

## Novel caged clusters of silicon: Fullerenes, Frank–Kasper polyhedron and cubic

VIJAY KUMAR

Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan and  
Dr Vijay Kumar Foundation, 45 Bazaar Street, K. K. Nagar (West), Chennai 600 078, India

**Abstract.** We review recent findings of metal (M) encapsulated caged clusters of Si and Ge obtained from computer experiments based on an *ab initio* pseudopotential method. It is shown that one M atom changes drastically the properties of Si and Ge clusters and that depending upon the size of the M atom, cages of 14, 15, and 16 Si as well as Ge atoms are formed. In particular  $M@Si_{16}$  silicon fullerene has been obtained for  $M = Zr$  and  $Hf$ , while a Frank–Kasper polyhedron has been obtained for  $M@X_{16}$ ,  $X = Si$  and  $Ge$ . These clusters show high stability and large highest occupied–lowest unoccupied molecular orbital (HOMO–LUMO) gaps which are likely to make these species strongly abundant. A regular icosahedral  $M@X_{12}$  cluster has also been obtained for  $X = Ge$  and  $Sn$  by doping a divalent M atom. Interactions between clusters are rather weak. This is attractive for developing self-assembled cluster materials.

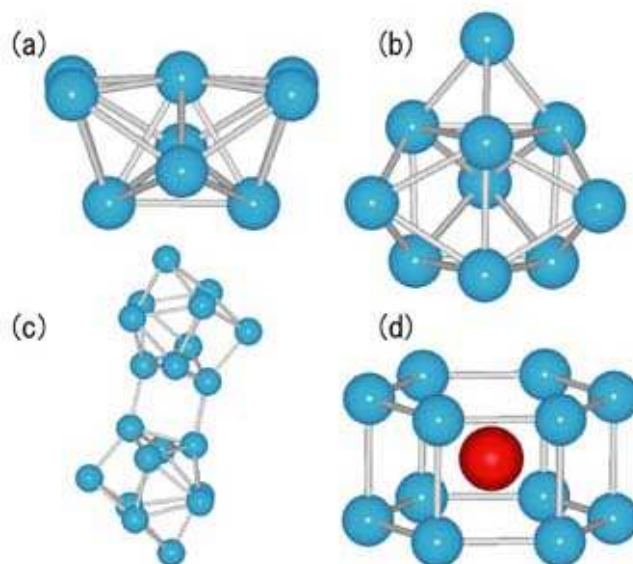
**Keywords.** Silicon; fullerenes; Frank–Kasper polyhedron; cubic.

### 1. Introduction

Silicon is the most important material for device applications. The continued shrinking size of devices has created great interest in understanding the properties of its nanoforms in order to find components of the future miniature devices. Extensive efforts have been devoted in recent years (Kumar *et al* 2002; Kumar and Kawazoe, to be published) to understand the properties of Si clusters and to find ways to produce novel nanostructures for miniature devices. The finding of visible luminescence in silicon nanoclusters is interesting for applications in optoelectronics, tunable lasers, tagging, displays etc. While the small clusters of Si tend to have close packed structures, clusters with 14–25 atoms have prolate structures in which  $Si_9$  or  $Si_{10}$  is the building block (Ho *et al* 1998; Mitas *et al* 2000). Beyond this size, compact 3-D structures are believed to be more favoured. Figure 1 shows the lowest energy structures of  $Si_9$ ,  $Si_{10}$  and  $Si_{20}$ . Studies (Röthlisberger *et al* 1994) on  $Si_{45}$  do show a fullerene-like (*f*) structure with a core of silicon atoms.

