Metal-Encapsulated Caged Clusters of Germanium with Large Gaps and Different Growth Behavior than Silicon

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Metal (M)-encapsulated caged clusters of Ge are studied using the *ab initio* pseudopotential plane-wave method and the generalized gradient approximation for the exchange-correlation energy. Depending upon the size of the M atom, we find Frank-Kasper polyhedral $M@Ge_{16}$ for $M =$ Ti, Zr, Hf, and capped decahedral or cubic $M@Ge_{14}$ and $M@Ge_{15}$ clusters for several M atoms. The growth behavior differs from the one found in $M@Si_n$ clusters. The highest-occupied–lowest-unoccupied molecular orbital gaps are, however, similarly large or even higher in some cases. $Cr@Ge_{16}$ and $Fe@Ge_{15}$ are magnetic. The weak interaction between the clusters makes such species attractive for cluster assembled materials.

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Clusters of semiconducting materials are currently of great interest for developing miniature devices. Silicon clusters have attracted much attention [1] in the quest for sustaining Si based technologies. It has led to the recent findings of novel M-encapsulated caged Si clusters [2,3] that have fullerenelike (f), cubic (c), and Frank-Kasper (FK) polyhedral structures which are very different from those of elemental Si clusters [4,5]. These results demonstrate that M doping changes the structure and properties of Si clusters in a dramatic way and opens up a new direction for developing new species for nanoscale applications. Small clusters of elemental Ge have similar structures as for Si, but the growth behavior is slightly different [6]. Recently M doping of Ge has been used [7] to obtain perfectly icosahedral clusters similar to those of metals. These have large density functional highest-occupied–lowest-unoccupied molecular orbital (HOMO-LUMO) gaps of about 2 eV, but Si shows a different behavior. Here we report for the first time M-encapsulated larger Ge caged clusters that have large gaps as for $M@Si_n$, leading to new possibilities of cluster assembled materials.

The calculations have been done using the *ab initio* ultrasoft pseudopotential plane wave method [8] with spin-polarized generalized gradient approximation (GGA) [9] for the exchange-correlation energy. A simple cubic supercell with 15 Å edge length is used with periodic boundary conditions and the Γ point, for the Brillouin zone integrations. The initial structures are taken from isomers of $M@Si_n$ [2,3] and a few other structures that are fully optimized using the conjugate gradient method. For M, we use Ti, Zr, Hf, Cr, Mo, W, Fe, Ru, Os, and Pb atoms that have an even number of valence electrons. The $3p$ and $4p$ atomic core states of Ti and Zr, respectively, are treated as valence.

Figure 1 shows the low lying isomers of M-encapsulated Ge clusters. For $Zr@Ge_{16}$, the f structure [2] transforms into the FK polyhedron [Fig. 1(a)] and, therefore, it differs from $Zr@Si_{16}$ for which the f isomer is of lowest energy. There are four interconnected hexagonal (h) rings of Ge atoms forming a truncated tetrahedron. Each of the rings is capped by a Ge atom that strongly binds with the M atom at the center. The Ge-Ge bonds on the four h rings are shorter (2.57 and 2.63 Å) as compared to the bonds (2.89 Å) between the ring and the capping atoms but slightly longer than the experimental bulk bond length of 2.44 Å. This is also expected as the mean coordination of Ge atoms on the cage is 5.25 as compared to 4 in the bulk. The bond length between the capping atoms and Zr is also shorter (2.87 Å) as compared to 3.05 Å between Zr and the ring atoms, suggesting strong bonds between the ring atoms and between Zr and the capping atoms. The HOMO-LUMO gap is large ($\approx$2 eV) and is surprisingly close (Table I) to the value (2.358 eV) for FK-$Ti@Si_{16}$ [2]. Moreover, *the gap for* $Zr@Ge_{16}$ *is significantly higher than 1.58 eV for the lowest energy isomer of* $Zr@Si_{16}$. Thus, M doping leads to unexpectedly different behaviors in clusters. The actual gap is expected to be even significantly higher and to lie in the visible range that makes this cluster interesting for optoelectronic devices.

