$,$^{34}$ several isomers of doped Si$_{nM}$ clusters are found in a narrow energy interval. The determination of the ground state geometry is then a difficult task, and calculated properties which are not directly related to the total energy will be averaged with adequate weights in order to check against experimental determinations at finite temperature.$^{13}$

In Table I are given the average bond distances Si-$M$ and Si-Si for several isomers of Si$_{nM}$ clusters. These distances are smaller for Si$_{16}$ and Si$_{15}$ clusters, and, for a given size $n$, the distance Si-$M$ decreases smoothly from Si$_n$Sc$^-$ to Si$_n$Ti to Si$_n$V$^+$, following the same tendency as the metallic bond radius of the atomic impurities, namely 1.63, 1.45, and

![FIG. 1. (Color online) Geometry of the few lowest energy isomers of Si$_{14}$M clusters. The index I in the label 14-I indicates the different geometries. Below each structure is given, for the three different types of dopant, the total energy difference with respect to the lowest energy configuration (eV), the HOMO-LUMO gap (eV), and the ordinal number of the isomer. In all structures the spin state is a singlet except for 14-VIII* which is a triplet (indicated by an asterisk).](image)

![FIG. 2. (Color online) Same as Fig. 1 for $n = 15$.](image)
1.31 Å for Sc, Ti, and V, respectively. The state of charge also has influence on the overall size of these clusters, as noted by Koyasu et al., being the anions larger than the cations. There are two or more maxima in the distributions of Si-M distances, depending on the isomeric geometry. For example, the maxima of $d_{\text{min}}^{M}$ for the isomers 16-I to 16-IV of $\text{Si}_{16}^{M}$ are indicated in Fig. 7, and correspond to well defined radial shells of Si atoms around the central M impurity. Thus, for the isomer 16-II (FK geometry) there are two atomic shells composed of 4 and 12 Si atoms, respectively, the first shell forming a perfect tetrahedron. It is interesting to note that the electronic charge distribution of a perfect tetrahedral molecule $X_{4}$ have zero dipole and quadrupole electric moments, and then behaves approximately as a spherical charge distribution.

The average Si-Si distance is also smaller for $\text{Si}_{16}^{M}$ and $\text{Si}_{15}^{M}$ clusters, and, for a given size and structure, is smaller for $\text{Si}_{n}^{V^{+}}$ than $\text{Si}_{n}^{\text{Ti}}$ and than $\text{Si}_{n}^{\text{Sc}^{-}}$ clusters. The distribution of Si-Si distances shows two maxima for $n \leq 16$, at about (roughly) 2.5 and 4.5 Å which are larger than the first and second neighbor Si-Si distances in bulk Si, respectively. In some cases there are three maxima, like in the 14-VIII isomer [the only structure which prefers spin triplet instead of spin singlet multiplicity (see below Sec. III A 1)], or the fullerene type 16-IV isomer, with maxima at about 2.5, 3.8, and 5.1 Å, in both cases. For $n=17,18$ isomers there is only one broad maximum in the Si-Si distance distributions.

I. $\text{Si}_{14}^{M}$ ($M=\text{Sc}^{-},\text{Ti},\text{V}^{+}$)

The structure of several low energy isomers of $\text{Si}_{14}^{M}$ clusters are represented in Fig. 1. For the first isomer of $\text{Si}_{14}^{M}$ we obtain a DHP structure decorated with a Si$_{2}$ dimer on a side. That structure is similar to the first isomer of ZrSi$_{14}$ found by Lu and Nagase, and to the second isomer of ZrSi$_{14}$ found by Wang and Han. The second, third, and fourth isomers of $\text{Si}_{14}^{\text{Sc}^{-}}$, with structures 14-II, 14-III, and...
respectively, were obtained by Torres et al. Not among these structures is the one for the second isomer of Si$_{14}$Ti or Si$_{14}$V$^+$, but 14-IV is adopted by the third isomer of Si$_{14}$Ti, and the fifth isomer of Si$_{14}$V$^+$. The structure of the second isomer of Si$_{14}$Ti is similar to the third isomer of Si$_{14}$V$^+$ and the seventh isomer of Si$_{14}$Sc$^-$. The structure of the fourth isomer of Si$_{14}$Ti, which is similar to the ninth isomer of Si$_{14}$Sc$^-$, was obtained by Kawamura et al. as the fifth isomer of Si$_{14}$Cr, and by Wang and Han as the first isomer of Si$_{14}$Zr.

