# Hydrogenated Silicon Fullerenes: Effects of H on the Stability of Metal-Encapsulated Silicon Clusters

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*Ab initio* calculations of H interaction on $Si_{12}M$, $Si_{18}M_2$ ($M = $ Cr, Mo, and W), and $Zr@Si_{16}$ fullerene ($f$) show relatively weak binding of H in agreement with experimental results of H free $Si_{12}M$ and $Si_{18}M_2$ clusters. Adsorption of H enhances $sp^3$ bonding between the Si atoms, weakens the $M$-Si cage interactions, and leads to distortions in the cages. $Si_{12}CrH_{12}$ has $4\mu_B$ magnetic moment in contrast to zero for $Si_{12}Cr$. Removal of the $M$ atom leads to stable empty cages of $Si_{12}H_{12}$, $f$-$Si_{16}H_{16}$, and $f$-$Si_{20}H_{20}$ with large highest occupied–lowest unoccupied molecular orbital gaps of 2.5–3.0 eV, making them attractive for optoelectronic applications.

Recent findings [1–3] of metal ($M$) encapsulated caged clusters of Si have opened up new avenues for developing novel nanoforms of Si for device applications. As compared to elemental Si clusters these have higher stabilities, high symmetries, as well as size selectivity that make them attractive for cluster assembled materials with desired properties. Understanding the stability of these clusters against reactants is important for applications. Here we report for the first time results of the stability of these novel clusters against interaction with H and predict empty cage hydrogenated Si fullerenes.

The study of H interaction on these clusters is important as two experiments have shown different abundances. Using silane and $M$ monomers as well as dimers, lack of interaction of $SiH_4$ was observed [3] for $Si_{12}M$ and $Si_{18}M_2$, $M = $ W and Mo making these H free clusters magic. However, laser vaporization of Si and the addition of $M(CO)_6$ to the He carrier gas led [4] to large abundances of $Si_{15}M$ and $Si_{16}M$ ($M = $ Cr, Mo, and W) with little intensities of $Si_{12}M$ and $Si_{18}M_2$. Therefore, the growth behavior of these clusters depends upon the nucleation conditions. The magic behavior of $Si_{15}M$ and $Si_{16}M$ was explained [2] to be due to the competitive growth of cubic ($c$) and fullerenelike structures. An important finding has been [1] the $M$ encapsulated Si fullerene ($f$) of $Zr@Si_{16}$. In this as well as the hexagonal ($h$) prism $Si_{12}M$ clusters all Si atoms are tricoordinated with other Si atoms besides the $M$ atom at the center. Similar to $C_{60}$, bonding between the Si atoms is $sp^2$-$sp^3$ type [5]. It is plausible that H can be associated on these clusters. This is important for the development of assemblies of such clusters on a substrate such as a clean or H covered Si surface.

The stability of $Si_{12}W$ was suggested [3] to be due to the 18 valence electron rule according to which each Si atom contributes an electron to W to make it a 18 valence electron closed electronic shell specie while the remaining three valence electrons on each Si form covalent bonds with three neighboring Si. However, *the charge transfer between M and the cage is small and the bonding is mainly covalent.* Further, the same argument cannot be used to understand the stabilities of $Zr@Si_{16}$ or $Fe@Si_{14}$ [1] as well as the 15 and 16 Si atom Cr, Mo, and W doped clusters [2]. It was shown [1,2,6] that besides the electronic structure, the size of the $M$ atom plays a crucial role to determine the size of the cage due to strong $M$-Si interactions. As Si atoms share charge with the $M$ atom, interaction of H is unlikely to be similar to, e.g., $SiH_4$. We find that H adsorption weakens $M$-Si interactions, enhances $sp^3$ bonding, and leads to distortions in the cages but the binding energy (BE) is relatively low. Removal of the $M$ atom leads to increased binding of H and stable high symmetry empty center hydrogenated Si $f$s with large band gaps. This is in contrast to most studies [7] on hydrogenated Si clusters that assume bulk structure with dangling bonds saturated by H.