For Hf and Ti also, the f isomer transforms into the FK structure. The corresponding Ge-Ge and M-Ge bond lengths are, respectively, (2.56, 2.63, and 2.88 Å) and (2.85 and 3.05 Å) for Hf and (2.54, 2.61, and 2.84 Å) and (2.78 and 3.04 Å) for Ti. In all the cases the gap is large (Table I) but notably smaller for Ti as compared to Zr or Hf due to a weaker interaction of Ti states with those of the Ge cage, the Ti atom being smaller and valence orbitals, shorter ranged. We further optimized a hexacapped decahedron (one pentagonal face uncapped) as decahedral (d) clusters are among the lowest energy isomers for $n = 14$ and 15. This transforms into the FK isomer for Hf and a tetracapped h antiprism with C_{3v} symmetry [Fig. 1(b)] for Zr. The latter is nearly degenerate with the FK isomer and has a gap of 1.998 eV [10]. Thus, *a smaller M atom or a bigger cage prefers the 16 atom FK structure.*

As the Ge_{16} cage is bigger than the one of Si_{16}, we tried to dope the f- and the FK-Ge_{16} cages with a larger atom such as Pb that is also tetravalent. Optimizations led to

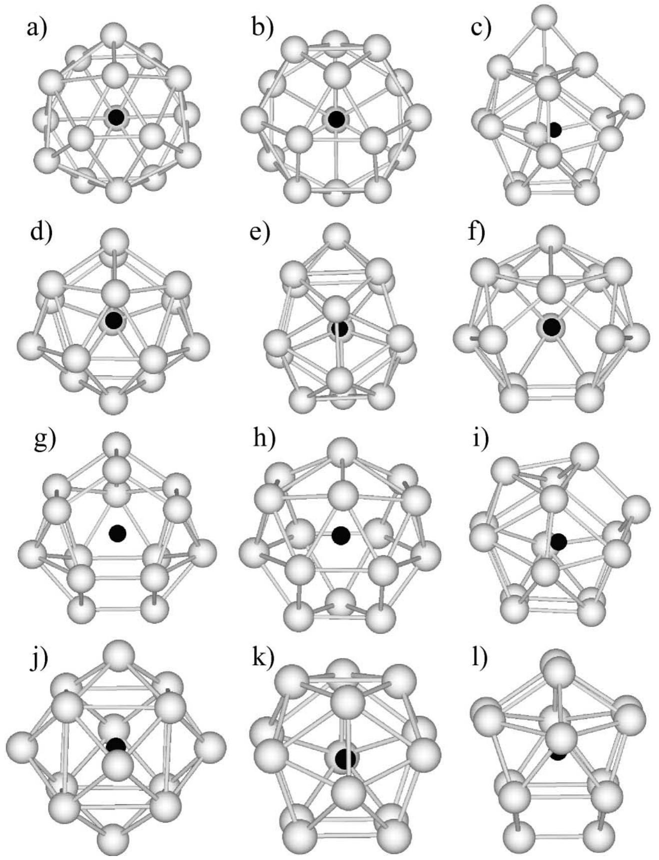

FIG. 1. Low lying isomers of M-encapsulated Ge_n clusters. (a) The FK polyhedron for M = Ti, Zr, and Hf and (b) tetracapped hexagonal antiprism for $n = 16$. (c) Shrinkage of the f-M@Ge_{16} cage for M = Cr, Mo, and W. (d) d-M@Ge_{15}, (e) $d1$-M@Ge_{15} for M = Ti, Zr, and Hf, (f) FK-type structure of M@Ge_{15} for M = Cr, Mo, W, Ru, and Os, (g) $d2$ isomer for M = Ru, Cr, and W, (h) FK1 isomer for Cr, Mo, and W, and (i) $d3$ isomer for Fe and Os. d, $d1$, $d2$, and $d3$ differ in the capping of faces. (j) c-M@Ge_{14}, (k) d-M@Ge_{14} for Cr, Mo, and W, and (l) d-M@Ge_{14}, M = Fe, Ru, and Os. For clarity, bonds connecting M (dark atom inside) to the cage are not shown.

