

Metal-Encapsulated Fullerene-like and Cubic Caged Clusters of Silicon

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We report metal-encapsulated caged clusters of silicon from *ab initio* pseudopotential plane wave calculations using generalized gradient approximation for the exchange-correlation energy. Depending upon the size of the metal (M) atom, silicon forms fullerene-like $M@Si_{16}$, $M = \text{Hf, Zr}$, and cubic $M@Si_{14}$, $M = \text{Fe, Ru, Os}$, caged clusters. The embedding energy of the M atom is ≈ 12 eV due to strong M -Si interactions that make the cage compact. Bonding in these clusters is predominantly covalent and the highest-occupied–lowest-unoccupied molecular orbital gap is ≈ 1.5 eV. However, an exceptionally large gap (2.35 eV) is obtained for $Ti@Si_{16}$ Frank-Kasper polyhedron. Interaction between these clusters is weak, making them attractive for cluster-assembled materials.

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Nanofoms of materials are currently of great interest to realize miniature devices. Nanoclusters are attractive building blocks for self-assembled structures as their properties can be manipulated by changing size, shape, and composition. Intense research has been carried out in recent years [1–4] on silicon clusters to understand their growth and size dependence of properties. These studies show that clusters in the range of 15–20 atoms have prolate structures. Very recently doping of transition metal atoms was used to find a new cluster, $Si_{12}W$ [5] that has a hexagonal prism open structure with a W atom at the center. Here we report for the first time the findings of three novel metal-encapsulated compact caged clusters of silicon: (1) fullerene-like (f) $M@Si_{16}$, (2) cubic (c) $M@Si_{14}$ and (3) surprisingly a Frank-Kasper (FK) tetrahedral structure, known for metallic systems, as the lowest energy structure of $Ti@Si_{16}$ with an exceptionally large gap of 2.358 eV that makes these clusters novel for atomic scale devices.

Fullerene-like forms of silicon have been sought soon after the discovery of C_{60} . However, unfavorable sp^2 hybridization makes cage structures of Si, such as the smallest dodecahedral fullerene for Si_{20} , unstable. R othlisberger *et al.* [6] obtained a fullerene-like shell structure of Si_{45} with a core of silicon atoms inside. Jackson and Nellermoe [7] attempted to stabilize Si_{20} with a Zr atom in the fullerene cage. However, our results show that $Zr@Si_{20}$ is not stable. We performed computer experiments on encapsulation of transition metal atoms having an even number of valence electrons [8] starting with Zr, being the largest in size, in f - Si_{20} . Optimization of $Zr@Si_{20}$ (Fig. 1a) leads to the shrinkage of the Si_{20} cage with a Si atom sticking out (Fig. 1b). Removal of this capping atom and reoptimization leads to a $Zr@Si_{17}$ cage with two Si atoms sticking out (Fig. 1c). Further removal of the two capping Si atoms and reoptimizations lead to a $Zr@Si_{16}$ cage with a capping by one Si atom (Fig. 1d). Again, removal of this capping atom and reoptimization lead to a compact symmetric f cage of $Zr@Si_{16}$ (Fig. 1e). This procedure of shrinkage and removal of atoms is

continued with smaller M atoms starting with the structure of $Zr@Si_{16}$. It further leads to the findings of caged $M@Si_{14}$ clusters. The calculations are performed using the *ab initio* ultrasoft pseudopotential plane wave method [9,10] within the spin-polarized generalized gradient approximation [11] for the exchange-correlation energy. A simple cubic supercell with size up to 18   is used with periodic boundary conditions and the Γ point, for the Brillouin zone integrations. The structures are optimized using the conjugate gradient method. In most cases we consider only the outer valence electrons but for Ti and Zr we also included, respectively, $3p$ and $4p$ atomic core states as valences.