The calculations have been done using the *ab initio* ultrasoft pseudopotential plane wave method [8,9] and generalized gradient approximation [10] for the exchange-correlation energy. We use a large simple cubic unit cell of side up to 18 Å and the $\Gamma$ point for the Brillouin zone integrations. The structures are optimized using the conjugate gradient method.

In $h$-$Si_{12}M$ we place 12 H atoms, one on each Si. The optimized structure shows [Fig. 1(a)] H induced distortions such that the hexagons are no longer regular. The interhexagon bonds are shortened to 2.25 (2.26) Å from 2.40 (2.40) Å in $Si_{12}W$ ($Si_{12}Mo$) whereas the bonds within a hexagon become alternately 2.28 (2.29) and 2.66 (2.63) Å as compared to 2.37 (2.38) Å in W (Mo) doped clusters. Thus, there is a pairing and strengthening of bonds with stronger covalency between some Si atoms while a few Si-Si bonds become weaker. Also the W-Si bond lengths increase from 2.66 to $\approx 2.71$ Å weakening the W-Si interactions. The H-Si bond length is 1.49 Å. For $Si_{12}CrH_{12}$, the Cr atom is displaced from the center of the
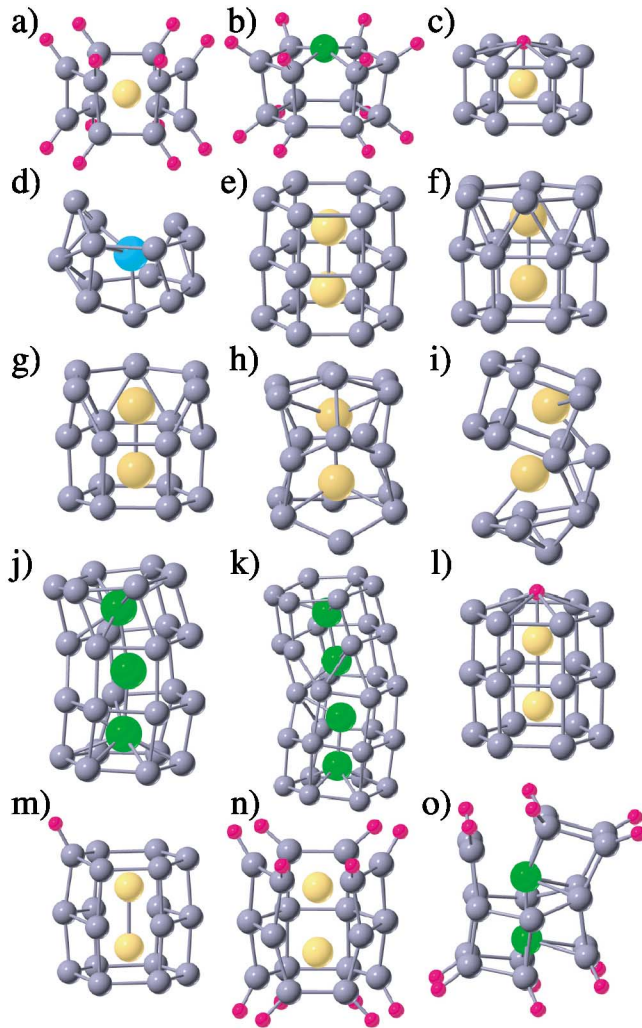
FIG. 1 (color). Optimized structures of (a) $Si_{12}MH_{12}$, $M =$ Mo, W, and Hf; (b) $Si_{12}CrH_{12}$; (c) H on W site of $Si_{12}W$; (d) $Si_{13}Mo$; (e) $Si_{18}M_2$, $M =$ Mo, and W; (f) an isomer of $Si_{18}W_2$; (g) $Si_{17}W_2$; (h),(i) isomers of $Si_{17}W_2$; (j) $Si_{24}Cr_3$; (k) $Si_{30}Cr_4$; (l) H on the W site of $Si_{18}W_2$; (m) H on a Si site of $Si_{18}W_2$; (n) $Si_{18}W_2H_{12}$; (o) $Si_{18}Cr_2H_{12}$. Red balls represent H atoms while the $M$ atom is yellow, green, or blue. Si-Si bonds with lengths less than 2.6 Å are connected.

