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Metal-encapsulated icosahedral superatoms of germanium and tin with large gaps: Zn@Ge₁₂ and Cd@Sn₁₂

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Metal (M)-encapsulated clusters of Ge and Sn, Zn@Ge₁₂ and Cd@Sn₁₂, are obtained from total energy calculations using *ab initio* pseudopotential plane wave method and generalized gradient approximation for the exchange-correlation energy. These have perfect icosahedral symmetry and large highest occupied–lowest unoccupied molecular orbital gap of about 2 eV. It lies in the optical region and makes these species attractive for cluster assembled optoelectronic materials. Calculations on silicon clusters doped with Be show a different behavior. © 2002 American Institute of Physics. [DOI: 10.1063/1.1447315]

Clusters of semiconducting materials are currently of great interest as building blocks to realize miniature devices by self-assembly. Their properties can be manipulated by changing size, shape and composition that provide flexibility to prepare devices with desired properties. In this direction, recently novel M-encapsulated silicon fullerene as well as cubic clusters have been obtained.¹ Their shape and size depend upon the atomic size of M that also determines the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap. The smallest highest symmetry cluster is an icosahedron (*i*). However, none of the clusters of silicon,² germanium³ and tin⁴ have icosahedral structure. Instead, in the size range of about 15 atoms, these have prolate structures.⁵ Here we show from computer experiments that M encapsulation can be used to prepare *superatoms* of Ge and Sn with perfect icosahedral symmetry and with exceptionally large band gaps of about 2 eV that lie in the optical region.

The calculations have been performed using *ab initio* ultrasoft pseudopotential plane wave method^{6,7} within spin-polarized generalized gradient approximation (GGA).⁸ A simple cubic supercell of size 15 Å is used with periodic boundary conditions and the Γ point, for the Brillouin zone integrations. The structures are optimized using the conjugate gradient method. We consider doping of Zn (Cd) in Ge₁₂ (Sn₁₂) for which several starting configurations are taken. These include *i*, decahedron (*d*), cuboctahedron (*c*), hexagonal prism (*h*) and hexagonal antiprism (*ha*) structures. For Ge, we consider only the outer valence electrons but, for other elements, *d* electrons are also included as valence. The converged structures are found to have zero spin.

The optimized structures are shown in Fig. 1. Their binding energies (BEs) with respect to free atoms, embedding energies (EEs) of the M atoms in the X₁₂ cage of M@X₁₂ clusters, and the HOMO–LUMO gaps are given in Table I. The EE is the negative of the difference of the total energy of the M@X₁₂ cluster and the sum of energies of the empty center cage of X₁₂ with the corresponding positions of X in M@X₁₂ and the isolated M atom. It is noted that the *c* and

the *d* atomic configurations relax to the *i* isomer in both the cases and lie lowest in energy while the *h* and the *ha* isomers lie more than 1 eV higher in energy (Table I). The latter two reconstruct significantly such that in the *h* isomer Ge atoms form two interacting chair structures of six atoms each as shown in Fig. 1(b), while in the *ha* isomer, the central Zn atom comes out and lies in the plane of Ge atoms as shown in Fig. 1(c). The overall layered triangular structure of this cluster is interesting and may be important for supported clusters. Similar results have been obtained for Cd doped Sn₁₂. These give us confidence that the perfect *i* structure obtained here is the ground state of Ge₁₂Zn and Sn₁₂Cd clusters. An important finding is the exceptionally large HOMO–LUMO gap of 2.212 eV (1.935 eV) for the icosahedral M-doped Ge (Sn) clusters. This should be compared with 0.744 eV experimental band gap in bulk Ge at 0 K and semimetallic behavior of Sn in bulk. Also the HOMO–LUMO gap of small Ge clusters⁹ and the GGA band gap in tin⁴ clusters are about 1 eV. Therefore, the large value of the band gap is unexpectedly high, particularly with M doping. The GGA band gap lies in the optical region and we expect the true value to be significantly higher. This result makes these high symmetry clusters very interesting for optoelectronic devices. The EE of Zn in the icosahedral Ge₁₂ cage is 3.388 eV that is more than the BEs of Ge clusters in this size range³ and significantly higher than the cohesive energy (1.35 eV/atom) of bulk Zn. It should be noted that there is no known binary alloy or compound of Ge with Zn. The atomic radius (1.37 Å) of Zn is slightly smaller than the value (1.39 Å) for Ge. However, in the icosahedral cluster, the Zn–Ge bond length (2.69 Å) is about 5% shorter than the Ge–Ge bond length (2.84 Å) that makes a perfect packing of 12 Ge atoms around Zn in the form of a regular *i*. We also considered doping of Zn atom at a vertex site in the icosahedral structure. However, it lies 1.898 eV higher in energy as compared to Zn at the center of *i*, again confirming the M-encapsulated icosahedral cage to be the ground state.