The structure of the second isomer of Si$_{14}$V$^+$ is shared with the sixth isomer of Si$_{14}$Ti and the 21st of Si$_{14}$Sc$^-$, and deserves special attention because it is the only case whose spin multiplicity is a triplet. The triplet-singlet energy difference for the optimized structure 14-VIII of Si$_{14}$M is 0.05, 0.18, and 0.42 eV for M=Sc$^-$, Ti, and V$^+$, respectively. The structure 14-VIII resembles the second isomer of Si$_{14}$Ti given by Kawamura et al. The structure 14-V, which is adopted by the fourth isomer of Si$_{14}$V$^+$ and the fifth of Si$_{14}$Sc$^-$, is not found among the low-lying energy isomers of Si$_{14}$Ti.

We have tested other structures of Si$_{14}$Ti given in the literature. Thus, the first isomer of Si$_{14}$Ti reported by Kawamura et al. corresponds to our twelfth, seventh, and ninth isomers for Sc$^-$, Ti, and V$^+$ impurities, respectively, with the energy difference 0.57, 0.53, and 0.39 eV, and spin zero. When we optimize that structure for the triplet spin state, there results a triplet-singlet energy difference of 0.62, 0.74, and 0.62 eV for M=Sc$^-$, Ti, and V$^+$, respectively. Similarly, the structure of the first isomer of Si$_{14}$Ti reported by Kawamura et al. corresponds to our isomers 16th, 10th, and 11th of Si$_{14}$M, with energy difference (with respect to the ground state) 0.63, 0.76, and 0.68 eV, and triplet-singlet energy difference 0.27, 0.10, and 0.09 eV, for M=Sc$^-$, Ti, and V$^+$, respectively. Finally, the cubic structure reported for the ground state of Si$_{14}$Fe corresponds to our 27th, 12th,

The structure 14-V, which is adopted by the fourth isomer of Si$_{14}$V$^+$ and the fifth of Si$_{14}$Sc$^-$, is not found among the low-lying energy isomers of Si$_{14}$Ti.

The structure of the second isomer of Si$_{14}$Ti (14-VI) is similar to the third isomer of Si$_{14}$V$^+$ and the seventh isomer of Si$_{14}$Sc$^-$. The structure of the fourth isomer of Si$_{14}$Ti, which is similar to the ninth isomer of Si$_{14}$Sc$^-$, was obtained by Kawamura et al. as the fifth isomer of Si$_{14}$Cr, and by Wang and Han as the first isomer of Si$_{14}$Zr.

The structure of the second isomer of Si$_{14}$V$^+$ (14-VIII) is shared with the sixth isomer of Si$_{14}$Ti and the 21st of Si$_{14}$Sc$^-$, and deserves special attention because it is the only case whose spin multiplicity is a triplet (see below, Sec. III B 2). The triplet-singlet energy difference for the optimized structure 14-VIII of Si$_{14}$M is 0.05, 0.18, and 0.42 eV for M=Sc$^-$, Ti, and V$^+$, respectively. The structure 14-VIII resembles the second isomer of Si$_{14}$Ti given by Kawamura et al. The structure 14-V, which is adopted by the fourth isomer of Si$_{14}$V$^+$ and the fifth of Si$_{14}$Sc$^-$, is not found among the low-lying energy isomers of Si$_{14}$Ti.

We have tested other structures of Si$_{14}$Ti given in the literature. Thus, the first isomer of Si$_{14}$Ti reported by Kawamura et al. corresponds to our twelfth, seventh, and ninth isomers for Sc$^-$, Ti, and V$^+$ impurities, respectively, with the energy difference 0.57, 0.53, and 0.39 eV, and spin zero. When we optimize that structure for the triplet spin state, there results a triplet-singlet energy difference of 0.62, 0.74, and 0.62 eV for M=Sc$^-$, Ti, and V$^+$, respectively. Similarly, the structure of the first isomer of Si$_{14}$Ti reported by Kawamura et al. corresponds to our isomers 16th, 10th, and 11th of Si$_{14}$M, with energy difference (with respect to the ground state) 0.63, 0.76, and 0.68 eV, and triplet-singlet energy difference 0.27, 0.10, and 0.09 eV, for M=Sc$^-$, Ti, and V$^+$, respectively. Finally, the cubic structure reported for the ground state of Si$_{14}$Fe corresponds to our 27th, 12th,
and 13th isomers of Si$_{14}$M for $M$=Sc$^-$, Ti, and V$^+$, respectively, with energy difference 1.43, 1.09, and 0.83 eV, and triplet-singlet energy difference 0.30, 0.20, and 0.08 eV, respectively. That structure was given by Kawamura et al.\textsuperscript{18} as the third isomer of Si$_{15}$Ti.