The lowest energy structures, binding energy (BE), embedding energy (EE) of M atom in the Si_n cage

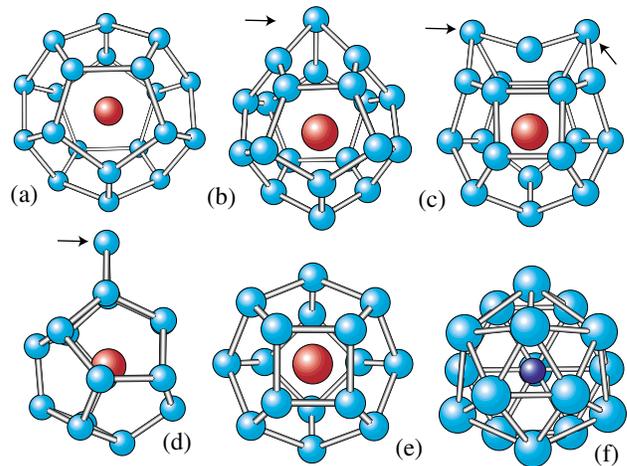


FIG. 1 (color). Shrinkage of the Si_{20} cage. (a) Dodecahedral Zr-encapsulated $Zr@Si_{20}$, (b)–(e) optimized structures of $Zr@Si_{20}$, $Zr@Si_{19}$, $Zr@Si_{17}$, and $Zr@Si_{16}$, respectively. The arrows indicate the atoms that were removed. The same structure is obtained for $Hf@Si_{16}$. (f) The Frank-Kasper polyhedral structure of $M@Si_{16}$ ($M = \text{Ti and Hf}$). The light blue balls represent Si atoms and the central atom is M . For clarity, bonds connecting M to the cage atoms are not shown.

of $M@Si_n$ cluster, and the highest-occupied–lowest-unoccupied molecular orbital (HOMO-LUMO) gaps of all the caged clusters studied here are given in Table I. Among these, Zr and Hf with atomic radii 1.61 and 1.59 Å, respectively, form the largest close packed f cage of 16 Si atoms. It has eight pentagonal and two square faces as compared to 12 pentagons in the dodecahedral Si_{20} and constitutes the *smallest* high symmetry f structure of silicon in which each atom on the cage is tricoordinated similar to the fullerenes. The BEs, EEs, and the HOMO-LUMO gaps are large (Table I) which make these clusters among the most stable. The isoelectronic f -Ti@Si₁₆ has a 1.495 eV HOMO-LUMO gap but the total BE and EE are about 1.3 eV lower, as compared to Zr and Hf encapsulation due to the smaller size of Ti (1.47 Å) that reduces interaction with the silicon cage. The Ti-Si (2.87 Å), Zr-Si (2.90 Å), and Hf-Si (2.89 Å) bond lengths are similar which shows that the Si₁₆ cage cannot be compressed further and that Ti is not optimally bonded in this cage. Also the Si-Si bond lengths in all three cases are in the range of 2.27–2.36 Å with less than 1% variation, which is indicative of covalent bonding (see below). In order to further check the stability of this structure, we considered the FK polyhedron (tetrahedral) with 16 coordinations that occur in complex alloys [12] of constituents with significantly different atomic sizes. Ionic relaxations of this structure lead to an isomer (Fig. 1f) of Ti@Si₁₆ that lies 0.781 eV lower in energy than the f isomer and to our surprise, it has an *exceptionally* large gap of 2.358 eV. In this structure the Ti atom has 4 Si atoms as nearest neighbors in a tetrahedral arrangement with a short bond length of 2.61 Å and 12 Si atoms (which form interlinked hexagonal rings) at a distance of 2.82 Å. The reduced Ti-Si bond lengths in this structure indicate covalent bonding that enhances the interaction of Ti with the Si cage. The Si-Si bonds are, however, elongated (2.37–2.66 Å) and have a mixed covalent-metallic bonding, as shown later. The BE of this higher (5 and 6) coordination cage is about 2 eV more than the f -Si₁₆ cage, leading to a lower EE of Ti in FK-Si₁₆. The isoelectronic FK-Hf@Si₁₆ is degenerate with the f

isomer, but the gap is significantly large (2.352 eV) as for Ti. However, FK-Zr@Si₁₆ lies 0.355 eV higher in energy than the f isomer. These results suggest that both Ti- and Hf-encapsulated clusters with FK polyhedron structure should be strongly abundant and that *Hf doping is unique to produce two different stable isomers with different bonding natures and significantly different large band gaps*.