Recent experiments (Hiura *et al* 2001) on reactions of silane gas with transition metals showed particular stability of  $Si_{12}W$  cluster that did not adsorb any hydrogen. It has a hexagonal (*h*) prism structure with W at the centre (figure 1). This structure is very different from the structures of elemental Si clusters. In another experiment (Beck 1989), coevaporation of Si and M led to large abundances of  $Si_{15}M$  and  $Si_{16}M$  clusters with  $M = Cr, Mo,$  and  $W$  and little intensities for  $Si_{12}M$  contrary to the results obtained with  $SiH_4$ . Also these results are markedly different from the abundance spectrum (Jarrold and

Bower 1988) of pure Si clusters which shows less intensities in the region of 12–16 atoms. Jackson and Neller-moe (1996) attempted to stabilize a dodecahedral  $Si_{20}$  cage with a Zr atom at the centre (figure 2(a)) and obtained a large binding energy (BE). However, studies by Kumar and Kawazoe (2001) showed distortions in this



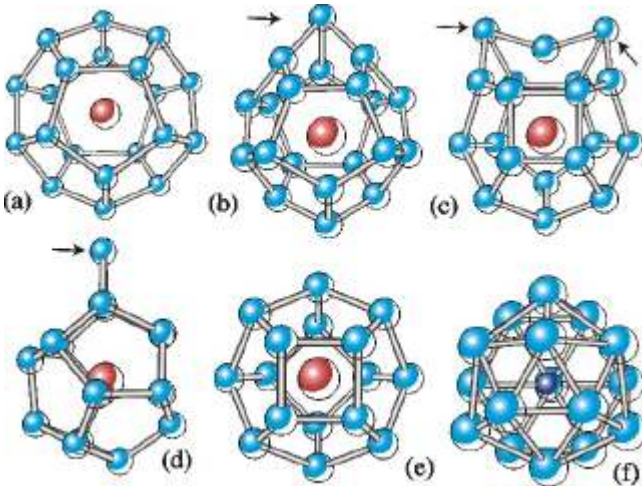
**Figure 1.** Lowest energy structures of (a)  $Si_9$ , (b)  $Si_{10}$ , (c) prolate structure of  $Si_{20}$  obtained from quantum Monte Carlo method (Mitas *et al* 2000), and (d)  $Si_{12}W$  with W (black filled circle) at the centre (Hiura *et al* 2001).

cage such that there is a tendency for the shrinkage of the cage (figure 2(b)).

Following this result and adopting an atom removal and cage shrinkage approach, novel M encapsulated caged  $f$ -M@Si $_n$  ( $n = 14$ – $16$ ) and cubic ( $c$ ) M@Si $_n$  ( $n = 14$  and  $15$ ) structures (the notation M@Si $_n$  is used to denote caged structures of  $n$  Si atoms around an M atom without cappings). The shape and size of these clusters depend upon the size of the M atom which also determines the gap. Also a Frank–Kasper ( $FK$ ) polyhedral M@Si $_{16}$ , (M = Ti and Hf) cluster has been found to have an exceptionally large gap of about 2.35 eV that makes this cluster attractive for opto-electronic materials. The embedding energy (EE) of the M atom in the cage is very large ( $\approx 12$  eV) that leads to a strong stability of these clusters. This together with the variable band gap and weak interaction between clusters make this new family of structures, interesting for self-assembled materials. Similar studies have been done on Ge and Sn clusters. In particular, doping of divalent M atoms has led to the finding of icosahedral ( $i$ ) clusters of Ge and Sn for the first time (Kumar and Kawazoe 2002a). In the following, we present a brief review of these results.

## 2. Computational approach

The calculations were performed using *ab initio* ultrasoft pseudopotential plane wave method (Kresse and Fürthmüller 1996). The exchange–correlation energy was calculated within the spin-polarized generalized gradient approximation (Perdew 1991). A simple cubic supercell with size up to 18 Å was used with periodic boundary



**Figure 2.** 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 silicon fullerene Zr@Si $_{16}$ , respectively. 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 = Ti and Hf). The atom in the cage is M (after Kumar and Kawazoe 2001).

conditions and the  $\Gamma$  point, for the Brillouin zone integrations. The structures were optimized using the conjugate gradient method. The relaxed structures were found to have zero spin in most cases.

