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Magic behavior of $Si_{15}M$ and $Si_{16}M$ (M=Cr, Mo, and W) clusters

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Ab initio electronic-structure calculations based on pseudopotential plane-wave method and generalized gradient approximation for the exchange-correlation energy are performed on Si_nM ($n=14-17$ and $M=$Cr, Mo, and W) clusters. We find an M-encapsulated silicon cage $M@Si_{15}$ derived from a *cubic* structure to be the optimally close packed for these elements. There are competing growth modes so that a *fullerenelike* capped cage of $Si_{16}M$ has the lowest energy leading to their *simultaneous* magic behavior in agreement with experiments. The binding energy, the highest occupied–lowest unoccupied molecular orbital gap and the embedding energy of M are large, giving rise to their strong stability and complete quenching of the magnetic moment of M. Similar cubic $M@Si_{15}$ structures are predicted for $M=$Ti, Hf, Zr, Ru, and Os.

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Recent findings[1] of novel metal encapsulated caged clusters of silicon remarkably show that the properties of silicon clusters can be modified drastically by *one* metal (M) atom and that the latter can be used to selectively prepare cages of specfic size and with specific properties making them attractive for nanodevice applications. These have fullerenelike (f) and cubic (c) shapes in sharp contrast to the prolate structures of elemental silicon clusters.[2,3] Also a hexagonal (h) prism shaped $W@Si_{12}$ cluster has been reported.[4] An exceptional finding[1] has been the large band gap of about 2.35 eV in the optical region for the Frank-Kasper (FK) polyhedral $M@Si_{16}$ cluster with $M=$Ti and Hf. Here we report Si_nM clusters with $n=14-17$ and $M=$Cr, MO, and W and explain the magic behavior of clusters with $n=15$ and 16 observed[5] more than a decade ago. Several other metals are also predicted to form $M@Si_{15}$ structures.

An interesting property of the metal-encapsulated silicon clusters is that the band gap varies significantly with M. This property can be used to develop novel silicon-based miniature devices. Also, studies of these mixed M-Si clusters open up new possibilities to understand phenomena occuring at M-Si interfaces that are important for technological applications.

We use first-principles ultrasoft pseudopotential method[6,7] with a plane-wave basis and generalized gradient approximation[8] with spin polarization for the exchange-correlation energy. The cluster is placed in a large simple cubic unit cell of side upto 18 Å. The Γ point is used for Brillouin-zone integrations. The low-lying atomic structures of these clusters are obtained by optimizing a few selected structures using the conjugate gradient method. Also we use the cage-shrinkage method[1] that led to the findings of the f-Zr@Si_{16} type metal-encapsulated silicon-cage clusters. Optimizations of this f structure with a smaller M atom such as Cr show that it is not optimally bonded unlike Hf and Zr. There is a shrinkage of the cage such that one Si atom caps a $M@Si_{15}$ cage as shown in Fig. 1(a). Removal of this capping atom and subsequent reoptimization lead to a stable f-$M@Si_{15}$ cage as shown in Fig. 1(b). It has 0.808 eV highest occupied and lowest unoccupied molecular orbital (HOMO-LUMO) gap and 3.883 eV/atom binding energy (BE). There are five pentagons, two squarelike, and four triangular faces. Ten silicon atoms have coordination 3 on the cage like in fullerenes, but five are fourfold coordinated due to the presence of triangular faces. An important result is the complete loss of the large magnetic moment of Cr atom. The embedding energy (EE) of Cr in the cage is large (8.936 eV) but significantly lower as compared to about 14 eV obtained[1] for Zr and Hf, due to the quenching of the magnetic moments. The Si-Si bond lengths are in the range of 2.27–2.34 Å indicating covalent bonding in this isomer. A few bonds are elongated with values of 2.47 and 2.72 Å. The Cr-Si bond lengths lie in the range of 2.60–2.96 Å. These are longer than the sum of the covalent radii, 1.18 and 1.36 for Si and Cr, respectively. Therefore, Cr is not optimally bonded with the silicon cage.

