

Thorium Encapsulated Caged Clusters of Germanium: Th@Ge_n , $n = 16, 18$, and 20Abhishek Kumar Singh,^{*,†} Vijay Kumar,^{‡,§} and Yoshiyuki Kawazoe[†]

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We report from ab initio calculations that thorium encapsulation can be used to stabilize highly symmetric cages of germanium with 16 and 20 atoms. The lowest energy structures of these clusters are different from the recently found silicon fullerenes and are similar to clusters found in bulk metallic alloys. The binding energies of these clusters are higher compared with the values for the elemental germanium clusters of comparable sizes, and this suggests a strong possibility of their experimental realization in large quantities. Also, Th@Ge_{16} has a large highest occupied–lowest unoccupied molecular orbital (HOMO–LUMO) gap of 1.72 eV that makes it interesting for optoelectronic applications.

Currently, great efforts are being made to develop and understand the properties of novel nanostructures of silicon and germanium in the search for suitable materials for future miniature devices. Highly stable clusters and cluster-assembled materials are promising, for new materials, having desired properties. Extensive research^{1–5} on clusters of Si and Ge shows that clusters with more than 11 atoms are generally not magic and that Si and Ge clusters have different growth behaviors,² though in bulk both have the same structure. Therefore, large-scale production of mass selected elemental clusters of Si and Ge is unlikely. In a recent development, a novel way to generate high stability magic clusters of Si and Ge has been found^{6–11} in which clusters are formed by the encapsulation of a metal atom. The selection of different metal atoms leads to the much desirable tunability in the properties of these clusters. Besides that, it has also been shown that some of these clusters could be assembled to form nanotubes.^{12–14}

The idea of encapsulation has been successfully imported to clusters of other elements, and promising results have also been obtained for Sn and Pb clusters.^{15,16} Thus far, the studies have been focused mostly on clusters in the range of 10–16 atoms. The largest known metal encapsulated cluster of Ge consists of 16 germanium atoms.⁹ The interaction between the metal atom and the cage in these clusters is very strong, and the relative sizes of the metal and the cage atoms are very important for the stabilization of a cage of a particular size, while the electronic configuration of the metal atom is important for the stability of a particular structure for a given number of cage atoms. The metal atom in these studies is generally a transition metal. To stabilize larger cages of Ge, lanthanide and actinide atoms are interesting because of their bigger size. In this study, we explore the encapsulation of the Th atom from the actinide

series as a representative case and show that it stabilizes some novel cages in the size range of 16–20 Ge atoms.

Recently, Th has been used¹⁰ to stabilize the dodecahedral fullerene structure of silicon. As we shall show, the structures and properties of Th encapsulated Ge clusters are quite different, but as in the case of silicon, Th@Ge_{20} is the largest cluster of Ge with the encapsulation of a single metal atom. We choose thorium as a dopant because it is one of the most important elements in the actinide series and occurs in nature in amounts sufficient to extract.¹⁷ Most importantly, it is the only element in the lanthanide and actinide series to have a most preferred oxidation state of 4+, which has been shown¹⁰ to be very important for the stabilization of dodecahedral silicon fullerene. Also, Th has been found to be the only element in the periodic table that stabilizes the Si_{20} fullerene in neutral form in icosahedral symmetry. The radius of the Th atom is one of the largest (1.80 Å), which is also an important factor in optimizing the strong metal–germanium interactions, as the Ge atom is 4% bigger than a Si atom.

We have performed ab initio calculations using the projected augmented wave method^{18,19} and a plane wave basis set within the spin-polarized density functional theory and the generalized gradient approximation (GGA)²⁰ for the exchange–correlation energy. The Brillouin zone is represented by the Γ -point. The conjugate gradient technique is used to optimize the structures without any symmetry constraints. The structures are considered to be converged when the force on each ion becomes 0.001 eV/Å or less. The reliability of the potentials has been tested for bulk Ge and Th. The calculated lattice parameters (5.46 and 5.05 Å) and cohesive energies (4.73 and 6.18 eV/atom) for Ge and Th, respectively, are in excellent agreement with the experimental values (5.43 and 5.08 Å) and (4.63 and 6.20 eV/atom).