## 3. The cage shrinking approach

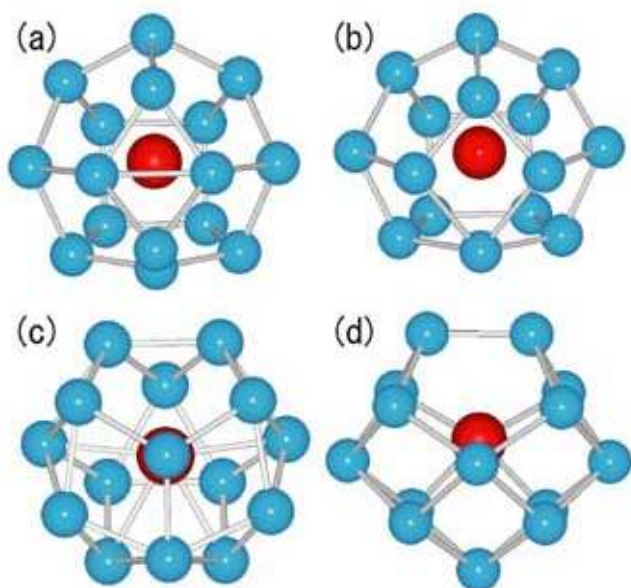
Zr is among the largest size atoms in transition M series. Its encapsulation in the smallest carbon fullerene cage structure of Si $_{20}$  (figure 2(a)) led to a Si atom sticking out (figure 2(b)) upon relaxation. Removal of this capping atom and reoptimization led to a Zr@Si $_{17}$  cage with two Si atoms sticking out (figure 2(c)). Further removal of the two capping Si atoms and reoptimizations led to the Zr@Si $_{16}$  cage with a capping by a Si atom (figure 2(d)). Again removal of this capping atom and reoptimization led to a compact symmetric  $f$  cage of Zr@Si $_{16}$  (figure 2(e)). This procedure of shrinkage and removal of atoms was continued with smaller M atoms starting with the structure of  $f$ -Zr@Si $_{16}$ . It further led to the findings of caged M@Si $_{14}$  and M@Si $_{15}$  clusters. The stability of these clusters was further checked by optimizing several other structures. This procedure was repeated for germanium also. Studies on 12-atom cage structures further led to the finding of  $i$  isomers.

## 4. Results

The close packed symmetric  $f$  cage of 16 Si atoms (figure 2(e)) has eight pentagonal and two square faces as compared to 12 regular pentagonal faces in the dodecahedral Si $_{20}$  (figure 2(a)). Each Si atom on the cage is tricoordinated similar to carbon fullerenes. The size of  $f$ -Zr@Si $_{16}$  is close to that of C $_{60}$ , but the former is lighter. The Si–Si bond lengths are slightly smaller than in bulk Si and the bonding is covalent. The encapsulation of M atom leads to a large gain in energy that makes these M doped clusters to be the most stable Si clusters known so far. The HOMO–LUMO gaps are also large (table 1) and this should make such clusters very abundant. The energy gain in adding one Si atom on  $f$ -Zr@Si $_{16}$  cage is only 3.211 eV and the BE of the Si $_{17}$ Zr structure (figure 3(d)), 4.109 eV/atom. This is lower than the value of 4.162 eV/atom for the  $f$ -Zr@Si $_{16}$  cage. Therefore,  $f$ -Zr@Si $_{16}$  shows

**Table 1.** BEs (eV/atom), EEs (eV), and HOMO–LUMO gaps (eV) of the  $f$  and  $FK$  isomers of M@Si $_{16}$  clusters.

Cluster	BE	EE	Gap
$FK$ -Ti@Si $_{16}$	4.135	11.269	2.358
$f$ -Ti@Si $_{16}$	4.089	12.733	1.495
$f$ -Zr@Si $_{16}$	4.162	13.965	1.580
$FK$ -Zr@Si $_{16}$	4.141	11.814	2.448
$f$ -Hf@Si $_{16}$	4.175	14.176	1.576
$FK$ -Hf@Si $_{16}$	4.171	12.399	2.352