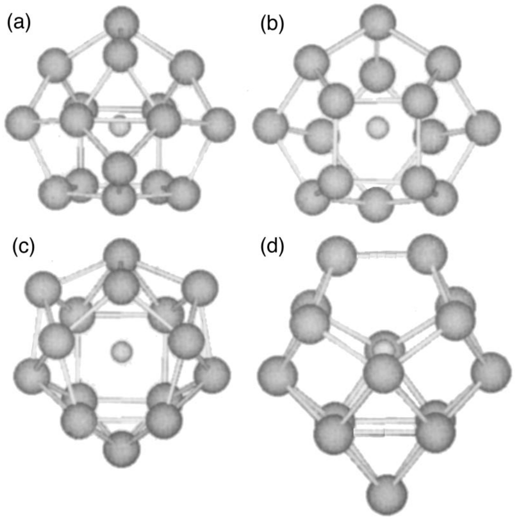

FIG. 1. (a) Optimized structure of $Si_{16}Cr$ starting from the f-Zr@Si_{16} cluster (Ref. 1) with Zr replaced by Cr. There is a shrinkage of the cage such that one Si atom caps a Cr@Si_{15} cage. (b) Relaxed f-Cr@Si_{15} after removal of the capping atom in (a), (c) lowest-energy structure of $M@Si_{15}$ ($M=$Cr, Mo, and W) obtained from a c isomer, and (d) lowest-energy structure of $M@Si_{15}$ (M $=$Ti, Zr, Hf, Ru, and Os) derived from c isomer. This is different from (c) in the way faces are capped. Optimizations of this structure with $M=$Cr, Mo, and W lead to isomers with higher energy.

TABLE I. BE (eV/atom), EE (eV), HOMO-LUMO gap (eV) of isomers of metal encapsulated 14–16 atom silicon clusters.

Cluster	BE	EE	Gap
f-$\mathrm{Si}_{16}\mathrm{Cr}$	−3.934	−8.817	1.244
f-$\mathrm{Si}_{16}\mathrm{Mo}$	−4.132	−12.091	1.195
f-$\mathrm{Si}_{16}\mathrm{W}$	−4.246	−14.053	1.208
c-$\mathrm{Cr@Si}_{15}$	−3.950	−8.867	1.537
f-$\mathrm{Cr@Si}_{15}$	−3.883	−8.936	0.808
c-$\mathrm{Mo@Si}_{15}$	−4.125	−13.037	1.659
f-$\mathrm{Mo@Si}_{15}$	−4.093	−12.524	0.779
$c1$-$\mathrm{W@Si}_{15}$	−4.250	−13.700	1.747
$c2$-$\mathrm{W@Si}_{15}$	−4.231	−13.797	1.377
f-$\mathrm{W@Si}_{15}$	−4.214	−14.481	0.780
c-$\mathrm{Ti@Si}_{15}$	−4.076	−10.454	1.237
c-$\mathrm{Zr@Si}_{15}$	−4.087	−12.998	1.287
f-$\mathrm{Zr@Si}_{15}$	−4.083	−13.415	1.179
c-$\mathrm{Hf@Si}_{15}$	−4.116	−14.507	1.262
f-$\mathrm{Hf@Si}_{15}$	−4.111	−14.904	1.175
c-$\mathrm{Ru@Si}_{15}$	−4.186	−12.358	1.164
c-$\mathrm{Os@Si}_{15}$	−4.250	−13.037	1.120
d-$\mathrm{Cr@Si}_{14}$	−3.917	−8.298	1.540
d-$\mathrm{Mo@Si}_{14}$	−4.086	−11.035	1.736
d-$\mathrm{W@Si}_{14}$	−4.224	−13.097	1.860

Following the earlier[1] result of a body-centered-cubic structure for $M@\mathrm{Si}_{14}$ with $M=\mathrm{Fe}$, Ru, and Os, we constructed a 15-atom Si cluster by placing one more Si on a face of the cube. Optimization with $M=\mathrm{Cr}$ led to its transformation into a structure shown in Fig. 1(c). It lies 1.071 eV lower in energy than the *f* isomer and has a large (1.537 eV) HOMO-LUMO gap suggesting its strong stability. This structure is completely different from the *f* isomer. There is a majority of triangular faces, one pentagon and three rhombii. The mean coordination of Si atoms on this cage is 4. The higher coordination of Si atoms in this structure leads to slightly elongated Si-Si bonds (2.36–2.57 Å). This range is more than the value of 2.35 Å for the covalently bonded silicon. It indicates development of some metallic character in this isomer as one can also expect from a higher coordination of Si atoms. The M-Si bond is, however, slightly shorter (2.54–2.83 Å) than in the *f* isomer with majority of bonds having the lower value. This leads to a better M-Si interaction in this structure. The EE of Cr in this cage is 8.867 eV. This is slightly lower than the value for the *f* cage, but there is a gain in the BE of the silicon cage by 1.14 eV that lowers the total energy of this cluster. The atomic states of Cr lie near the HOMO of the silicon cage and interact covalently. This lowers the energy of the silicon cage states in a range of about 2 eV below the HOMO, the deeper states remaining nearly unchanged.