TABLE I. Binding energies (BEs) (eV/atom), embedding energies (EEs) (eV), and HOMO-LUMO gaps (eV) of low lying isomers of M doped Ge_n clusters. d-Cr@Ge_{16} and $d3$-Fe@Ge_{14} have a magnetic moment of $2\mu_B$ each.

Cluster	BE	EE	Gap
FK-Ti@Ge_{16}	3.597	10.608	1.790
FK-Zr@Ge_{16}	3.649	11.674	1.955
FK-Hf@Ge_{16}	3.658	11.774	1.979
FK-Pb@Ge_{16}	3.118	3.702	1.169
FK-Cr@Ge_{16}	3.350	6.196	0.463
d-Ge_{16}Mo	3.534	10.069	1.217
d-Ge_{16}W	3.622	11.550	1.274
d-Ti@Ge_{15}	3.567	10.174	1.386
d-Zr@Ge_{15}	3.619	11.250	1.508
d-Hf@Ge_{15}	3.632	11.393	1.523
FK-Cr@Ge_{15}	3.367	7.089	1.070
FK-Mo@Ge_{15}	3.584	10.565	1.204
FK-W@Ge_{15}	3.680	12.181	1.278
$d3$-Fe@Ge_{15}	3.448	7.289	0.778
$d2$-Ru@Ge_{15}	3.643	11.494	1.131
$d3$-Os@Ge_{15}	3.697	12.394	1.219
d-Cr@Ge_{14}	3.368	6.835	1.179
d-Mo@Ge_{14}	3.582	10.133	1.390
d-W@Ge_{14}	3.690	11.760	1.519
c-Fe@Ge_{14}	3.445	7.388	1.109
d-Ru@Ge_{14}	3.661	11.915	1.565
d-Os@Ge_{14}	3.723	12.843	1.610

a significant distortion of the FK isomer. It lies 0.224 eV lower in energy than the f isomer. The latter shrinks such that a few atoms cap a smaller Ge cage. This shrinkage of the cage with encapsulation of a bigger atom is first surprising but is very likely due to the charge transfer from the Pb atom to the cage that effectively reduces its size. Further studies with smaller M atoms such as Mo, Fe, Ru, and Os also show shrinkage of the f cage and significant distortions of the FK cage. This is also due to the partial occupation of the HOMO in the tetrahedrally symmetric FK cluster. Therefore, smaller cages are preferred for these M atoms. This result is also supported by the higher binding energies (BEs) of smaller cages.

For W, the f isomer shrinks into a capped d structure [Fig. 1(c)] that has the lowest energy. A capped c isomer [2] transforms into a d structure with slightly different capping such that a Ge atom on a pentagonal face is moved to a side face adjoining another capping atom. It lies only 0.041 eV higher in energy with a 1.227 eV gap. For Mo, the FK isomer is distorted and lies only 0.093 eV higher in energy than the lowest energy capped d isomer. For Cr, however, the FK isomer with a magnetic moment of $2\mu_B$ is of lowest energy. It is due to the fact that the existence of magnetic moments tends to elongate the bonds. The Ge-Ge and Cr-Ge bond lengths lie in the range of 2.55–3.02 and 2.73–3.28 Å, respectively. The nonmagnetic solution lies 0.323 eV higher in energy. The f structure shrinks to the d isomer as for W and Mo [Fig. 1(c)] and lies 0.321 eV higher in energy than the magnetic FK isomer. *This is the first case that a FK magnetic isomer is found to be of lowest energy.* For Fe and Ru, the FK isomer shrinks and the cage is significantly distorted. Thus, *M-encapsulated Ge clusters prefer d or FK structures that are more common in metallic systems than f isomers normally encountered in covalently bonded clusters.* The FK isomer is the best for M@Ge_{16} with M = Ti, Zr, and Hf.