**Figure 3.** (a) Optimized structure of  $f\text{-M@Si}_{16}$  with  $M = \text{Cr}$ . There is a shrinkage of the silicon cage, (b) the capping silicon atom in (a) is removed and the structure, reoptimized to obtain the  $f\text{-Cr@Si}_{15}$  isomer, (c) the  $c$  isomer of  $\text{Cr@Si}_{15}$  that has the lowest energy, (d) lowest energy isomer of  $\text{M@Si}_{15}$ ,  $M = \text{Ti}$ ,  $\text{Zr}$ ,  $\text{Hf}$ ,  $\text{Ru}$ , and  $\text{Os}$ . Structures of  $\text{Si}_{16}\text{M}$  and  $\text{M@Si}_{15}$  for  $M = \text{Mo}$  and  $\text{W}$  are similar (after Kumar and Kawazoe 2002b).

magic behaviour. Similar results were obtained for the isoelectronic  $\text{Hf@Si}_{16}$ . However, encapsulation of  $\text{Ti}$  in the  $f$  cage does not lead to closest packing due to its smaller size and an  $FK$  polyhedron (figure 2(f)) was found to be 0.781 eV lower in energy. It has tetrahedral symmetry with four connected capped hexagons of  $\text{Si}$ . The  $\text{Ti-Si}$  bond lengths in this structure are slightly reduced and it enhances interaction of  $\text{Ti}$  with the  $\text{Si}$  cage. The  $\text{Si-Si}$  bonds are, however, elongated (2.37–2.66 Å) and have a mixed covalent-metallic character. This isomer has an exceptionally large gap of 2.358 eV that lies in the visible range. It is likely that the actual gap would be significantly higher as the approximate density functional methods tend to underestimate the gap. Similar calculations were performed for  $M = \text{Hf}$  and  $\text{Zr}$ . The isoelectronic  $FK\text{-Hf@Si}_{16}$  was found to be nearly degenerate with the  $f$  isomer, but its HOMO–LUMO gap is as large (2.352 eV) as for  $M = \text{Ti}$ . However,  $FK\text{-Zr@Si}_{16}$  lies 0.355 eV higher in energy than the  $f$  isomer. These results suggested that both  $\text{Ti}$  and  $\text{Hf}$  encapsulated  $\text{Si}$  clusters with  $FK$  polyhedron structure should be strongly abundant and that  $\text{Hf}$  doping is unique to produce two different stable degenerate isomers with different bonding natures and significantly different band gaps. These are the only cages with 16 silicon atoms that are formed with even electron transition  $M$  atoms. In the case of

other  $M$  atoms, 16 silicon atom clusters are possible but either these are not of lowest energy or there are distortions or the cage shrinks with capping of some  $\text{Si}$  atom(s). Interaction between two  $f$  clusters has been found to be relatively weak with 1.345 eV BE and a reduction in the gap. However, for  $FK$  isomers, this interaction is very weak (0.048 eV) and the gap remains large, making these species attractive for self-assembly.

Encapsulation of smaller  $M$  atoms such as  $\text{Cr}$ ,  $\text{Mo}$ , and  $\text{W}$  led to the shrinkage of  $f\text{-M@Si}_{16}$  to  $\text{M@Si}_{15}$  cage with a capping atom (Kumar and Kawazoe 2002b) as shown in figure 3(a). Removal of the capping atom and subsequent reoptimization led to a stable  $f\text{-M@Si}_{15}$  cage (figure 2(b)). The HOMO–LUMO gap is small (0.808 eV) and the BE, 3.883 eV/atom. The EE of  $\text{Cr}$  in the cage is large (8.936 eV) but significantly lower than  $\approx 14$  eV obtained for  $\text{Zr}$  and  $\text{Hf}$  (table 1) due to complete quenching of the magnetic moment of  $\text{Cr}$ . The  $\text{Si-Si}$  bond lengths are in the range of 2.27–2.34 Å indicating covalent bonding in this isomer. A few bonds are, however, elongated with values of 2.47 and 2.72 Å. The  $\text{Cr-Si}$  bond lengths lie in the range of 2.60–2.96 Å. These values are more than the sum of the covalent radii, 1.18 and 1.36 of  $\text{Si}$  and  $\text{Cr}$  atoms, respectively. Therefore,  $\text{Cr}$  is not optimally bonded in this  $f$  silicon cage.

