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A relativistic density functional study of Si_n (n = 7–13) clusters with rare earth ytterbium impurity

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ABSTRACT

Geometries, relative stabilities, HOMO–LUMO gaps, and growth-pattern of $YbSi_n$ (n = 7–13) clusters have been systematically studied. The calculated results show that Yb atom always prefers capping on the surface site of the silicon frame and no cagelike geometries are found up to n = 13, and that the most stable $YbSi_n$ (n = 7–13) clusters keep basically the analogous frameworks as the low-lying Si_{n+1} clusters. The relative stabilities of $YbSi_n$ (n = 7–13) clusters are studied, $YbSi_n$ (n = 8, 10, and 13) clusters have stronger relative stabilities in comparison with the corresponding neighbors. Furthermore, the charges in the most stable $YbSi_n$ (n = 7–13) clusters are transferred from Yb atom to silicon frame. Interestingly, the inserted Yb raises the chemical activities, increases the metallic in character of $YbSi_n$ clusters. In addition, the most stable charged $YbSi_n$ (n = 8–10, 13) geometries are deformed their neutral geometries.

1. Introduction

Silicon clusters have been extensively investigated both experimentally and theoretically because they are employed as the building blocks for developing new silicon-based nanomaterials with tunable properties [1–17]. Unlike the carbon fullerene cages, the hollow cagelike Si_n geometries are unstable due to the lack of sp^2 hybridization of valence orbitals. In order to stabilize the silicon cageframes, some guest atoms (for example: transition metal atoms) stuffed inside the silicon cageframes are needed.

Beck had already successfully produced mixed metal–silicon cluster ions [18], MSi_n^+ (M = Cr, Mo, and W), by the laser vaporization supersonic expansion technique, and they found that the transition metal (TM) atom doped silicon clusters were more stable towards photofragmentation than the bare Si_n clusters of the same size. Subsequently, Hiura et al. [19] reported the formation of a series of Si_n cagelike clusters with endohedral transition metal impurities, in the form of $TM@Si_n^+$, (TM = Hf, Ta, W, Re, Ir, etc.; n = 9, 11, 12, 13, 14). Their first-principles calculations further showed that WSi_{12} is a very stable isomer due to the electronic and geometrical shell closures. Rare earth Tb doped Si_n^- ($6 \leqslant n \leqslant 16$) were reported experimentally by aid of various experimental technical methods [20]. Recently, the photoelectron spectra of the chromium-doped silicon cluster anions, $CrSi_n^-$ (n = 8–12) [21], were measured; experimental measurements on vertical detachment energies showed that the $CrSi_{12}$ unit with chromium atom being encapsulated inside the Si_{12} cageframe has enhanced stability. Motivated by these experimental results, many computational investigations have been carried out for metal doped silicon clusters [22–35]; the calculated values indicated that the TM in the lowest-energy $TMSi_n$ geometries occupied a gradual Si_n sinking site, and the site varies from the TM surface-absorbed forms to the TM-encapsulated forms with the size of Si_n atoms being increased. Moreover, the charge-transfer between TM atom and Si_n framework depends on different kinds of doped TM and cluster size, and the stabilities for the specific-sized TM–silicon clusters have been enhanced after the TM is doped into the Si_n frames. The computational studies of the small-sized neutral and charged $YbSi_n$ (n = 1–6) clusters with various spin states were carried out by using the relativistic density function theory (RDFT) method [23].

In order to further investigate the various properties of the large-sized $YbSi_n$ (n = 7–13) clusters, we performed a detailed investigation of equilibrium geometries, charge-transfer properties, relative stabilities in terms of the calculated fragmentation energies [$D(n, n-1)$], averaged atomic binding energies [$E_b(n)$], ionization potentials (IPs), electron affinities (EAs), and the HOMO–LUMO gaps of the middle-sized $YbSi_n$ clusters by using the relativistic density functional method with a generalized gradient approximation.

2. Computational details

All geometry optimizations and electronic properties are calculated by utilizing the Amsterdam Density Functional package (ADF)