The large HOMO–LUMO gap and the stability of these clusters make them behave like superatoms. To further check this, we performed calculations for Ge₁₃Zn by adding a Ge

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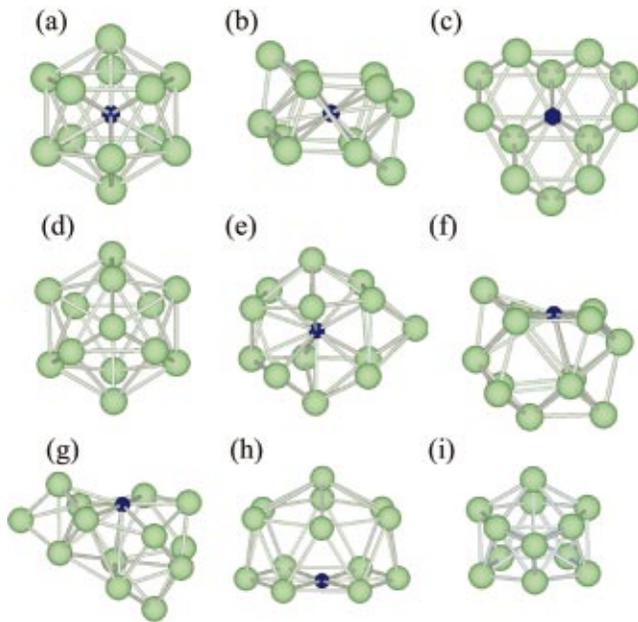


FIG. 1. (Color) (a) M-encapsulated i -M@X₁₂. (b) and (c) The optimized structures of h -M@X₁₂ and ha -M@X₁₂, respectively [(M,X) = (Be,Si), (Zn, Ge), and (Cd, Sn)]. Smaller dots represent M atoms. The d and c isomers of (Zn, Ge) and (Cd, Sn) converge to the i isomer. There is a reconstruction of the h and ha structures. In the h structure, the X atoms develop chair-type structure, whereas in the structure derived from ha , the M atom lies almost in the plane of the X atoms for Si and Ge and slightly above for Sn. The d isomer of (Be, Si) converges to the structure shown in (i) and has the lowest energy. (d) to (g) the relaxed capped i , d , h , and ha structures of X₁₃M, for Ge. For Sn the ha isomer is different and is shown in (h). The d isomer has the lowest energy.

atom on one of the faces of the i -Zn@Ge₁₂. The converged structure is shown in Fig. 1(d). The BE of this additional Ge atom is only 2.0 eV as compared to the BE of 3.097 eV/atom for Zn@Ge₁₂, confirming the magic nature of Zn@Ge₁₂. Further calculations on d , h and ha isomers of Ge₁₃Zn show the relaxed d isomer [Fig. 1(e)] to be 0.386 eV lower in energy while the h isomer with a capping of one hexagonal face, 0.335 eV higher in energy. The relaxed structure [Fig. 1(f)] is a capping of the h isomer of Zn@Ge₁₂ [Fig. 1(b)], but Zn is significantly displaced outwards. The ha structure,

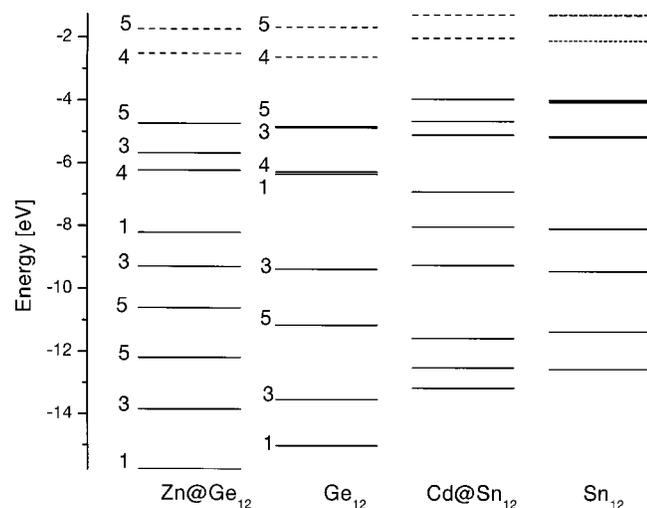


FIG. 2. Kohn-Sham energy spectra of the i -Zn@Ge₁₂, i -Cd@Sn₁₂ and the i cages of Ge₁₂ and Sn₁₂ at the corresponding positions. The broken lines show the LUMO states and the numbers, the degeneracies of the states.