Similar calculations have been carried out for $M=\mathrm{Mo}$ and W. It is found that the f-$M@\mathrm{Si}_{16}$ cage[1] is stable for these dopings, but a capped cage structure [Fig. 1(a)] has lower energy similar to Cr. Repetition of the optimizations for $M@\mathrm{Si}_{15}$ with $M=\mathrm{Mo}$ and W, respectively, shows a decrease in the HOMO-LUMO gap (0.779 and 0.780 eV) in the *f* isomer but an increase to 1.659 and 1.747 eV in the *c* derived structure.[9] Therefore, for $M@\mathrm{Si}_{15}$ ($M=\mathrm{Cr}$, MO, and W), the isomer obtained from a *c* structure has the lowest energy and large HOMO-LUMO gap.[10] The EEs for Mo and W in the silicon cage are large (13.037 and 13.700 eV, respectively) and the M-Si and Si-Si bond lengths are similar (2.61–2.85 and 2.40–2.66, and 2.61–2.86 and 2.39–2.65, respectively). These are slightly elongated as compared to Cr due to a slightly bigger size of these atoms. The bonding properties for these isoelectronic dopings are similar. These results are in agreement with the observed strong abundance of these clusters.

The strong stability of a cluster generally implies that addition of one more atom is energetically not favorable. However, experiments show equally strong abundance of $\mathrm{Si}_{16}M$ that is surprising, knowing that $M@\mathrm{Si}_{15}$ has a large gap. Strong stability of $M@\mathrm{Si}_{16}$ ($M=\mathrm{Ti}$, Hf, and Zr) cage was obtained[1] earlier in the *f* and FK structures. For $\mathrm{Si}_{16}M$ ($M=\mathrm{Cr}$, Mo, and W), we performed several calculations including the FK polyhedron, the *f* structure, a *c* structure with cappings as well as capping of some low-lying isomers of $M@\mathrm{Si}_{15}$. The lowest-energy structure is shown in Fig. 1(a). The FK, *f*, and *c* structures have $2\mu_B$ magnetic moment and small HOMO-LUMO gaps except for c-$\mathrm{W@Si}_{16}$ that has zero magnetic moment and 0.691 eV gap. These isomers are unlikely to be abundant. Their BEs are also nearly the same but significantly above the lowest-energy isomer [Fig. 1(a)]. The latter has a HOMO-LUMO gap of about 1.2 eV (Table I) and zero spin in all the three cases. The BE is nearly the same as for $M@\mathrm{Si}_{15}$ clusters. These results again confirm that even though, the 16 coordinated structures, $M@\mathrm{Si}_{16}$ are possible for $M=\mathrm{Mo}$ and W and locally stable, isomers with a capping of a 15-atom cage have lower energies. Therefore, a 15-atom cage is the optimal closest packing around these M atoms. Interestingly, an isomer obtained from capping of the lowest-energy 15-atom silicon-cage structure lies about 1 eV higher in energy. This again shows magic behavior of $M@\mathrm{Si}_{15}$. *An important result that emerges from these calculations is that there are competing growth modes that give rise to very different structures of the M-encapsulated 15- and 16-atom silicon clusters and their simultaneous strong abundances.*

In order to further establish the magic nature of $M@\mathrm{Si}_{15}$ and $\mathrm{Si}_{16}M$, we studied Si_nM ($n=14$ and 17) species using several initial configurations. These included c- and f-$M@\mathrm{Si}_{14}$ isomers, capped *h* prism and decahedral (*d*) cluster for $n=14$, and cappings of several $\mathrm{Si}_{16}M$ structures for $n=17$. The low lying structures are shown in Fig. 2. For $n=14$, we find a *d* structure [Fig. 2(a)] with cappings on two pentagonal and two square faces to be of lowest energy in all the three cases. These have large BEs and large HOMO-LUMO gaps (Table I). The M-Si and Si-Si bond lengths in this cage have values 2.55–2.79 and 2.40–2.52, 2.62–2.82 and 2.40–2.58, and 2.62–2.81 and 2.40–2.58 Å for Cr, Mo, and W, respectively. These are similar to those obtained for $M@\mathrm{Si}_{15}$ except that the upper values are slightly reduced. Several other structures derived from the *c* and *f* isomers obtained[1] for Fe, Ru, and Os as well as the one derived from the *h* isomer have $2\mu_B$ magnetic moment and lie close in