Another 15-atom  $\text{Si}$  cage was attempted from a body centred cubic structure by placing one more  $\text{Si}$  atom on a face of the cube with  $M$  at the centre. Optimization with  $M = \text{Cr}$  led to the structure shown in figure 3(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. The mean coordination of  $\text{Si}$  atoms on this cage is 4. The higher coordination of  $\text{Si}$  atoms in this structure leads to slightly elongated  $\text{Si-Si}$  bonds (2.36–2.57 Å). This range is more than the value of 2.35 Å for the covalently bonded bulk silicon and suggests development of some metallic character in this isomer as one would also expect from a higher coordination of  $\text{Si}$  atoms. The  $M\text{-Si}$  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  $M\text{-Si}$  interaction in this structure. The valence states of  $\text{Cr}$  atom lie near the HOMO of the  $\text{Si}$  cage and interact covalently with the latter and the nearby states. This leads to a lowering of the energy of the  $\text{Si}$  cage states in a range of about 2 eV below the HOMO but the deeper states are only weakly perturbed. The same holds true also for other  $M$  atoms.

Similar calculations on  $\text{M@Si}_{16}$  with  $M = \text{Mo}$  and  $\text{W}$  showed the capped caged structure of figure 3(a) to be the lowest in energy similar to  $\text{Cr}$ . Optimizations for  $\text{M@Si}_{15}$  with  $M = \text{Mo}$  and  $\text{W}$ , respectively, showed an increase in the gap to 1.659 and 1.747 eV in the  $c$  derived structure. Therefore, for  $\text{M@Si}_{15}$  ( $M = \text{Cr}$ ,  $\text{Mo}$ , and  $\text{W}$ ),

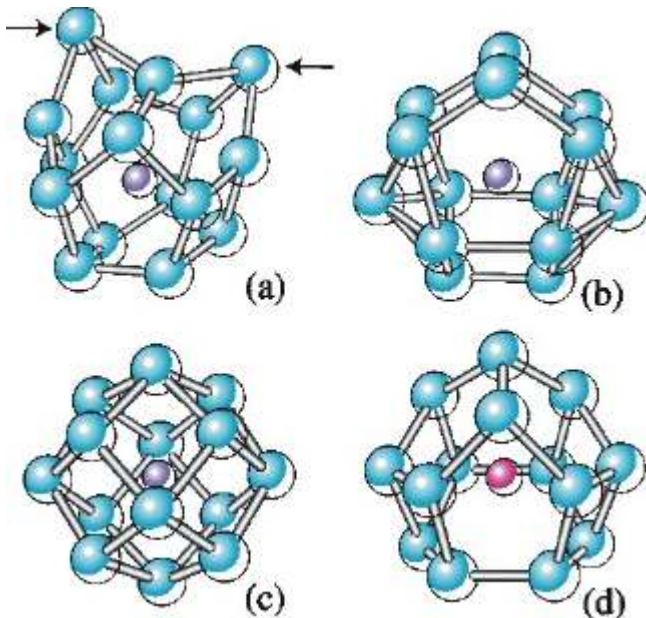
the isomer obtained from a  $c$  structure has the lowest energy and large HOMO–LUMO gap. The bonding properties of these clusters with isoelectronic dopings are similar. The different growth modes of 15 and 16 Si atom clusters lead to their simultaneous large abundances as observed (Beck 1989). Strikingly, these are the only two clusters with high intensities in experiments and beyond this size there is very low intensity of other clusters. These results show the importance of the  $M@Si_{15}$  cage for these  $M$  atoms and suggest that the only other significantly stable cluster with a capping is  $Si_{16}M$  that has large gap. Therefore, it is highly likely that such caged clusters can be uniquely produced for developing cluster assembled materials with desired properties as the shape, size, and band gap can be varied with a suitable choice of  $M$ . Further calculations (Kumar and Kawazoe 2002b) on  $M = Ti, Zr, Hf, Ru,$  and  $Os$  for the 15-atom silicon cage give a slightly different  $c-M@Si_{15}$  structure with large BEs and about 1.2 eV HOMO–LUMO gaps.