prism towards the center of a $h$ face [Fig. 1(b)] as Cr is smaller. This optimizes the Cr-Si interactions. *Interestingly H adsorption induces $4\mu_B$ magnetic moment on this cluster as compared to zero in $Si_{12}Cr$.* The magnetic polarization is predominantly around the Cr ion, though small polarization is induced around the Si and H ions [Figs. 2(a) and 2(b)]. The highest occupied–lowest unoccupied molecular orbital (HOMO-LUMO) gap is 0.930 eV which suggests that this hydrogenated magnetic cluster is quite stable. The hydrogenated clusters with W or Mo, however, have zero moment. Therefore, Cr encapsulated clusters behave differently from those with Mo or W.

Following an increase in the $M$-Si bond lengths upon H adsorption, we studied doping of a larger $M$ atom, Hf. The
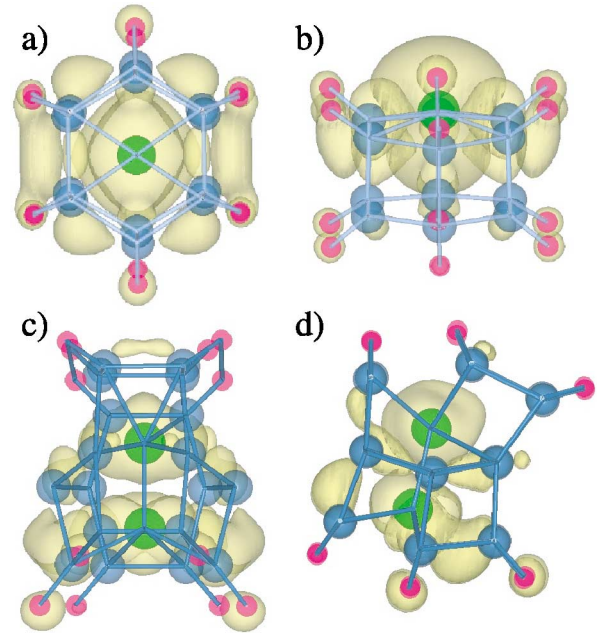


FIG. 2 (color). Two views of the isosurfaces of spin polarization for $Si_{12}CrH_{12}$ (a),(b) and $Si_{18}Cr_2H_{12}$ (c),(d) with the value of 0.004.

structure of $Si_{12}HfH_{12}$ is similar to the one in Fig. 1(a) with a large HOMO-LUMO gap of 1.345 eV as compared to 0.129 eV and $2\mu_B$ magnetic moment for $Si_{12}Hf$.

The H adsorption enhances $sp^3$ bonding between the Si atoms and increases the HOMO-LUMO gap (Table I) from 0.900 (1.340) to 1.636 (1.747 eV) for Mo (W), but for Cr, the increase is only marginal (0.847 to 0.930 eV)

TABLE I. BEs (eV/atom) and the HOMO-LUMO gaps (eV) of different clusters. $Si_{12}CrH_{12}$ and $Si_{18}Cr_2H_{12}$ have magnetic moments of $4\mu_B$ and $2\mu_B$, respectively. For hydrogenated clusters, the BE is for H. (1) and (2) refer to adsorption on W and Si in $Si_{18}W_2H$ and adsorption on square and ring Si atoms in $Zr@Si_{16}H_8$, respectively.