2. Si$_{15}$M ($M$=Sc$^-$, Ti, V$^+$)

A few low-lying energy isomers of Si$_{15}$M are represented in Fig. 2. Structure 15-I for the ground state is similar to the ones obtained previously for the second isomer of Si$_{15}$Ti,\textsuperscript{18} and for the third isomer of Si$_{15}$Cr.\textsuperscript{17} The second isomer of Si$_{15}$Sc$^-$ and Si$_{15}$Ti (structure 15-II) is similar to the first isomer of Si$_{15}$Ti in Ref. 18. The second isomer of Si$_{15}$V$^+$ (structure 15-III, shared with the third isomer of both Si$_{15}$Sc$^-$ and Si$_{15}$Ti), is similar to the second isomer of Si$_{15}$Cr.\textsuperscript{17} The structure 15-IV is formed by adding a Si atom to the lateral dimer of structure 14-I, resulting in a Si$_3$ unit which binds laterally to the DHP structure. That geometry resembles the sixth and eighth isomers of neutral ZrSi$_{15}$ of Ref. 19. The structure 15-V of the third isomer of Si$_{15}$V$^+$, which is shared with the seventh isomer of Si$_{15}$Sc$^-$ and the fifth isomer of Si$_{15}$Ti, was obtained previously by Kawamura et al.\textsuperscript{18} as the third isomer of Si$_{15}$Ti.

The structures 15-I and 15-II remind the cubic structure of Si$_{14}$Fe\textsuperscript{16,22} with an additional Si atom. That cubic structure was also obtained by Kawamura et al.\textsuperscript{17} for the third isomer of Si$_{15}$Cr.

3. Si$_{16}$M ($M$=Sc$^-$, Ti, V$^+$)

Several low-lying energy isomers of Si$_{16}$M are represented in Fig. 3. For the first and second isomers of Si$_{16}$M we obtain the structures 16-I and 16-II, and they are practically degenerate, especially for $M$=V$^+$. Note that structure 16-I was not found in our preliminary work\textsuperscript{34} for Si$_{16}$Sc$^-$. Structures 16-I and 16-II were obtained by Kumar and co-workers\textsuperscript{16,18} as the second and first isomers, respectively, of Si$_{15}$Ti. The structure 16-II is the Frank-Kasper (FK) polyhedron, with a nearly spherical structure and $T_h$ symmetry.\textsuperscript{2} It consists of a central M atom surrounded by 16 Si atoms within two closely spaced shells: one with 12 atoms (all equidistant from central), and another shell with 4 Si atoms forming a perfect tetrahedron. The structure 16-I can be seen as a distortion of the FK polyhedron (16-II), with the triangle along the threefold symmetric axis rotated by 30°. The structure 16-III can be seen as three pentagons in three parallel layers plus a capping Si atom, or, equivalently, as a polygonal prism with the rectangular faces capped with a Si atom, plus a Si atom capping a pentagonal basis. That structure is not stable for Si$_{16}$V$^+$, and evolves toward the FK geometry when we take 16-III as the initial geometry of Si$_{16}$V$^+$. The third isomer of Si$_{16}$V$^+$ adopts the structure 16-IV, which is shared with the fourth isomer of Si$_{16}$Sc$^-$ and Si$_{16}$Ti. It coincides with the fullerene-like structure obtained previously as the third isomer of Si$_{15}$Ta$^+$,\textsuperscript{18} and the first isomer of Si$_{16}$W.\textsuperscript{21} The interplay between the electronic properties of $n=16$ isomers and their symmetry will be analyzed in Sec. III B 3.

4. Si$_{17}$M ($M$=Sc$^-$, Ti, V$^+$)

A few low-lying energy isomers of Si$_{17}$M are represented in Fig. 4. We are not aware of previous calculations reporting that type of structure, except our previous work.\textsuperscript{34} In the structures 17-I and 17-II a dimer and a trimer, respectively, binds the lateral faces of the DHP motif. We note that the sequences of V$^+$ and Ti doped isomers departs considerably from the sequence for Sc$^-$ doped clusters, and the apparent tendency towards sphericity observed for the low-lying energy isomers of Si$_{15}$M and Si$_{16}$M disappears.