For the stabilization of a 20-atom Ge cage with the encapsulation of a Th atom, we consider two different initial structures: (i) a dodecahedral fullerene cage with Th at the center (Figure 1a(I)) and (ii) a 20-atom cage structure (Figure 1a(II)) that is found in the bulk $\text{Ce}_5\text{Mg}_{42}$ phase.²¹ Both structures

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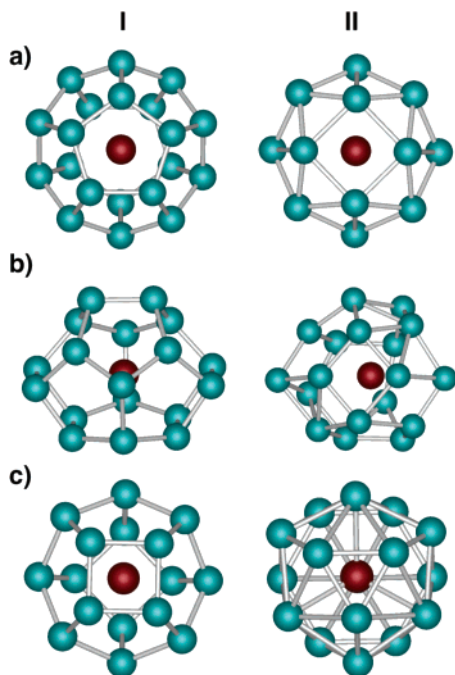


Figure 1. Optimized structures of (a) Th@Ge₁₆, (b) Th@Ge₁₈, and (c) Th@Ge₂₀ clusters. I and II represent the fullerene-like and close packed structures considered in this study. The structures in column II have the lowest energies. Turquoise (maroon) balls represent the Ge (Th) atom.

are stable. However, unlike Si, the second structure becomes 0.74 eV lower in energy than the fullerene isomer. A similar behavior was obtained earlier with transition metal encapsulation in a 16-atom cage of Ge⁷ that was found to be different from Si. Thus, similar to the elemental clusters of Ge and Si, at the nanoscale, the slight difference in size and bonding nature also leads to very different behaviors of metal encapsulated Si and Ge clusters. In the case of the dodecahedral Th@Ge₂₀ fullerene cage, the electron counting for the completion of electronic shell is satisfied,¹⁰ as is the case for Th@Si₂₀. Therefore, it can be expected that the dodecahedral fullerene cage of Ge would be stabilized. However, due to the larger atomic size of Ge, the size of the cage becomes slightly bigger and this could lead to a reduction in Ge–Th interactions. The optimized Ge–Ge and Ge–Th bond lengths are 2.48 and 3.48 Å, respectively. The doping energy (14.11 eV), defined as the difference between the energy of Th@Ge₂₀ and the sum of energies of the Ge₂₀ cage with the same atomic positions as in the doped cage and the Th atom, still remains high. The HOMO–LUMO gap also increases from 0.57 eV in the case of Th@Si₂₀ fullerene to 1.32 eV. In the other isomer (Figure 1a(II)), the Ge–Ge bond length increases to 2.61, 2.81, and 2.94 Å due to the higher coordination of Ge atoms on the cage, while the Ge–Th bond length reduces to 3.27, 3.36, and 3.45 Å compared to the values in the fullerene cage. In this way, the interaction between the Ge cage and the Th atom is better optimized. The HOMO–LUMO gap is reduced slightly to 1.11 eV. Also, the doping energy of Th in this case is 13 eV, which is less than the gain in energy for the fullerene isomer. Despite this, the binding energy (BE) in this cage (3.56 eV/atom) is more than the value (3.53 eV/atom) for the fullerene isomer because the BE of the 4-fold symmetric closer packed Ge cage is higher than that of the fullerene cage.