Optimizations of the f - $M@Si_{16}$ structure with smaller M atoms such as Fe, lead to a cage of Si₁₄ with a capping by two Si atoms, as shown in Fig. 2a. This has a 1.294 eV HOMO-LUMO gap and no magnetic moment. Removal of these two capping atoms and reoptimization of the remaining structure lead to a caged Fe@Si₁₄ cluster (Fig. 2b) which could be described as a decahedron (d) with capping of four Si atoms. The atomic coordination on the shell varies from 3 to 5 due to the presence of triangular faces. The Si-Si and Fe-Si bond lengths vary in the range of 2.31–2.71 and 2.61–2.86 Å, respectively, representing a mixed covalent-metallic bonding in this structure. We further studied a capped hexagonal prism structure but it transforms into a symmetric body-centered cubic packing (side 3.0 Å) upon relaxation with the Fe atom surrounded by 14 Si atoms (Fig. 2c). The nearest neighbor Si-Si and Fe-Si bond lengths are 2.4 and 2.6 Å, respectively. This structure lies 0.566 eV lower in energy than the d isomer and represents, to our knowledge, the first cubic cluster of silicon. The HOMO-LUMO gap is more than 1 eV which makes it a very stable specie. The EE is, however, significantly lower than the value for Zr@Si₁₆, presumably due to the quenching of the magnetic moment of the Fe

TABLE I. BE (eV/atom), EE (eV), HOMO-LUMO gap (eV) of lowest energy isomers of studied clusters.

Cluster	BE	EE	Gap
FK-Ti@Si ₁₆	-4.135	-11.269	2.358
f -Zr@Si ₁₆	-4.162	-13.965	1.580
f -Hf@Si ₁₆	-4.175	-14.176	1.576
FK-Hf@Si ₁₆	-4.171	-12.399	2.352
c -Fe@Si ₁₄	-4.018	-8.404	1.162
c -Ru@Si ₁₄	-4.194	-11.136	1.409
f -Ru@Si ₁₄	-4.184	-12.939	1.488
c -Os@Si ₁₄	-4.259	-12.111	1.453
f -Os@Si ₁₄	-4.258	-14.024	1.576

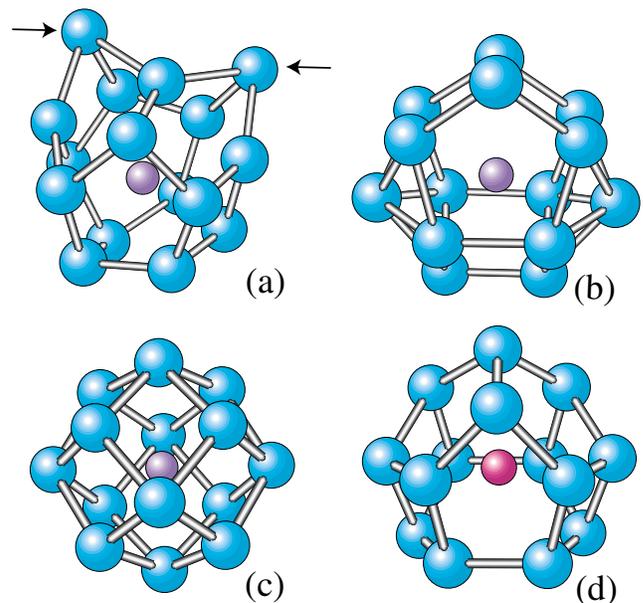


FIG. 2 (color). Shrinkage of f -Fe@Si₁₆ structure. (a) optimized Si₁₆Fe with two Si atoms capping (arrows), (b) d - $M@Si_{14}$, $M = Fe$ and Ru, (c) c -Fe@Si₁₄, and (d) f -Os@Si₁₄. The c structures of Ru and Os are similar to (c).