5. Si$_{18}$M ($M$=Sc$^-$, Ti, V$^+$)

Several low energy isomers of Si$_{18}$M are represented in Fig. 5. The lowest energy isomer for Si$_{18}$Sc$^-$ and Si$_{18}$Ti has the structure 18-I, which can be seen as a DHP structure with three silicon dimers on alternating lateral faces. Instead, the first isomer of Si$_{18}$V$^+$ adopts the more elongated structure 18-V. As for Si$_{17}$M clusters, the low-lying isomers of Si$_{18}$M departs from sphericity more than the Si$_{17}$M and Si$_{16}$M clusters. Thus, in the range $n=14$–18, the optimal coordination of the $M$ impurity to Si atoms of Si$_n$M clusters is found for $n=15,16$.

B. Electronic properties of Si$_n$M clusters ($M$=Sc$^-$, Ti, V$^+$; $n$=14–18)

1. Energies and stability

In Fig. 6 is represented, for the lowest energy isomer of Si$_n$M clusters, the evolution with the cluster size $n$ of several quantities: the binding energy per atom [$E_b$, Eq. (1)], the addition energy of an $M$ impurity to a Si$_n$ cluster [$E_{ad}$, Eq. (2)], the addition energy of a Si atom to a Si$_{n-1}$M cluster [$E_{ad}^2$, Eq. (3)], the second difference of the total cluster energy [$\Delta_2E_n$, Eq. (4)], and the energy difference between the LUMO and HOMO orbital eigenvalues, $\Delta_{\text{pop}}$. For comparison purposes, these quantities are also represented for pure Si$_n$ clusters. The ground state energy of pure Si$_n$ clusters was taken from our preliminary work.\textsuperscript{34} As a matter of fact, we have calculated again the low-lying energy isomers of Si$_n$ and found some new isomers. In particular, for the ground state of Si$_{14}$ we obtain a new structure with 0.07 eV lower energy than the ground state structure reported previously.\textsuperscript{34}

That new structure is similar to the second isomer of Si$_{14}$ found by Bazterra and co-workers.\textsuperscript{15} We can see for the various properties plotted in Fig. 6 a completely different trend with size of pure versus doped Si clusters.

In panel (b) of Fig. 6 we see that $\Delta_2E_n$ has a positive peak at $n=16$ for $M$=Sc$^-$, Ti, V$^+$, and a negative value at $n=17$. These facts, according to the usual interpretation of the cluster mass spectra,\textsuperscript{38} indicate a high abundance of Si$_{18}$M relative to their neighbors clusters, which agrees with the mass spectrometry experiments of Nakajima and co-workers.\textsuperscript{31,32} In Fig. 6 we can see peaks also at $n=16$ for the binding energy per atom [panel (a)] and for the HOMO-LUMO gap [panel (c)], which can be considered additional signatures of the special stability of Si$_{18}$M clusters. Our HOMO-LUMO gap values at $n=16$ are smaller than those found by Reveles and Khana,\textsuperscript{31} and for the isomers 16-I to 16-III of Si$_{16}$Ti is slightly larger than the value 1.9 eV estimated from photoelectron spectroscopy experiments.\textsuperscript{31,33} This fact can be surprising in view of the empirically known tendency of LDA...
and GGA calculations to underestimate the band gap of bulk semiconductors, which apparently cannot be applied to the HOMO-LUMO gap of small doped silicon clusters.

On the other hand, the addition energies of a Si atom to a pure Si$_{n-1}$ and to a doped Si$_{n-1}M$ cluster, have comparable magnitudes but the trend with size is different, and they are systematically smaller than the addition energy of a $M$ impurity to Si$_n$, as seen in panel (d) of Fig. 6.

2. Spin and charge population analysis

All structures in Figs. 1–5 correspond to spin zero, except 14-VIII of Fig. 1, which is a triplet for the three doped clusters, as was already mentioned in Sec. III A 1. For Si$_{14}$V$^+$ that triplet structure is near degenerate with the singlet 14-I structure.

We have investigated also the energy difference between singlet and triplet states of the isomer 16-II of Si$_{16}M$, whose equilibrium geometry is a Frank-Kasper (FK) polyhedron with spin zero: by forcing a spin 1 and relaxing the structure, we obtain equilibrium geometries which depart from the FK structure, having 1.4, 1.2, and 1.4 eV higher energy for Si$_{16}$Sc$^-$, Si$_{16}$Ti, and Si$_{16}$V$^+$, respectively.