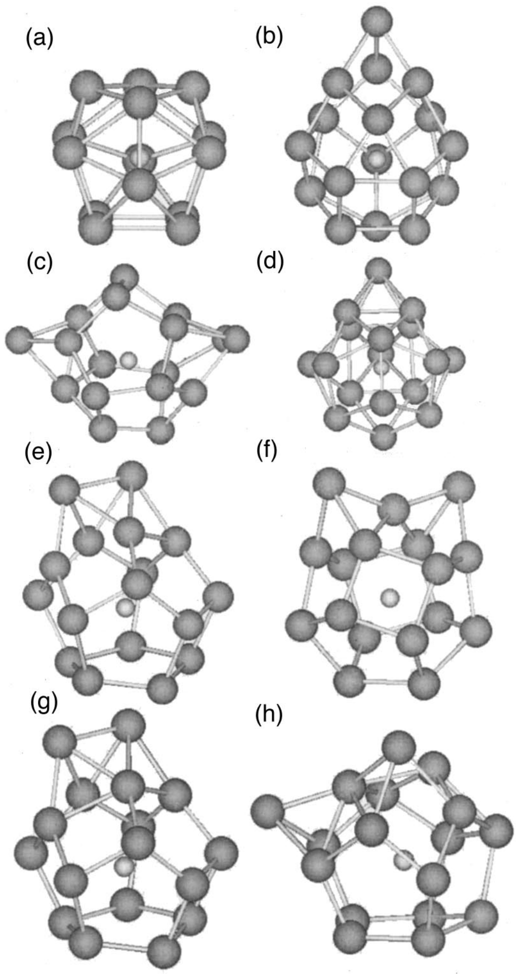

FIG. 2. (a) Lowest-energy structure of $M@\mathrm{Si}_{14}$ ($M=$Cr, Mo, and W), (b) an isomer of $\mathrm{Si}_{17}M$ ($M=$Cr, Mo, and W) obtained from capping of FK-$M@\mathrm{Si}_{16}$ Ref. 1), (c) relaxed Si_{17}Cr obtained from capping of f-$M@\mathrm{Si}_{16}$, (d) optimized d-Si_{17}Cr, (e) optimized capped f-Mo@Si_{16}, (f) optimized d-Si_{17}Mo, (g) optimized capped f-W@Si_{16} [similar to (e)], and (h) optimized d-Si_{17}W. Isomers (c), (f), and (g) have the lowest energies.

energy with each other but about 1 eV higher than the lowest-energy isomer. Therefore, the lowest-energy structures for $M@\mathrm{Si}_{14}$ ($M=$Cr, Mo, and W) are different from those reported earlier[1] for Fe, Ru, and Os. For $\mathrm{Si}_{17}M$, we studied cappings of FK-$M@\mathrm{Si}_{16}$ and f-$M@\mathrm{Si}_{16}$, a d structure with face capping and capping of some low-lying $\mathrm{Si}_{16}M$ structures. The lowest-energy structures for $M=$Cr, Mo, and W are different (Table II). These are shown in Fig. 2. It can be seen that all these are cappings of a subunit in which M atom has fewer Si nearest neighbors. These results give further support that a 15-atom cage is optimal for Cr, Mo, and W. The HOMO-LUMO gap for Cr doping is about 1 eV, but it reduces to 0.82 and 0.651 eV for Mo and W, respectively. These results suggest that the 17-atom Si clusters may be reactive, in agreement with their low abundance in experiments.