Studies (Kumar and Kawazoe 2001) with further smaller  $M$  atoms,  $Fe, Ru,$  and  $Os$  showed the  $f-M@Si_{16}$  cage to shrink to  $M@Si_{14}$  with two Si atoms capping (figure 4(a)). Removal of these two capping atoms and subsequent optimizations led to a  $f-M@Si_{14}$  cage (figure 4(b)) which is better described as a capped decahedron (d). It was, however, found that a body centred cubic structure (figure 3(f)) had lower energy and larger HOMO–LUMO gap. But in the case of  $M = Ru$  and  $Os$ ,

both the  $f$  and  $c$  isomers are nearly degenerate. The BE, EE and the HOMO–LUMO gaps of these clusters are given in table 2. Though,  $M@Si_{15}$  structure has also been obtained for  $M = Ru$  and  $Os$ , it is not close packed. These calculations suggested the 14-atom Si cage to be optimal for  $M = Fe, Ru,$  and  $Os$ . Calculations with  $M = Ni, Pd,$  and  $Pt$  also gave cubic structure to be of lowest energy, but there is a magnetic moment of  $2\mu_B$  and the HOMO–LUMO gap is small ( $< 0.5$  eV). Therefore, these clusters are unlikely to be abundant.

Similar studies (Kumar and Kawazoe 2002c) have been carried out on germanium clusters. In this case the  $f-M@Ge_{16}$  structure transforms into the  $FK$  polyhedron which again has a large HOMO–LUMO gap of about 2 eV similar to the Si based clusters. The 14- and 15-atom clusters have a tendency to prefer capped decahedral structures. It is due to the weaker covalent character of Ge. The lowest energy structures of 14, 15, and 16 Ge atom cages are shown in figure 5. Again there is a large gain in the binding energy as compared to the elemental Ge clusters.

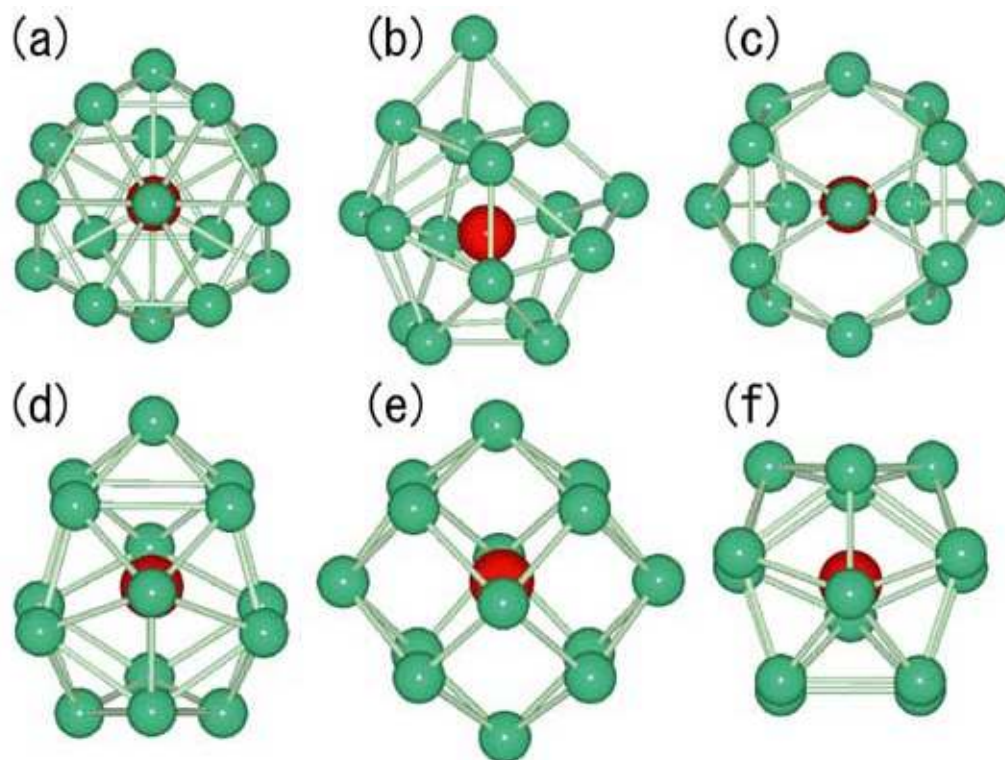
Further studies have been carried out on 12 atom cages with  $M$  encapsulation. For  $Si_{12}M$ ,  $M = Cr, Mo,$  and  $W$ , a  $h$  prism (figure 1(d)) has the lowest energy. The BE and gaps are 3.84, 4.02, and 4.18 eV and 0.85, 0.90, and 1.34 eV, respectively. These gaps are lower than the values obtained for the 15- and 16-atom Si cages except for  $Si_{12}W$ , but the BE of the 15- and 16-atom cages are higher than the corresponding value for the  $Si_{12}M$  cluster. Therefore, 15- and 16-atom cages are more stable than  $Si_{12}M$  in agreement with the finding of the laser evaporation experiments. As the sizes of these  $M$  atoms are significantly larger than that of Si, these cannot form close packed structures with 12 Si atoms. This is, however, possible with smaller  $M$  atoms. Further studies (Kumar and Kawazoe, to be published) of H interaction with these clusters show weak bonding in agreement with the absence of hydrogenated species of  $Si_{12}M$ . Calculations (Kumar and Kawazoe 2002a; and to be published) on several other  $M$  atoms led to the finding of  $i$  clusters of Ge and Sn with large gaps by doping divalent  $M$  atoms such as  $Be, Zn, Mg,$  and  $Ca$ .