TABLE I. BE (eV/atom), EE (eV), HOMO-LUMO gap (eV) of some low energy isomers of M@X₁₂.

Cluster	BE	EE	Gap
i -Zn@Ge ₁₂	3.132	3.388	2.212
h -Ge ₁₂ Zn	3.026	2.515	1.446
ha -Ge ₁₂ Zn	3.044	2.950	1.469
i -Cd@Sn ₁₂	2.770	2.941	1.935
h -Sn ₁₂ Cd	2.615	2.424	1.076
ha -Sn ₁₂ Cd	2.660	2.503	1.155
i -Be@Si ₁₂	3.689	5.350	1.565
d -Be@Si ₁₂	3.737	5.417	1.319
h -Si ₁₂ Be	3.716	4.847	1.712
ha -Si ₁₂ Be	3.713	5.403	1.811

with one face capped, transforms into a disordered structure [Fig. 1(g)] and is nearly degenerate with the d isomer, but the gap is 1.302 eV as compared to 1.065 eV for the latter. These results show that the BE of the additional Ge atom is significantly smaller than the value for the i -Zn@Ge₁₂ cluster.

Calculations on i -Cd@Sn₁₂ show a regular i with Cd-Sn and Sn-Sn bond lengths of 3.06 and 3.22 Å, respectively, to be the closest packing for this cluster. These bond lengths are close to the sum of the covalent radii, 1.58 and 1.52 Å, of Sn and Cd atoms, respectively. The h and the ha isomers lie, respectively, 1.997 and 1.422 eV higher in energy and have similar structures [Fig. 1(b) and 1(c)] as obtained for the case of Ge. Also the configuration with Cd at a vertex site lies 1.437 eV higher in energy than Cd at the center of the icosahedral cluster. The EE of Cd in Sn₁₂ cage is 2.940 eV that is comparable to the BE (about 2.88 eV/atom) for Sn₁₂ and Sn₁₃ clusters⁴ and much larger than the cohesive energy (1.16 eV/atom) of bulk Cd. This large value of EE of Cd at the center makes the icosahedral structure stable. In this case there is also no known alloy or compound of Sn with Cd. We also checked several structures for Sn₁₃Cd and the d isomer is found to have the lowest energy. The energy to add one more Sn atom on Sn₁₂Cd is 1.861 eV that is significantly smaller as compared to the BE of 2.77 eV/atom for Cd@Sn₁₂ cluster, making the latter, magic. The

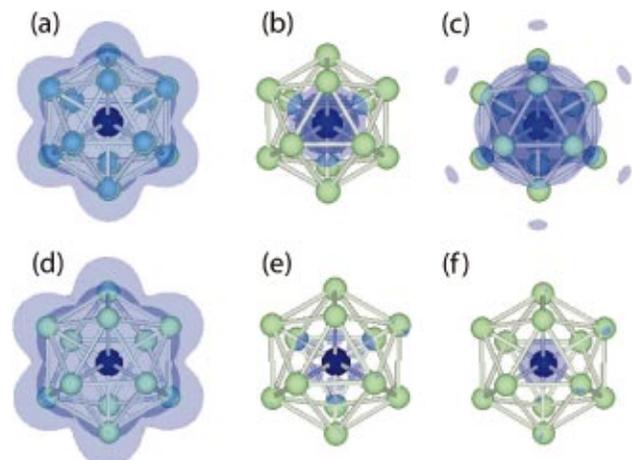


FIG. 3. (Color) Constant electronic charge density surfaces for (a) i -Zn@Ge₁₂ and (d) i -Cd@Sn₁₂. (b), (e) The excess and (c) and (f) depletion of charge as compared to the overlapping electronic charge densities of M and X₁₂ at the respective positions in Zn@Ge₁₂ and Cd@Sn₁₂, respectively. The densities for different surfaces are: (a) 0.15, (b) 0.015, (c) 0.001, (d) 0.12, (e) 0.015 and (f) 0.015 e/Å.

capped *i* isomer lies 0.165 eV higher in energy. The *h* isomer distorts very much and becomes an open structure while the *ha* isomer [Fig. 1(h)] is stable and lies 0.76 eV higher in energy as compared to the *d* isomer. This *ha* isomer is different from the distorted structure of Ge₁₃Zn and shows that Sn clusters have more metallicity.