To further check the stability of other cages and to find the optimal size of the cage for Th encapsulation, we extend our studies to cages of 16 and 18 Ge atoms. For the case of Th@Ge₁₈, we have studied two geometrical isomers: (i) a fullerene-like isomer with a hexagon, two squares, and eight

pentagons (Figure 1b(I)) and (ii) a closer packed cage (Figure 1b(II)) which is found generally in metallic alloys, and it is lowest in energy with a BE of 3.48 eV/atom and a HOMO–LUMO gap of 0.72 eV. Therefore, unlike Si, Ge prefers more metallic cages as the lowest energy structures with Th encapsulation. Similar to the case of Ge₂₀ cages, the closer packed cage also lies about 0.30 eV lower in energy than the fullerene-like cage (BE = 3.46 eV/atom). Though the fullerene cage can be stabilized, there is a signature of strain in the structure due to the lack of symmetry. The doping energy in the fullerene-like isomer remains high (12.83 eV), but it goes down by 1.07 eV as compared to the case of the 20-atom fullerene cage. For Th@Ge₁₆, we study Frank–Kasper (FK) and fullerene cages that have been found⁶ to be the most preferred structures for metal encapsulated 16-atom silicon clusters with tetravalent transition metal atom doping such as Ti, Zr, and Hf. We obtain a tetrahedral FK isomer (Figure 1c(I)) with a BE of 3.50 eV/atom that is 1.27 eV lower in energy than the fullerene-like isomer (Figure 1c(II)) (BE = 3.43 eV/atom). In the FK structure, the HOMO–LUMO gap is 1.72 eV which is significantly smaller compared with the Zr@Ge₁₆ cage which also has the FK polyhedral structure.⁷ Also, the gap in the fullerene-like isomer reduces significantly to 0.82 eV. These results again show the preference of Ge for closer packed structures similar to those found in metallic alloys even for larger size atoms such as Th. The doping energy for the FK cage is 11.06 eV, while for the fullerene-like isomer it is 12.42 eV. These values of the doping energies are quite comparable to those for Hf, Zr, and Ti atom doped clusters.⁷ The BE for this cluster has a higher value than the lowest energy cage for Th@Ge₁₈. This is due to the higher symmetry in the FK cage that leads to better bonding in the Th@Ge₁₆ cluster. The relatively large HOMO–LUMO gap of the FK cluster among all of the metal encapsulated germanium clusters makes it promising for high abundance as well as for optical properties. However, from the point of view of the BE, the Th@Ge₂₀ cluster is the best.

To further find the optimal size of the Ge cage with Th doping, we also dope Th in a high symmetry 24-atom Ge cage having the C₂₄ fullerene structure and Th at the center. Optimization of this cluster leads to the shrinkage of the cage such that three atoms pop out, showing that a cage with 24 Ge atoms is too big for Th. This suggests that Ge₂₀ is the largest cage that can be stabilized by the doping of a metal atom. A similar behavior has been obtained for silicon.¹⁰

To elucidate the bonding nature in these cages, we have performed charge density analysis (Figure 2). It is seen from the total as well as the difference in the charge densities of the doped clusters and the overlapping densities of Th and the empty cages with the corresponding atomic positions as in the case of the doped clusters that the charge is accumulated between the Th atom and the cages. In the case of fullerene-like cages (Figure 2b, d, and f for Th@Ge₂₀, Th@Ge₁₈, and Th@Ge₁₆, respectively), there is a dip in the total and excess charge densities at the center of the faces. This dip is indicative of the directional bonding and clearly represents the dominance of the covalent nature of bonding in these isomers. The charge densities in closer packed cages (Figure 2a, c, and e for Th@Ge₂₀, Th@Ge₁₈, and Th@Ge₁₆, respectively) have relatively uniform distributions of charge compared with the charge density in the fullerene-like isomers. The accumulation of charge between the Th atom and the cage is due to the covalent bonding between the orbitals of the Th atom and the cage. For Th@Ge₁₆, this also leads to a large HOMO–LUMO gap.

To understand the origin of the large gap in the 16-atom cage, we show in Figure 3 the electronic states of the lowest energy Th@Ge₂₀, Th@Ge₁₈, and Th@Ge₁₆ isomers and the states of