atom. This also finds support from the fact that substitution of the isoelectronic Ru or Os leads to higher EE and higher BE. In these cases the f and c isomers are nearly degenerate (Table I). Ru behaves more like Fe. The f isomer of Os@Si₁₄ (Fig. 2d), however, has a hexagon, four pentagons, and four quadrilaterals, such that each Si atom is tricoordinated on the cage as in fullerenes. It can also be viewed as a dimer capped hexagonal prism. The Si-Si and Os-Si bond lengths vary in the range of 2.31–2.44 Å and 2.68–2.87 Å, respectively. The HOMO-LUMO gap (1.576 eV) and the BE (4.258 eV/atom) are among the largest in this covalently bonded cluster. The d -Os@Si₁₄ structure of Fe is also degenerate. The c isomer has side 3.05 Å with Si-Si and Os-Si bond lengths to be 2.44 and 2.65 Å, respectively. The HOMO-LUMO gap (1.453 eV) and the BE (4.259 eV/atom) are also large. c -Ru@Si₁₄ is similar to Os encapsulation and both these clusters are expected to be strongly abundant. Further studies of a 15-atom Si cage with $M = \text{Ru}$ and Os show shrinkage to a c -Si₁₄ cage with a capping by a Si atom, indicating that for these elements the Si₁₄ cage is the optimal.

The constant electronic charge density surfaces show (Figs. 3a and 3c) high density in the Si-Si bonds of f isomers of M @Si₁₆ as well as the c isomers of M @Si₁₄

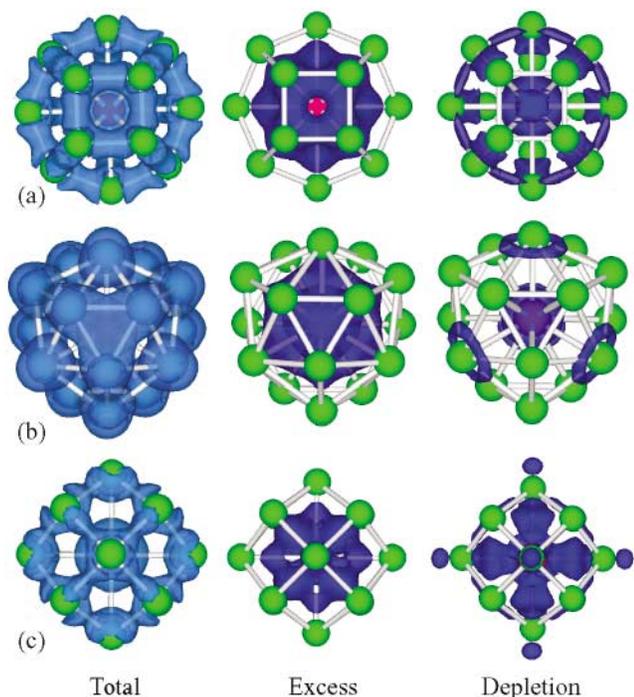


FIG. 3 (color). Constant electronic charge density surfaces for (a) f -Zr@Si₁₆, (b) FK-Ti@Si₁₆, and (c) c -Os@Si₁₄. The second and third columns show, respectively, the excess and depletion of charge as compared to the overlapping densities of M and Si _{n} in M @Si _{n} clusters. The densities for different surfaces are: (a) 0.4, 0.015, 0.015 $e/\text{Å}^3$, (b) 0.35, 0.020, 0.020 $e/\text{Å}^3$, and (c) 0.4, 0.022, 0.022 $e/\text{Å}^3$. Balls (visible green/red as well as shadowed) represent Si/M ions.