The Mulliken population analysis of our equilibrium structures for Si$_nM$ clusters reveals that the spin charge cancellation occurs locally, for each atom and each orbital. In the four panels of Fig. 7 is represented, for the four isomers 16-I to 16-IV of Si$_{16}$ given in Fig. 3, the total charge accumulation and partial $s$-, $p$-, and $d$-orbital charge accumulation per Si atom (compared to the nominal valence of free Si atom), as a function of the radial distance to the cluster center. The radial shells are well defined for these structures, and the corresponding shell radii are smaller for V$^+$ than for Ti, and for Sc$^-$ doped Si$_{16}M$. This trend was discussed above in Sec. III A.
In the isomeric geometries of Si\textsubscript{16}V\textsuperscript{+}, the electrons flow from Si atoms to V\textsuperscript{+} cation, whereas in the isomers of Si\textsubscript{16}Sc\textsuperscript{−} the electrons flow from Sc\textsuperscript{−} anion to the Si atoms, as a consequence of the relative electronegativity of these elements. The loss of s-orbital charge of Si atoms is larger for Si\textsubscript{16}V\textsuperscript{+} than for Si\textsubscript{16}Sc\textsuperscript{−}, but the corresponding gain of p-orbital (d-orbital) charge is smaller (larger) for the cation than for the anion clusters. For Si\textsubscript{16}Ti, it results in an intermediate situation among those for Si\textsubscript{16}Sc\textsuperscript{−} and Si\textsubscript{16}V\textsuperscript{+}. From Fig. 7 we can recognize a covalent bonding for Si\textsubscript{16}V\textsuperscript{+} a part of the t\textsubscript{1} in the HOMO and LUMO compound spherical model. Similarly, the bonding and antibonding orbitals 1\textsubscript{a} and 2\textsubscript{a} of the FK structure, the splitting of the mono electronic levels of O\textsuperscript{+}(3) in the D\textsubscript{3} irreducible representation is: 49 (s\textsubscript{1}(1), p\textsubscript{1}(2), d\textsubscript{e}(t\textsubscript{2}), f\textsubscript{e}(a\textsubscript{1}+t\textsubscript{1}+t\textsubscript{2}), g\textsubscript{e}(a\textsubscript{1}+t\textsubscript{1}+t\textsubscript{2}), h\textsubscript{e}(e\textsubscript{1}+t\textsubscript{1}+t\textsubscript{2}), i\textsubscript{e}(a\textsubscript{1}+a\textsubscript{2}+e\textsubscript{1}+t\textsubscript{1}+t\textsubscript{2})... This can be seen clearly in the total density of states (DOS) of Si\textsubscript{15}Sc\textsuperscript{−} represented in the upper panel of Fig. 8(b), where the electronic levels are grouped and then labeled according to the spherical model. In the middle and lower panels of Fig. 8(b) is shown the partial density of states (PDOS) for Sc\textsuperscript{−} atom and Si cage, and the contribution of 3d, 4s, and 4p orbitals of Sc\textsuperscript{−} to the PDOS, respectively. We see that the valence electrons of Si\textsubscript{16}Sc\textsuperscript{−} accommodate within the sequence of levels 1s, 1p, 1d, 1f, 2s, 1g, 2p, 2d, 1h, 3s, 3p, 1l... of the spherical potential model, producing a shell closing of 68 electrons when completing the orbital 2d, which is the HOMO. This HOMO is the bonding orbital resulting from the hybridization of the 3d electron of Sc\textsuperscript{−} with the 2d (e\textsubscript{1}+t\textsubscript{2}) orbital of the Si FK cage, whereas the antibonding hybrid orbital forms a part of the t\textsubscript{1} components of the LUMO, which is grouped in a 1h state of the spherical model. Similarly, the 4s orbital of Sc\textsuperscript{−} hybridizes with the orbital 2s of the FK structure, giving the bonding orbital 2s and the antibonding 3s orbital of the compound Si\textsubscript{15}Sc\textsuperscript{−}.