An interesting aspect is that clusters with 14-atom Si cage have the largest HOMO-LUMO gaps but these are not so strongly abundant in experiments as the 15 and 16 silicon atom clusters. In order to understand this, we note that the BE of the $M@\mathrm{Si}_{15}$ cage is 0.033, 0.039, and 0.026 eV/atom more than the value for the $M@\mathrm{Si}_{14}$ cages with $M=$Cr, Mo, and W, respectively. The EE of the M atom in the Si_n cage is significantly less in the $n=14$ cage as compared to the value for $n=15$ (Table I). Further, we calculated the second-order difference in energy, $\Delta_2E(n)=2E(n)-E(n+1)-E(n-1)$ for $n=15$ and 16. Here $E(n)$ is the total energy of a $M@\mathrm{Si}_n$ or Si_nM cluster. These are -0.768 and -0.284, -0.472 and -0.975, and -0.461 and -1.256 eV for Cr, Mo, and W, respectively. Therefore, both $M@\mathrm{Si}_{15}$ and $M@\mathrm{Si}_{16}$ are magic as observed.[5] Strikingly, these two are the only clusters with high intensities in experiments and beyond this size there is very low intensity of other clusters. It shows the importance of the $M@\mathrm{Si}_{15}$ cage for these M atoms and that the only other significantly stable cluster with a capping is $\mathrm{Si}_{16}M$ that has large gap. Therefore, *such caged clusters are ideally placed to be uniquely produced for developing materials with desired properties as the shape, size, and gap can be varied by a suitable choice of M.*

TABLE II. BE (eV/atom) and HOMO-LUMO gap (eV) of low-lying isomers of $\mathrm{Si}_{17}M$ clusters. d-Si_{17}Cr has a magnetic moment of $2\mu_B$ while for all others it is zero.

Cluster	BE	Gap
f-Si_{17}Cr	-3.904	1.059
FK-Si_{17}Cr	-3.895	0.989
d-Si_{17}Cr	-3.841	0.233
d-Si_{17}Mo	-4.083	0.820
f-Si_{17}Mo	-4.065	0.641
FK-Si_{17}Mo	-4.057	1.095
f-Si_{17}W	-4.172	0.651
d-Si_{17}W	-4.168	0.548
FK-Si_{17}W	-4.161	1.098

Further calculations have been carried out on $M=$Ti, Hf, Zr, Ru, and Os for the 15-atom silicon cage. All of these form c-$M@\mathrm{Si}_{15}$ structures with large BE and about 1.2 eV HOMO-LUMO gap (Table I). However, this structure [Fig. 1(d)] is slightly different from the lowest-energy isomer of Cr@Si_{15}. For Zr and Hf, the f isomer is nearly degenerate while in all other cases, the c structure is about 0.5–1.0 eV lower in energy. We also tried Fe, Pd, and Pt. However, in all these cases the structures get distorted and for Fe, there is a magnetic moment of $2\mu_B$ as well as the gap is very small.

In summary, we have reported metal-encapsulated silicon-cage $M@\mathrm{Si}_{15}$ and $\mathrm{Si}_{16}M$ clusters with $M=$Cr, Mo, and W. The 15-atom silicon cage is found to be optimal close packing for these metal atoms. There are competing growth modes such that an isomer obtained from a body-centered-cubic unit has the lowest-energy for $M@\mathrm{Si}_{15}$, whereas for $\mathrm{Si}_{16}M$, an isomer with a capped fullerenelike cage lies lowest in energy. This leads to their simultaneous magic behavior in agreement with experiments. These two clusters are special as clusters with $n>16$ will have silicon atoms in the second layer. This leads to small HOMO-LUMO gaps so that the clusters become reactive. Therefore, there is a high size selectivity of the metal-encapsulated silicon clusters that could be exploited for device applications. The bonding nature of the cages in the two structures are somewhat different, but the stability of the cages primarily arises from a strong interaction with M atom that also completely quenches the magnetic moments of M and leads to large HOMO-LUMO gaps. Similar cubic $M@\mathrm{Si}_{15}$ structures are predicted for $M=\mathrm{Ti}$, Hf, Zr, Ru, and Os with similar properties. We hope our results would encourage experimentalists to look for the high abundances of these clusters.

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[9] Another cubic structure (see Ref. 10) was obtained for $\mathrm{W}@\mathrm{Si}_{15}$ with 0.019 eV/atom lower BE and 1.377 eV HOMO-LUMO gap.

[10] Several calculations were performed on M doped 15 and 16 Si atom clusters. These details will be published separately. V. Kumar and Y. Kawazoe (unpublished).