To understand the bonding nature in these clusters, we show the Kohn–Sham energy spectra of the empty centered X₁₂ icosahedron and the M-encapsulated clusters in Fig. 2. It is noted that the partially occupied HOMO of the empty centered cage is fivefold degenerate and can accommodate two electrons. There is a large gap of about 2 eV above the HOMO. A divalent atom such as Zn and Cd at the center of the Ge and Sn cages has strong covalent bonding with the *s* character state of the cage that lies at −6.35 and −5.16 eV, respectively. The *d* state of the M atom is very localized and is weakly affected by interaction with the cage. However, the *s* and the *p* orbitals overlap significantly with the orbitals of the cage and get upshifted. The strong hybridization of the *s* state leads to a bonding state at around −8.2 and −6.9 eV for Zn@Ge₁₂ and Cd@Sn₁₂ clusters, respectively, and an antibonding state in the unoccupied region of the spectra. Other occupied states of the cage are less perturbed as can be seen in Fig. 2. This leads to a transfer of charge of 2 electrons to the HOMO and a large HOMO–LUMO gap in these doped clusters that is close to the value in the empty cage.

In Fig. 3 we show the electronic charge density surfaces for the two clusters. The total charge density is delocalized similar to the case of clusters of metals, but the known results of magic behavior for 2, 8, 40, ... valence electrons in a jellium model⁵ do not hold. There is a significant change in the ordering of the states that leads to the magic behavior with 50 e. The difference in the charge density of the M@X₁₂ and the overlapping charge densities of M and X₁₂ at the respective positions shows an excess of charge in between the M ion and X₁₂ cage with a depletion of charge from the cage and in the vicinity of the M ion. This leads to covalent character of bonding between the cage and M atom. The excess of charge is more in the case of Zn@Ge₁₂ as compared to Cd@Sn₁₂.

In order to check if the same would hold true for the isoelectronic Si, we studied doping of Si₁₂ with Be that is slightly smaller in size than Si. It is found that the *i* isomer is stable, but it is not the ground state. The *d* isomer relaxes to a partial *i* in which a vacancy is created at a vertex and an atom caps a face as shown in Fig. 1(i). This has the lowest energy (Table I) among the different structures we studied. This different behavior as compared to Ge and Sn could be due to a stronger covalent character of bonding in Si. The HOMO–LUMO gap is 1.319 eV. Also in the *i* isomer, the HOMO–LUMO gap is 1.565 eV that is surprisingly smaller than the values for the M-doped Ge and Sn clusters, making

the latter two ideal icosahedral species. The relaxed *h* and *ha* isomers of M-doped Si₁₂ are similar to those obtained for Ge and Sn (Fig. 1), but the difference in energy as compared to the lowest energy isomer is only 0.27 and 0.315 eV, respectively. This is a significant reduction as compared to the values for Ge and Sn clusters. However, the HOMO–LUMO gaps are larger (Table I) with values of 1.711 and 1.811 eV for the *h* and *ha* isomers, respectively. This can be interesting for preparing supported clusters. Further calculations on doping Zn or Cd in Si also do not give *i* isomer to be of lowest energy. These results of different M atoms in X₁₂ cages would be published separately.

In summary, we have found icosahedral M-encapsulated superatoms, Zn@Ge₁₂ and Cd@Sn₁₂, of Ge and Sn with exceptionally large HOMO–LUMO gaps of about 2 eV that lie in the optical region. The high symmetry and large gaps make these clusters attractive for self-assembled nanodevices. Similar calculations on Be@Si₁₂ show a regular *i* to be stable but it has an unexpectedly smaller gap than in the case of M-doped Ge and Sn. The lowest energy structure is one in which Be has a lower coordination. However, a planar structure lies close in energy and has a higher HOMO–LUMO gap that may be important for supported clusters. Similar results may hold for negatively (positively) charged monovalent (trivalent) doping of X₁₂. We hope that our results would stimulate experiments to look for these clusters.

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