**Figure 4.** Shrinkage of  $f-Fe@Si_{16}$  structure: (a) optimized  $Si_{16}Fe$  with two Si atoms capping (marked with arrows), (b)  $d-M@Si_{14}$ ,  $M = Fe$  and  $Ru$ , (c)  $c-Fe@Si_{14}$ , and (d)  $f-Os@Si_{14}$ . The  $c$  structures of  $Ru$  and  $Os$  are similar to (c) (after Kumar and Kawazoe 2001).

**Table 2.** BEs (eV/atom), EEs (eV), HOMO–LUMO gaps (eV) of low lying isomers of selected clusters.

Cluster	BE	EE	Gap
$f-Si_{16}Fe$	4.010	9.426	1.294
$f-Si_{16}Ru$	4.188	12.445	1.230
$f-Si_{16}Os$	4.252	13.551	1.246
$c-Fe@Si_{14}$	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



**Figure 5.** Optimized structure of  $M@Ge_n$  clusters. (a) FK polyhedron for  $n = 16$  and  $M = \text{Ti, Hf, and Zr}$ , (b) capped decahedral isomer for  $n = 16$  and  $M = \text{Cr, Mo, and W}$ , (c) and (d) are two closely lying decahedral isomers for  $n = 15$ , (e) and (f) are cubic and decahedral isomers for  $n = 14$  (after Kumar and Kawazoe 2002c).

## 5. Summary

In summary, we have presented a brief review of the recently found transition  $M$  atom encapsulated silicon and germanium caged clusters from computer experiments based on an *ab initio* method. These form 14-, 15-, and 16-atom cages with  $M$  at the centre, depending upon the size of the  $M$  atom. The shape and the HOMO–LUMO gap depend upon  $M$ . Most notable among these are the fullerene-like, cubic, and Frank–Kasper polyhedral structures. Interaction between the fullerene-like cages is relatively weak while interaction between the Frank–Kasper polyhedral clusters is van der Waals type. Further icosahedral clusters of Ge and Sn have been obtained with divalent  $M$  atom encapsulation. These results show that one  $M$  atom changes the properties of elemental Si and Ge clusters drastically. It has opened up new avenues for the development of elements of nanodevices. Also these results can shed new light on the understanding of metal–semiconductor interfaces as well as the development of nanowires for which metal particles are used as catalyst. The strong stability of these clusters results from strong  $M$ –Si interactions that also fix the size of the cage. It is likely that these clusters can be pro-

duced exclusively in large quantities. The HOMO–LUMO gaps in these clusters are large and in particular for the FK isomer, these lie in the visible range. This is attractive for opto-electronic applications.

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