An analogous analysis can be performed for the isomers 16-I and 16-III of Si\textsubscript{16}Sc\textsuperscript{−}, both of them having D\textsubscript{3} symmetry. The splitting of the mono electronic levels of O\textsuperscript{+}(3) in the D\textsubscript{3} irreducible representation is: 49 (s\textsubscript{1}(1), p\textsubscript{1}(2), d\textsubscript{e}(t\textsubscript{2}), f\textsubscript{e}(a\textsubscript{1}+a\textsubscript{2}+e\textsubscript{1}), g\textsubscript{e}(a\textsubscript{1}+a\textsubscript{2}), h\textsubscript{e}(a\textsubscript{1}+a\textsubscript{2}+e\textsubscript{1}), i\textsubscript{e}(a\textsubscript{1}+a\textsubscript{2}+2e\textsubscript{1})... Similar quantities as in Fig. 8(b) are represented in Fig. 8(a) for the isomer 16-I of Si\textsubscript{15}Sc\textsuperscript{−}. We see that the occupied levels of the spherical potential model, up to the HOMO level, follow the same sequence as for the FK structure 16-I, despite the fact that their splitting is different. The DOS of D\textsubscript{3} isomers differs from the T\textsubscript{d} (FK) one in the sequence and/or the fine structure of the unoccupied levels of the spherical model. For 16-I, the hybridization of 4s of Sc\textsuperscript{−} with the part a\textsubscript{1} of the 1h of the Si cage, leads to the occupied 2s bonding orbital and the antibonding orbital a\textsubscript{1} in the LUMO 1h of the compound. Similarly, the bonding and antibonding orbitals formed by the hybridization of 3d of Sc\textsuperscript{−} and the a\textsubscript{1}+2e part of 1h of the D\textsubscript{3} Si cage forms levels, respectively, in the HOMO and LUMO compound spherical model orbitals. This picture of the bonding of nearly spherical Si\textsubscript{16}M clusters is also obtained for M=Ti, V\textsuperscript{+}, as can be seen by inspection of Fig. 9, where it is represented the DOS, PDOS, and orbital-PDOS of structures 16-I, 16-II, and 16-IV isomers of Si\textsubscript{16}V\textsuperscript{+}.

For nonspherically shaped clusters the bonding cannot be based on the l-selection rule, as can be seen by inspection of Fig. 8(c) for isomer 16-V of Si\textsubscript{16}Sc\textsuperscript{−}, and Fig. 8(d) for isomer 17-I of Si\textsubscript{17}Sc\textsuperscript{−}. In these figures one cannot recognize a definite symmetry, and it is clear that the 3d orbital of the im-
purity is fragmented among several levels near the HOMO and, mainly, at higher energies than the HOMO. Comparing the projected density of states of the impurity in Figs. 8 and 8(d), with that in Figs. 8(a) and 8(b), we see that the weight of the 3d character near the HOMO level is smaller for nonspherical shaped clusters.
and anionic Si_{14}V^−, the ground state structure is 14-VIII within doublet and singlet spin state, respectively, being 0.21 and 0.60 eV lower in total energy than structure 14-I within doublet and singlet spin state, respectively. Nevertheless, 14-I still is an equilibrium energy structure of these clusters. The energy difference between Si_{14}V and Si_{14}V^−, when both are in the relaxed structure 14-I, is 2.67 eV, which is ~0.4 eV smaller than the adiabatic affinity reported in Table II.

In the case $n=16$ we performed the above mentioned optimization process taking as initial geometries the four isomers 16-I to 16-IV of Fig. 3. We obtained for the optimized geometries of Si_{16}Sc, Si_{16}Ti^+, and Si_{16}V^−, the same structures as the initial ones, but within a different energetic sequence. For Si_{16}Sc that sequence is just the inverse as that for Si_{16}Sc^−, that is, 16-IV, 16-III, 16-II, and 16-I, being 16-II slightly deformed from the FK structure, and near degenerate with 16-I. The energy difference between Si_{16}Sc and Si_{16}Sc^−, when both are in the same (relaxed) structure, is 3.50, 3.43, 3.41, and 3.16 eV, for structures 16-I, 16-II, 16-III, and 16-IV, respectively. The difference of these values with that reported in Table II is due to the structural relaxation of Si_{16}Sc^− after the loss of one electron. For Si_{16}Ti^- the sequence of structures with increasing energy is 16-I, 16-IV, 16-III, and 16-II, being the structure 16-II unstable and evolving towards 16-I. The energy difference between Si_{16}Ti and Si_{16}Ti^-, when both are in the same (relaxed) structure, is 1.80, 1.89, and 2.28 eV, for structures 16-I, 16-III, and 16-IV, respectively. The difference of these values with the one reported in Table II is due to the structural relaxation of Si_{16}Ti^− after charging with an extra electron. For Si_{16}V^- the sequence of isomers with increasing energy is 16-IV, 16-I, and 16-II, being the.