| Cluster | BE | Gap | Cluster | BE | Gap |
|---|---|---|---|---|---|
| $Si_{12}Cr$ | 3.835 | 0.847 | $Si_{12}CrH_{12}$ | 2.559 | 0.930 |
| $Si_{12}Mo$ | 4.016 | 0.900 | $Si_{12}MoH_{12}$ | 2.488 | 1.636 |
| $Si_{12}W$ | 4.183 | 1.340 | $Si_{12}WH_{12}$ | 2.413 | 1.747 |
| $Si_{12}Mo$ | 3.987 | 0.953 | $Si_{18}W_2H$ (1) | 1.140 | 0.340 |
| $Si_{17}W_2$ | 4.341 | 0.516 | $Si_{18}W_2H$ (2) | 2.028 | 0.183 |
| $Si_{18}Cr_2$ | 3.915 | 1.153 | $Si_{18}Cr_2H_{12}$ | 2.370 | 0.382 |
| $Si_{18}Mo_2$ | 4.170 | 1.011 | $Si_{18}Mo_2H_{12}$ | 2.320 | 0.763 |
| $Si_{18}W_2$ | 4.374 | 1.129 | $Si_{18}W_2H_{12}$ | 2.287 | 0.947 |
| $Si_{24}Cr_3$ | 3.900 | 0.387 | $Zr@Si_{16}H_8$ (1) | 2.575 | 0.859 |
| $Si_{30}Cr_4$ | 3.931 | 0.358 | $Zi@Si_{16}H_8$ (2) | 2.462 | 0.784 |
| $Si_{12}H_{12}$ | 2.777 | 2.564 | $Zr@Si_{16}H_{16}$ | 2.571 | 0.692 |
| $Si_{16}H_{16}$ | 2.962 | 2.881 | $SiH_4$ | 3.455 | 8.495 |
| $Si_{20}H_{20}$ | 2.926 | 2.911 | Si-H ($1\mu_B$) | 3.183 | 1.052 |
| $Si_{29}H_{24}$ | 2.950 | 2.616 | W-H ($5\mu_B$) | 2.893 | 1.558 |

due to a reduction in the symmetry as well as spin polarization. The BE per H decreases from 2.559 to 2.488 and 2.413 eV in going from Cr to Mo and W. Therefore, *H has the weakest bonding on $Si_{12}W$* in agreement with the observation of H free clusters. These values are significantly lower than the BE of 3.455 eV per H in $SiH_4$. Also the BE of one H on top of $M$ in $Si_{12}M$ [Fig. 1(c)] is only $\approx 2$ eV for all $M$ as compared to 2.893 eV for W-H and 3.183 eV for Si-H molecules. Therefore, $SiH_4$ is unlikely to be dissociated on this cluster. The BE of H on $Si_{12}M$ is only marginally favorable as compared to the $H_2$ molecule. Therefore, there is only a weak tendency for H adsorption on $Si_{12}M$ and under the experimental conditions of finite temperatures, H is unlikely to be adsorbed on these clusters in agreement with experiments. The energy gain by the addition of a Si atom on $Si_{12}Mo$ [Fig. 1(d)] to form $Si_{13}Mo$ is 3.611 eV as compared to the BE of 4.016 eV/atom for $Si_{12}Mo$. Therefore, the BE/atom for $Si_{13}Mo$ decreases as compared to $Si_{12}Mo$, making $Si_{12}Mo$ a magic cluster. The same is expected to hold for $M =$ Cr and W. The open structure of this cluster is due to significantly bigger size of the $M$ atom as compared to Si such that a closed cage is not possible.