The embedding energy (EE) of M in the Ge_n cage, defined as $E(M@\mathrm{Ge}_n)$-$E(\mathrm{Ge}_n)$-$E(M)$, $E(X)$ being the energy of the X species, is given in Table I. In most cases it is large ($\approx$10–12 eV) but smaller than the values for M-encapsulated Si clusters. The EE of Pb is much smaller than the values for other M atoms, suggesting the importance of d electrons in the strong bonding of M with the Ge cages. Also for Cr, the EE is significantly smaller as compared to other transition M atoms because its large atomic magnetic moment is partially quenched, the energy cost to transform the magnetic ground state of Cr atom into a nonmagnetic state being 5.87 eV within GGA.

For $n = 15$, the low lying isomers are generally d type (Fig. 1). For $M =$ Ti, Zr, and Hf a d isomer with cappings [Fig. 1(d)] has the lowest energy. It is similar to the M@Si$_{15}$ structure [3] for $M =$ Cr, Mo, and W. Two different structures converge to this isomer, giving us confidence that it is the lowest energy structure of this cluster. The BEs and EEs (Table I) are comparable to those of M@Ge$_{16}$. The HOMO-LUMO gaps are large ($\approx$1.5 eV). These are also larger than the values for M@Si$_{15}$, $M =$ Ti, Zr, and Hf that have a c structure [3]. The c isomer of M@Ge$_{15}$, $M =$ Ti, Zr, and Hf relaxes to a pentacapped $d1$ structure [Fig. 1(e)] that is nearly degenerate with the one shown in Fig. 1(d). The HOMO-LUMO gaps in these isomers have similar values. Continuation of optimization with $M =$ Cr, Mo, and W shows that these have different structures having nearly the same energy. For Cr and Mo, the f structure shrinks such that one Ge atom caps a 14-atom Ge cage. It lies significantly higher in energy than the lowest energy FK-type isomer [Fig. 1(f)]. An isomer with the structure of Fig. 1(d) lies very close in energy for Cr but has a slightly larger gap (1.126 eV). For Mo, a $d2$ isomer [Fig. 1(g)] lies only 0.032 eV higher in energy with a gap of 1.333 eV, while a FK-type isomer [Fig. 1(h)] lies 0.112 eV higher with a gap of 1.296 eV. The mean Ge-Ge and M-Ge bond lengths in these isomers also have similar values. Though there is significant variation in the bond lengths, a majority of Ge-Ge bonds are in the range of 2.5–2.7 Å. A few bonds are elongated with values of about 2.9 Å. Similarly, the M-Ge bonds have values of about 3.0 Å, but there are some short bonds also with values of about 2.8 Å. For W, the lowest energy isomer is the same [Fig. 1(f)], but $d2$ [Fig. 1(g)] is nearly degenerate. Also $d1$ [Fig. 1(e)] lies only 0.08 eV higher in energy with a gap of 1.388 eV. The FK-like structure [Fig. 1(h)] also lies only 0.088 eV higher in energy and has a larger gap of 1.418 eV. *The results of structures, energies, and bond lengths suggest mixed metallic-covalent bonding character in these clusters such that a higher coordination of Ge is generally energetically more favored.*

The lowest energy isomers of M@Ge$_{15}$, $M =$ Fe, Ru, and Os are also d type. For Fe, two different structures based on the f and c isomers of M@Si$_{15}$ converge to the same $d3$ structure [Fig. 1(i)]. This is degenerate with the FK isomer [Fig. 1(f)]. Both have a net magnetic moment of $2\mu_B$. These magnetic solutions lie $\approx$0.2 eV lower in energy than the nonmagnetic states and have a significant gap of about 0.77 eV. Therefore, the magnetic isomers should be stable and observable. The lowest energy structure ($d3$ in Table I) of Os@Ge$_{15}$ is shown in Fig. 1(i). The FK isomer [Fig. 1(f)] lies 0.081 eV higher in energy and has a slightly higher gap (1.377 eV). For Ru, the $d2$ isomer [Fig. 1(g)] has the lowest energy. The FK isomer lies only 0.071 eV higher in energy with a gap of 1.258 eV. Thus the structures of these clusters are similar and have zero magnetic moment except for Fe. The EEs and the BEs of Ru and Os clusters are among the largest. Our results suggest that the FK isomer [Fig. 1(f)] is a favored cagelike packing for many M doped Ge caged clusters.