and these are, therefore, covalently bonded. The difference in the self-consistent electronic density of M @Si _{n} and the overlapping densities of M and Si _{n} at the respective positions shows an excess of charge in the M -Si bonds and a slight depletion of charge from some Si-Si bonds in M @Si₁₆ and from the central region of the faces in M @Si₁₄. Some depletion of charge occurs in the vicinity of the M . Therefore, strong M -Si bonds are created in these structures, as it is also clear from the large EE of M atoms (Table I). In the FK-Ti@Si₁₆ isomer, there is covalent-metallic bonding, as seen from Fig. 3b. The Si-Si bonds forming hexagonal rings are short (2.37–2.43 Å) and have covalent bonding, whereas the remaining four Si atoms have elongated bonds (2.65 Å) with other Si atoms and the bonding is not covalent, as can be seen from the lower density (Fig. 3b). Similar to the f isomer, there is charge transfer from the silicon cage and an excess in between the metal ion and the cage leading to strong M -Si bonding. Some charge is depleted in the vicinity of the Si and M ions. The Si₁₆ cages in both the f and FK structures have a magnetic moment of $4\mu_B$ and can share four electrons to create closed shell clusters. Most of their states, except near the HOMO, remain nearly unchanged upon M encapsulation. Tetravalent atoms such as Zr, Hf, and Ti, therefore, make strong covalent bonding with these states of the cage leading to a large gap. This result is similar to the stabilization of the tetrahedral C₂₈ cage by Zr encapsulation [13] with about 12 eV EE [14]. However, in Zr@C₂₈ there is charge transfer from Zr to C₂₈. The c -Si₁₄ cage, however, has only two unpaired electrons and, therefore, covalent bonding with Fe, Ru, and Os leads to large gaps [15].

Further studies on the interaction between two f -Zr@Si₁₆ clusters joined at the square faces in a prism configuration and two FK-Ti@Si₁₆ clusters joined at edges in a tetrahedron configuration show that the optimized structures (Fig. 4) keep the caged structures of clusters intact. In the case of f isomers, the Si-Si bond length between the two clusters is 2.52 Å and the BE of the dimer, is only 1.345 eV, suggesting a weak interaction. The gap is, however, reduced to 0.673 eV. On the other hand, the converged structure for two FK-Ti@Si₁₆ cages has long intercage Si-Si bonds of 4.04 Å and the BE is only 0.048 eV. Therefore, the interaction between these two clusters is a van der Waals type, indicating strong magic behavior. The gap in this dimer also remains large (2.211 eV). Therefore, we expect self-organized assemblies of these clusters to be a good possibility.

In summary, we have reported the findings of three new classes of metal-encapsulated M @Si _{n} clusters with high stability and large HOMO-LUMO gaps: fullerene-like and Frank-Kasper tetrahedral for $n = 16$ and cubic, as well as fullerene-like for $n = 14$. The size of the silicon cage is found to depend strongly upon the size of the M atom since the M -Si interactions are very strong and lead to compact structures. A novel finding is the

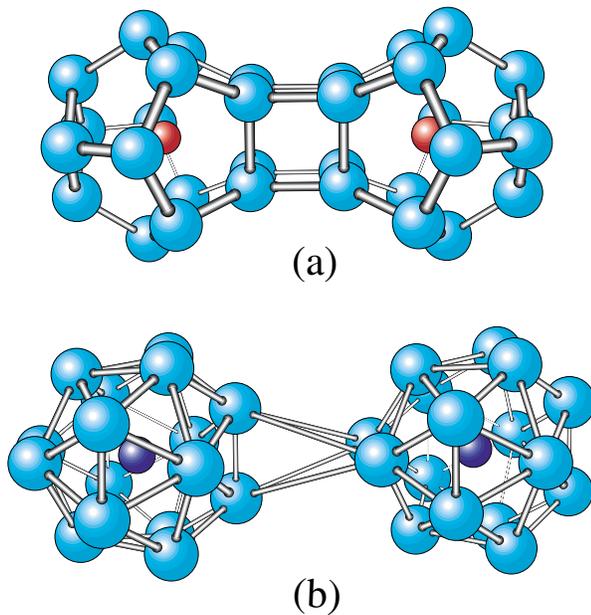


FIG. 4 (color). The optimized structures of dimers of (a) f -Zr@Si₁₆ and (b) FK-Ti@Si₁₆.

Frank-Kasper polyhedron of Ti@Si₁₆ and Hf@Si₁₆ clusters with an exceptionally large gap of about 2.35 eV. The weak cluster-cluster interactions, metallic as well as covalent bonding and the possibilities of a varying band gap with M , make these clusters attractive for cluster-assembled materials. We hope our results will stimulate experiments to look for these clusters.

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