TABLE II. The calculated adiabatic electron affinity (EA_{cal}, in eV) of neutral Si_{n}Sc, Si_{n}Ti, and Si_{n}V clusters. The structures of the lowest energy state for the anion and neutral species are indicated in parentheses using the labels of Figs. 1–5. For Si_{10}Ti are also given experimental values (EA_{exp}) from Ohara et al.\textsuperscript{30}

<table>
<thead>
<tr>
<th>Size</th>
<th>EA_{cal}</th>
<th>EA_{cal}</th>
<th>EA_{cal}</th>
<th>EA_{cal}</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>3.17 (I-I)</td>
<td>2.72 (I-I)</td>
<td>2.56±0.15 (VIII-VIII)</td>
<td>3.06 (VIII-VIII)</td>
</tr>
<tr>
<td>15</td>
<td>3.21 (I-I)</td>
<td>2.57 (I-I)</td>
<td>2.78±0.13 (I-I)</td>
<td>2.36 (I-I)</td>
</tr>
<tr>
<td>16</td>
<td>3.31 (I-I)</td>
<td>1.88 (IV-I)</td>
<td>1.81±0.10 (IV-I)</td>
<td>3.03 (IV-I)</td>
</tr>
<tr>
<td>17</td>
<td>3.09 (I-I)</td>
<td>2.57 (I-I)</td>
<td>2.47±0.13 (II-II)</td>
<td>2.58 (II-II)</td>
</tr>
<tr>
<td>18</td>
<td>2.91 (I-I)</td>
<td>2.79 (I-I)</td>
<td>2.82±0.12 (V-V)</td>
<td>2.85 (V-V)</td>
</tr>
</tbody>
</table>
geometry 16-IV similar to that obtained by Reveles and Khana. The structure 16-II of Si$_{16}$V$^-$ results to be a spin triplet. When we optimize the initial geometry 16-II of Si$_{16}$V$^-$ forcing a spin singlet state, it results in a different equilibrium structure at 0.45 eV higher energy than the triplet 16-II isomer. The structures of the neutral Si$_{16}$V isomers are obtained by relaxing the structures 16-IV, 16-I, and 16-II of the anion Si$_{16}$V$^-$ after subtracting one electron, resulting in the same structures with the same sequence of increasing energy as the anion clusters. The energy difference between Si$_{16}$V and Si$_{16}$V$^-$ in the same structure (relaxed for each cluster) is 1.97, 1.90, and 3.03 eV, for structures 16-I, 16-II, and 16-IV, respectively. We see in Fig. 3 that structure 16-IV has a smaller HOMO-LUMO gap for all impurities than 16-I, 16-II, and 16-III structures. Thus, for neutral Si$_{16}$Sc and Si$_{16}$Ti clusters within 16-IV, we obtained HOMO-LUMO gap values 0.36 and 0.65 eV, respectively, to be compared with 1.04 eV obtained for both Si$_{16}$Sc$^-$ and Si$_{16}$Ti$^-$V. This reduction of the HOMO-LUMO gap for the neutral Si$_{16}$Sc and Si$_{16}$V clusters agrees qualitatively with the experimental trend obtained by Koyasu and co-workers (see Fig. 6 in that reference).

We see in Table II that our results for the adiabatic electron affinities compare well with the experimental values for Si$_{16}$Ti, Si$_{16}$Sc, and Si$_{16}$V, respectively. For these FK isomers, we obtain 1.91, 2.09, and 2.25 eV, respectively. Thus, 1.91 eV.

The calculated vertical (adiabatic) electron affinity of Si$_{16}$Sc is 3.56 (3.31) eV, which compare well with the experimental detachment energy of Si$_{16}$Sc$^-$, which corresponds to the upper limit of the EA of Si$_{16}$Sc. Another experimental value for the adiabatic detachment energy of Si$_{16}$Ti$^-$, 2.03±0.09, was given by Koyasu et al. Two different theoretical estimations of the EA of Si$_{16}$Ti yield the value 1.91 eV.

The calculated vertical (adiabatic) electron affinity of Si$_{16}$V is 3.56 (3.31) eV, which compare well with the experimental detachment energy of Si$_{16}$Sc$^-$, which corresponds to the upper limit of the EA of Si$_{16}$Sc. Another experimental value for the adiabatic detachment energy of Si$_{16}$Ti$^-$, 2.03±0.09, was given by Koyasu et al. Two different theoretical estimations of the EA of Si$_{16}$Ti yield the value 1.91 eV.