For M@Ge$_{14}$ we tried several initial configurations including the c, f, and h antiprism structures. For Ti, the c isomer [Fig. 1(j)] is nearly degenerate with an f isomer and the HOMO-LUMO gaps are similar. The f isomer transforms into a double capped distorted d structure and the h isomer, to the c structure. For Zr, the c isomer is slightly distorted and is lowest in energy. The h isomer after distortion lies only 0.049 eV higher in energy. For Hf, the structures are significantly distorted. All of these have smaller gaps of about 1 eV or less and our results suggest that 14 atom Ge clusters are not the most preferred for these M atoms. For Cr, Mo, and W, the f isomer transforms to a tetracapped d structure [Fig. 1(k)] that has the lowest energy. It is the same structure as for M@Si$_{14}$, $M =$ Cr, Mo, and W [3]. It is also similar to the $d1$-M@Ge$_{15}$ isomer. The c and h isomers of Cr with $2\mu_B$ magnetic moment are lower in energy than the corresponding nonmagnetic solutions, but these are $\approx$1 eV higher than the one obtained from the f isomer. The c and h isomers of Mo and W transform to the lowest energy d structure, suggesting a large basin of attraction for it. For Ru, and Os, the d isomer with a slightly different capping [Fig. 1(l)] has the lowest energy. The c isomer of Ru and Os lies 0.241 and 0.340 eV higher in energy, respectively. For Fe, the c isomer lies 0.045 eV lower in energy than the d isomer. The HOMO-LUMO gaps for the d isomer (1.565 and 1.610 eV, respectively) of Ru and Os are also among the largest. These results show that the c and d isomers are the most preferred for M@Ge$_{14}$.

A comparison of energies for $n = 14$, 15, and 16 shows a larger gain in energy in going from $n = 14$ to 15 as compared to the energy gain in going from $n = 15$ to 16. Therefore, *15 atom Ge clusters are magic for all M dopings.*

In order to understand the stability of these clusters, we show in Fig. 2 the electronic states of FK-Zr@Ge$_{16}$, d-Zr@Ge$_{15}$, FK-W@Ge$_{15}$, and d-W@Ge$_{14}$ all of which have high stability. A comparison with the states of the corresponding empty center Ge cages shows that in all the cases deeper lying states are weakly perturbed by M encapsulation and the main effect is a shift of the states. This is more prominent in the range of a few eV around the HOMO. For FK-Zr@Ge$_{16}$, there are four down-spin LUMO states of the Ge$_{16}$ cage that interact covalently with the valence states (at -4.28 and -2.85 eV) of the Zr atom such that the four valence electrons of Zr get shared leading to the complete occupation of the bonding states and a large HOMO-LUMO gap that is seen also for the Ge$_{16}$ cage. For d-Zr@Ge$_{15}$, the Ge$_{15}$ cage has a zero magnetic moment and a large gap after two LUMO states. The latter interact covalently with the states of the Zr atom and the bonding states (fully occupied) get shifted to significantly higher binding energies leading to a large HOMO-LUMO gap and the stability of this cluster. Similar results hold for the isoelectronic Ti and Hf. In order