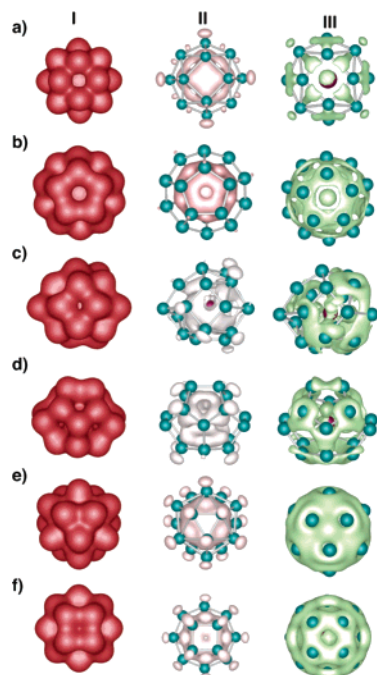


Figure 2. Isosurfaces of (I) the total electronic charge density, (II) the excess charge, and (III) the depletion of charge. Parts a, c, and e show isosurfaces of the charge densities corresponding to the lowest energy closed packed cages, while parts b, d, and f correspond to the fullerene-like covalently bonded cages of Th@Ge₂₀, Th@Ge₁₈, and Th@Ge₁₆, respectively.

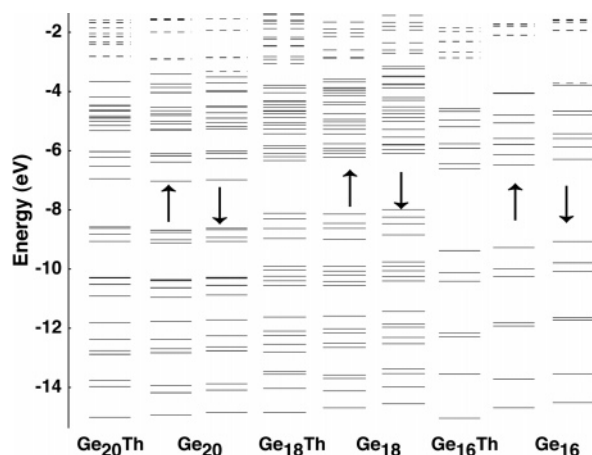


Figure 3. Electronic energy states of the lowest energy Th@Ge₂₀, Th@Ge₁₈, and Th@Ge₁₆ clusters and the corresponding up-and-down spin states of the Ge₂₀, Ge₁₈, and Ge₁₆ empty cages. The broken lines show the unoccupied states.

the corresponding empty cages. A comparison of these results shows that Th doping does not very significantly change the deeper lying states except in the case of Th@Ge₁₆. This gives an indication that Th interacts more strongly with the Ge₁₆ cage. However, in general, states lying within a range of a few electronvolts of the HOMO change (Figure 3) more significantly and this is largest again for the Ge₁₆ case. As has been discussed earlier²² for the case of Ti@Si₁₆ using a spherical potential model for the cage, the strong interaction is due to the strong hybridization between the Th d orbitals and the 2d orbitals of the Ge₁₆ cage, which form the HOMO of the undoped cage. The hybridization leads to the bonding orbital getting shifted to higher binding energies and being fully occupied, while the antibonding orbitals are unoccupied, resulting in a large HOMO–LUMO gap (note also the large gap above the HOMO of the empty Ge₁₆ cage). The tetrahedral symmetry of this cluster

leads to a narrower distribution of states as compared to the case of Th@Ge₁₈ and Th@Ge₂₀ for which the states are quite spread (Figure 3). For Ge₁₈ and Ge₂₀ empty cages, the gap above the HOMO is rather small. It is because the HOMO does not correspond to complete occupation of an electronic shell even after doping. The electronic states of the fullerene-like cages follow a similar trend, as has been discussed in the case of silicon.¹⁰

In summary, we have shown for the first time that highly symmetric cage clusters of Ge in the range of 16–20 atoms can be stabilized by the encapsulation of Th. Th@Ge₂₀ is found to be the largest cluster of Ge that can be stabilized with the doping of a single metal atom. Unlike silicon, a clear preference for closed packed metallic cages is found in Ge clusters due to the small difference in the atomic sizes and bonding natures of Ge and Si. These clusters have larger HOMO–LUMO gaps than the values obtained for Th encapsulated Si clusters in the same size range, and it is the largest for Th@Ge₁₆ with a GGA value of 1.72 eV. The actual gap can lie in the visible region, giving a strong possibility for their application in photonics and optical devices. We hope that the current intense activity and recent experimental advances in the area of metal encapsulated clusters will make the realization of these clusters in the laboratory possible.

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