$Si_{18}M_2$ has a $h$ double prism structure [Fig. 1(e)]. An isomer with the central hexagon in an antiprism configuration relative to the remaining two transforms to the double prism structure upon optimization. Another isomer with one of the outer hexagons in the antiprism structure [Fig. 1(f)] lies 0.32 eV higher in energy and has a gap of 1.146 eV as compared to 1.129 eV for the double $h$ isomer. Calculations on $Si_{17}W_2$ with a double $h$ prism, a capped decahedral isomer, and a few other structures [Figs. 1(g)–1(i)] give a slightly distorted $h$ double prism [Fig. 1(g)] with a Si atom missing to be of lowest energy. The HOMO-LUMO gap is 0.581 eV only with zero spin. The large gain of 5.006 eV in forming $Si_{18}W_2$ from $Si_{17}W2$ leads to the strong stability of the former. Interestingly in $Si_{18}M_2$, the HOMO-LUMO gap decreases for $M =$ W, but increases to 1.153 (1.011) eV from 0.847 (0.900) eV for $Si_{12}M$, $M =$ Cr (Mo). The bond lengths for $M =$ Mo and W are very nearly the same with the central (outer) hexagon Si-Si and Si-$M$ bonds being 2.50 (2.41 Å) and 2.79 (2.66 Å), respectively. The interhexagon bond lengths are 2.37 Å while the $M$-$M$ bond is 2.47 Å. However, for $M =$ Cr, these are shorter with the values of 2.44 (2.36 Å) and 2.68 (2.66 Å), respectively. The interhexagon bonds are 2.34 Å while the Cr-Cr bond is 2.20 Å. The short bond lengths in these dimers are due to the strong $d$ bonding in the middle of a $d$ series. This as well as the higher coordination of Si atoms leads to the elongation of the Si-Si and Si-$M$ bonds in the central hexagon. The BE increases to 3.915, 4.170, and 4.374 eV/atom for $Si_{18}M_2$ from 3.835, 4.016, and 4.183 eV/atom for $Si_{12}M$, $M =$ Cr, Mo, and W, respectively. As the increase in the band gap is large for $Si_{18}Cr_2$, we studied $Si_{24}Cr_3$ [Fig. 1(j)]. But the BE as well as the

gap decreases to 3.90 eV/atom and 0.387 eV, respectively, which suggests that $Si_{18}Cr_2$ is more preferred. Calculations on $Si_{30}Cr_4$ [Fig. 1(k)] show a slight increase in the BE to 3.931 eV/atom, but the HOMO-LUMO gap is only 0.358 eV. Therefore, it is likely to be reactive. The short Cr-Cr bonds lead to significant distortions in these nanowire-type structures.

H adsorption on the W and Si sites of $Si_{18}W_2$ [Figs. 1(l) and 1(m)] give the BEs to be only 1.140 and 2.028 eV, respectively, making H adsorption quite unfavorable as compared to $SiH_4$ or $H_2$ molecule. Similarly the BE of H on Mo is only 1.190 eV, but for Cr it is 1.511 eV. When 12 H are placed on the 12 Si atoms of the outer hexagons, the BE is 2.287, 2.320, and 2.370 eV per H for W, Mo, and Cr, respectively. Again the bonding is weakest on W doped clusters. We infer that H adsorption is unfavorable on these clusters, in agreement with the experimental finding of H free $Si_{18}W_2$. Adsorption of H distorts [Fig. 1(n)] the $h$ double prism structure for $M =$ Mo and W in a similar way as found for $Si_{12}MH_{12}$. However, for $Si_{18}Cr_2H_{12}$, the distortions are more significant [Fig. 1(o)] due to the short Cr-Cr bond and an increase in the Si-Si bond lengths. There is a net spin moment of $2\mu_B$ on this cluster predominantly around the Cr ions as shown in Figs. 2(c) and 2(d). A spin isomer with $10\mu_B$ magnetic moment lies 0.921 eV higher in energy while an isomer with zero spin lies 0.313 eV higher in energy. Also contrary to an increase in the gap for $Si_{12}MH_{12}$, there is a decrease to 0.947, 0.763, and 0.382 eV for W, Mo, and Cr, respectively. Therefore, Mo and Cr doped clusters are likely to be less favorable against further aggregation.