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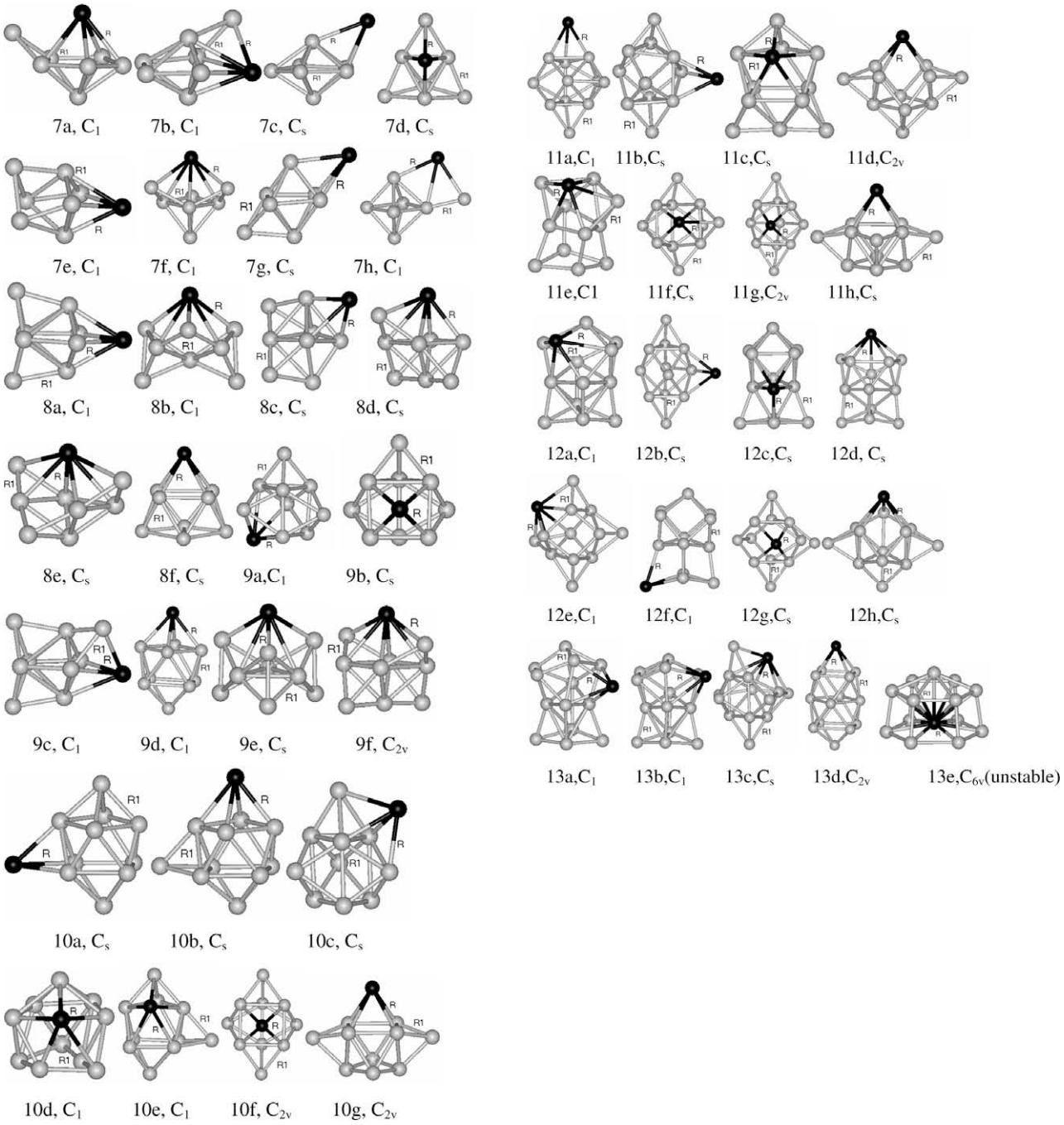

Fig. 1. All the equilibrium geometries of $YbSi_n$ (n = 7–13) clusters.

[36], which can perform the density functional theory (DFT) calculations of atoms, molecules, and clusters. The relativistic effects are of importance because $YbSi_n$ clusters involve in a heavy rare earth atom (Yb). A combined scalar or spin–orbit relativistic (SR) zero orders regular approximation (ZORA) [37,38] has been taken into accounts and a frozen-core triple-zeta basis sets plus polarization function (TZP) is employed for the $YbSi_n$ clusters. But, the comparison of the bonding energy of $YbSi_n$ clusters at respective the scalar relativistic and spin–orbit approximations show that the application of the spin–orbit operator lowers simultaneously the bonding energy by approximately 0.16 eV, therefore, the spin–orbit coupling effect was not considered for which having no effect substantively on total bonding energies of $YbSi_n$ clusters. For the ytterbium and silicon atoms, the inter-shell orbitals are kept frozen up to 5p and 2p subshells, respectively. Except where explicitly states, all calculations are based on the local density approximation (LDA) [39] augmented with the Becke–Perdew's exchange and correlation functionals [40,41].

For each of a cluster, the stability is reassured by the calculated harmonic vibrational frequencies. If the unstable geometry with one imaginary frequency is found, a relaxation along the coordinates of the imaginary vibrational mode is rearranged until a true local minimum is finally reached. Therefore, geometries and total energies for each stable cluster and its stable isomers actually correspond to the local minima. As the number of isomers is increased quickly with the cluster size, it is very difficult to obtain the global minimum simply according to the calculated total bonding energies of the isomers. To acquire the most stable $YbSi_n$ (n = 7–13)