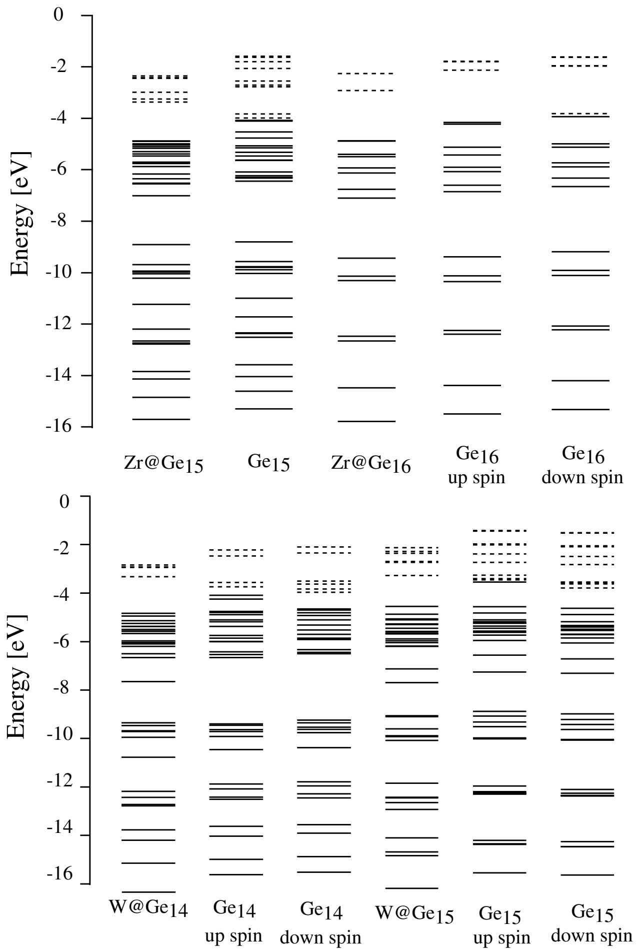

FIG. 2. Electronic states for M@Ge$_n$ clusters and Ge cages. Broken lines show a few unoccupied states. The up-spin states of Ge$_{16}$ have threefold and twofold nearly degenerate HOMO states. The down-spin HOMO is twofold degenerate but occupied by only one electron. The LUMO is threefold degenerate. For Ge$_{15}$, the net spin is zero. There are two LUMO states just above HOMO. The most significant effect of doping is on the states near the HOMO. Similar results are shown for 14 and 15 atom clusters with W and Ge$_n$ empty cages. See text for details.

to understand the stability of clusters with other M atoms, we show the spectrum of FK-W@Ge$_{15}$. There are six spin states of the Ge$_{15}$ cage above HOMO followed by a significant gap. These interact with the valence states of the W atom leading to 3-spin degenerate states at higher binding energies followed by a large gap. In the case of d-W@Ge$_{14}$ also, there are six unoccupied spin states of the Ge$_{14}$ cage followed by a significant gap. Again interaction with the W atom leads to fully occupied bonding states followed by a large gap. These results support the covalent character of bonding between the M atom and the Ge cages as was also found in the case of M@Si$_n$ [2].

A study of the interaction between two FK-Ti@Ge$_{16}$ clusters in a crossed edge structure [2] shows that the structure of the individual clusters remains nearly unchanged. The BE between the clusters is only 0.047 eV suggesting van der Waals–type bonding with long (4.50 Å) nearest neighbor bond lengths between the two clusters. The HOMO-LUMO gap also remains large with the value of 1.729 eV. Therefore, these clusters offer new possibilities for cluster assembled materials with large gaps.

In summary, we have found M-encapsulated caged clusters of Ge with large gaps of up to about 2 eV in the FK polyhedron structure. The gap can be varied by a suitable choice of the M atom. An interesting finding is that the gap for the Zr@Ge$_{16}$ cluster is even higher than the value for the lowest energy isomer of Zr@Si$_{16}$. In general the growth behavior of M@Ge$_n$ is different from M@Si$_n$ clusters. A 15 atom Ge cluster is found to be magic with all M dopings. There is a preference for the FK-type cage with 16 atoms and d-type cages for 14 and 15 atom Ge clusters as in metallic systems. The more extended nature of the Ge valence orbitals as compared to those of Si tends to increase the metallic nature in the bonding. The M-Ge interactions are strong but weaker than M-Si interactions. Fe@Ge$_{15}$ and Cr@Ge$_{16}$ are magnetic and the interaction between the FK clusters is weak that makes these clusters attractive for novel cluster assembled materials.

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