For $f$-Zr@$Si_{16}$, we consider three cases: (1) in which one H is placed on each of the eight Si atoms forming two square faces, or (2) on the remaining eight Si atoms forming a ring, and (3) on all the 16 Si atoms. The optimized structures (Fig. 3) show some distortion of
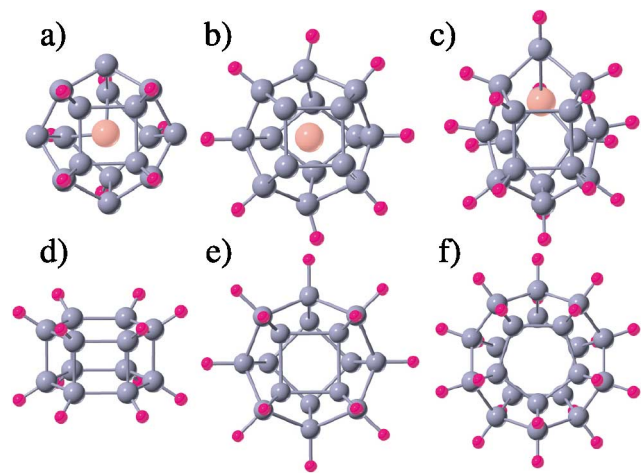


FIG. 3 (color).   Optimized structures of (a) $Si_{16}ZrH_8$ (H on eight square Si atoms), (b) $Si_{16}ZrH_8$ (H on eight ring Si atoms), (c) $Si_{16}ZrH_{16}$, (d) $Si_{12}H_{12}$, (e) $Si_{16}H_{16}$, and (f) $Si_{20}H_{20}$.

the cage in case 1 [Fig. 3(a)] and an increase in the Si-Si bond lengths (2.32-2.61 Å) leading to an elongation of the cage structure. The Zr atom is displaced closer to one of the square faces. The BE of H is 2.575 eV per H and the gap decreases to 0.859 eV. In case (2) [Fig. 3(b)], Si-Si bonds are in the range of 2.27 to 2.48 Å as compared to 2.29 to 2.38 Å in Zr@Si$_{16}$. The increase in the Si-Si bond lengths leads to an increase in the $M$-Si bonds. Therefore, the energy of the cluster is lowered by displacing the $M$ atom towards the wall of the cage in order to optimize the $M$-Si interactions. The BE of H is 2.462 eV per H and the gap reduces to 0.784 eV from 1.58 eV for $f$-Zr@Si$_{16}$. Adsorption of H on all the Si atoms [Fig. 3(c)] leads to a significant distortion of the cage due to an increase in the Si-Si bond lengths. This makes the $M$ atom move close to the cage. The BE of H is 2.571 eV per H and the gap reduces to 0.692 eV. Therefore, with an increase in the number of H, the bonding of the cage with the $M$ atom is reduced while the interaction with H is slightly enhanced due to an increase in the $sp^3$ bonding character. In general the BE of H on Zr@Si$_{16}$ is also low as compared to the value for SiH$_4$ and it is only slightly favorable as compared to H$_2$. It is unlikely that H$_2$ will get dissociated on these clusters. However, in an environment of atomic H, there is a possibility of the cage getting significantly distorted.