The HOMO-LUMO gap of Si$_{16}$M FK (16-II) clusters calculated by Khana and Reveles is 2.26, 2.34, and 2.42 eV for Si$_{16}$Sc$^-$, Si$_{16}$Ti, and Si$_{16}$V$^+$, respectively. For these FK isomers, we obtain 2.12, 2.17, and 2.25 eV, respectively. However, for the near degenerate 16-I structure of these clusters, we obtain 1.91, 2.09, and 2.25 eV, respectively. Thus, we hope that the measurement of magnitudes which are strongly dependent on the HOMO-LUMO gap, as the dipole polarizability, will allow one to discriminate the isomers 16-I and 16-II in the case of Si$_{16}$Sc$^-$.

In Table III is given the calculated electric dipole moment at zero temperature for the four lowest energy isomers of Si$_{16}$M (M = Sc$^-$, Ti, V$^+$), and their Boltzmann weighted average at room temperature. In principle, the geometry 16-II of Si$_{16}$Sc$^-$ can be discriminated from the others, particularly from geometry 16-III, by means of experiments. In practice, the averaged values should be compared against experimental dipole moments at finite temperature.

### IV. CONCLUSIONS

We have studied the structural and electronic properties of the low-lying energy isomers of doped Si$_{16}$M (M = Sc$^-$, Ti, V$^+$) clusters in the range $n=14$–18, and we have obtained several new geometries of low-lying isomers. In particular, most of the Si$_{16}$M isomers for $n=14$, 17, 18, and several of the isomers for $n=15$ and 16, are here reported for the first time. The metal impurity becomes encapsulated in all cases, and the geometries have no relation to those of pure silicon clusters.

The lowest energy isomers of Si$_{16}$M are nearly spherical shaped and they have smaller $M$-Si average distance than those clusters with neighbors sizes. This fact correlates with the higher relative stability of Si$_{16}$M with respect to their neighbor sizes. That enhanced stability was found in experiments, and is corroborated in this paper by means of first-principles calculations leading to positive peaks in the second difference of total energies of Si$_{16}$M clusters at $n=16$.

We have reported and discussed the trends with the cluster size of the binding energy, the addition energy of the impurity $M$ to pure Si clusters, the adiabatic electron affinity, the HOMO-LUMO gap, and other electronic properties of these clusters, such as the charge transfer among the metal atom and the Si cage, and the dipole moments of different Si$_{16}$M isomers. A detailed comparison of the bond properties and partial density of states is given for the few lowest energy isomers of Si$_{16}$M clusters in the context of the spherical potential model. That study allows us to identify the interplay among geometrical and electronic factors which determine the high abundance (stability) of Si$_{16}$M clusters detected in the experiments.

With respect to the interpretation of the experimental results in terms of the 20 electron rule by Reveles and Khana, or in terms of the 1-selection rule, we think that both offer complementary views, and both are based on first-principles calculations with 68 valence electrons for Si16M clusters, which is also a magic number of electrons. Our interpretation is not so drastic as that by Reveles and Khana, in the sense that these authors attach three electrons per Si atom to the Si16 cage and one electron per Si atom forms a bond with the impurity $M$. Instead, we insist on the combination of the 3d electrons of the impurity with $d$ electrons of the Si cage forming a bonding orbital at the HOMO level of the cluster.

Our results for the adiabatic electron affinity of neutral species of Si$_{16}$M clusters are in very good agreement with

### Table III. The calculated dipole moment (Debye) for the four lowest energy isomers of Si$_{16}$M, and their Boltzmann weighted average, $\langle 16 \rangle$.

<table>
<thead>
<tr>
<th>Si$_{16}$M</th>
<th>Si$_{16}$Sc$^-$</th>
<th>Si$_{16}$Ti</th>
<th>Si$_{16}$V$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16-I</td>
<td>0.108</td>
<td>0.019</td>
<td>0.022</td>
</tr>
<tr>
<td>16-II</td>
<td>0.002</td>
<td>0.055</td>
<td>0.025</td>
</tr>
<tr>
<td>16-III</td>
<td>0.545</td>
<td>0.336</td>
<td></td>
</tr>
<tr>
<td>16-IV</td>
<td>0.119</td>
<td>0.015</td>
<td>0.678</td>
</tr>
<tr>
<td>$\langle 16 \rangle$</td>
<td>0.175</td>
<td>0.029</td>
<td>0.024</td>
</tr>
</tbody>
</table>
available experimental measurements.\textsuperscript{31,32} We have also calculated the dipole moment of various nearly degenerate isomeric structures of Si\textsubscript{16}V\textsuperscript{2+}, Si\textsubscript{16}Ti, and Si\textsubscript{16}Sc\textsuperscript{2+} clusters, as well as their average values using Boltzmann weights at room temperature.

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