Noting the tendency of improved $sp^3$ bonding upon H adsorption as well as the weakening of the $M$-Si interactions, we removed the $M$ atom in the hydrogenated clusters so that all four valence electrons of Si could participate in covalent bonding. The optimized empty cages (Fig. 3) of Si$_{12}$H$_{12}$, Si$_{16}$H$_{16}$, and Si$_{20}$H$_{20}$ have high symmetries with all Si atoms nearly tetrahedrally bonded. There are large HOMO-LUMO gaps (Table I) and a slight decrease in the Si-Si bond length in Si$_n$H$_n$ with an increase in $n$ due to improved $sp^3$ bonding. It also increases the HOMO-LUMO gap. The BE per Si-H bond also increases to 6.551, 6.748, and 6.804 eV for $n = 12$, 16, and 20, respectively, as compared to 3.182 eV for the Si-H molecule. The BEs of H as compared to the ground states of Si$_{12}$, Si$_{16}$, and Si$_{20}$ are 2.777, 2.962, and 2.926 eV, respectively. It is comparable to the value of 2.950 eV for the case of Si$_{29}$H$_{24}$ that has 2.616 eV HOMO-LUMO gap. Si$_{29}$H$_{24}$ emits light [11] in the visible range. Accordingly, we expect these hydrogenated Si $f$s to be also photoluminescent in the visible range. Equiatomic concentrations of Si and H have been found [12] to be most preferred in Si$_n$H$_n$ at temperatures of about 700 K for $n = 10$–20 while higher (lower) fractions of H are preferred at low (high) temperatures suggesting competition with 3D bulklike structures at low temperatures. The structures of equiatomic clusters were suggested to be cage type. Si$_{14}$H$_{14}$ with a $f$ structure of Si$_{14}$ (same as predicted in [1] for Si$_{14}$Os) with all Si atoms having threefold coordination was found to be lower in en-

ergy than a heptaprism, lending further support to our conclusion.

In summary, we find stable hydrogenated Si fullerenes with empty centers and large HOMO-LUMO gaps that make these species interesting for optoelectronic applications. These results agree with the observed preference for equiatomic Si$_n$H$_n$ clusters at about 700 K. Interaction of H on Si$_{12}M$ and Si$_{18}M_2$, $M =$ Cr, Mo, and W as well as $f$-Zr@Si$_{16}$ is relatively weak, and dissociation of SiH$_4$ is not favorable in agreement with the experimental finding of H free Si$_{12}M$ and Si$_{18}M_2$. The BE is only slightly higher than the value for H$_2$ making dissociation of H$_2$ unlikely. Under the experimental conditions of finite temperatures, the probability of associating H on these clusters is still lower. The adsorption of H enhances $sp^3$ bonding and weakens the $M$-Si cage interactions leading to distortions in the cages. The HOMO-LUMO gap increases significantly for Si$_{12}M$H$_{12}$, $M =$ Mo, and W while Si$_{12}$CrH$_{12}$ develops a magnetic moment of $4\mu_B$ as well as a significant HOMO-LUMO gap contrary to complete quenching of Cr moments in Si$_{12}$Cr. Si$_{18}$Cr$_2$H$_{12}$ also has a magnetic moment of $2\mu_B$ providing an interesting way to develop magnetic species for nanostructures of semiconductors.

[1] V. Kumar and Y. Kawazoe, Phys. Rev. Lett. **87**, 045503 (2001).

[2] V. Kumar and Y. Kawazoe, Phys. Rev. B **65**, 073404 (2002).

[3] H. Hiura, T. Miyazaki, and T. Kanayama, Phys. Rev. Lett. **86**, 1733 (2001).

[4] S. M. Beck, J. Chem. Phys. **90**, 6306 (1989).

[5] V. Kumar, C. Majumder, and Y. Kawazoe, Chem. Phys. Lett. **363**, 319 (2002).

[6] V. Kumar and Y. Kawazoe, Phys. Rev. Lett. **88**, 235504 (2002).

[7] See, e.g., A. Puzder, A. J. Williamson, J. C. Grossman, and G. Galli, Phys. Rev. Lett. **88**, 097401 (2002), and references therein.

[8] G. Kresse and J. Furthmuller, Phys. Rev. B **54**, 11 169 (1996).

[9] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[10] J. P. Perdew, in *Electronic Structure of Solids' 91*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991), p. 11.

[11] G. Belomoin *et al.*, Appl. Phys. Lett. **80**, 841 (2002).

[12] G. A. Rechtsteiner, O. Hampe, and M. F. Jarrold, J. Phys. Chem. B **105**, 4188 (2001).