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## Stability of alkali-encapsulating silicon cage clusters

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We report a computational study of the possibility to form alkali-encapsulating Si clusters  $A@Si_n$  with  $n=10-20$ . We predict and quantify the stability for lithium, sodium, and potassium atoms encapsulated in silicon cage. The structure and electronic properties are discussed. An electronic charge transfer from the alkali atom to the  $Si_n$  cage is observed. The  $A@Si_n$  cluster is formed of a positive charge located on the alkali surrounded by a negative one distributed on the whole Si cage. For each size the predicted stability of such structure is discussed and compared with that of surface-bound alkali isomers. The alkali-encapsulating Si clusters  $A@Si_n$  are found to be stable but lying much higher in energy as compared to surface-bound alkali isomers. © 2007 American Institute of Physics. [DOI: 10.1063/1.2790018]

### I. INTRODUCTION

Extensive experimental and theoretical studies on silicon clusters have been carried out in the last decade because silicon is the most important semiconductor material in microelectronic industry. A motivation to the studies of atomic clusters comes from the expected possibilities to use the clusters as building blocks for fabrication of new nanostructures with controlled electronic properties, which can be manipulated by changing size, shape, and composition. In particular, caged structures such as the very known carbon fullerenes are very attractive. Unfortunately, bare Si cage structures are not stable or lie high in energy because the  $sp^2$  hybridization is unfavorable. Due to their  $sp^3$  nature, the Si atoms tend to bind themselves and favor compact structures very far from fullerene cages.<sup>1-3</sup> Even the endohedral structures  $Si_p@Si_m$  predicted recently<sup>4,5</sup> for  $Si_n$ ,  $n=p+m$ , with  $n > 30$  are quite different from fullerene cages. However, the recent experimental evidences<sup>6-10</sup> of the formation of stable Si cages in which Si atoms encage a metal atom, as suggested before by theoretical calculations,<sup>11</sup> open new perspectives to build cluster-assembled materials. Hiura *et al.*<sup>6</sup> have reported that the transition metal atoms  $M$  reacted with silane ( $SiH_4$ ) to form encapsulating  $Si_n$  cage of  $M@Si_n$  with  $n$  between 9 and 14 depending on the transition metal atom. Ohara *et al.*<sup>7</sup> have revealed that one transition metal atom can be encapsulated inside the  $Si_n$  cage at  $n \geq 15$  from results of the adsorption reactivity and photoelectron spectroscopy. Uchida *et al.*<sup>8</sup> have shown that  $TaSi_{12}^+$  has a geometrically closed Si network without dangling bonds and also that scanning tunneling microscope (STM) observations reveal that  $TaSi_{10-13}H_x^+$  clusters would have a stable Si cage structure with a Ta atom at the center. Very recently, Jaeger *et al.*<sup>9</sup> have shown that the photodissociation of  $CrSi_{15}^-$  and  $CrSi_{16}^-$  eliminates silicon atoms rather than chromium atom, indicating that the Cr is not located on the  $Si_n$  surface but is covered with Si atoms.

From the theoretical point of view, several calculations<sup>11-24</sup> have suggested that the  $Si_n$  cage can be stabilized by encapsulating a guest atom in the center of the cage. The idea is to put one or more atoms in the center of the cluster to stabilize the cage thanks to the overlap between the electron orbitals of the doped atom and those of Si atoms. If the Si-dopant bindings are stronger than the Si-Si ones, then the Si atoms may surround the dopant atom. Hence, the covalent bondings between the guest atom and Si atoms are responsible for the cage formation and the stability. Consequently, the first studies have investigated the stability of  $Si_n$  cage encapsulating a transition metal atom with open  $d$  electronic shell, the latter being expected to form covalent bondings with silicon atoms. Kumar and Kawazoe<sup>13</sup> have investigated the metal-encapsulated cagelike  $M@Si_n$  with  $M = Hf, Zr, Fe, Ru, Os$  and  $n = 14, 16$ . The size of the encapsulating silicon cage was found to be very dependent on the size of the doped atom since the  $M-Si$  interactions are very strong and lead to compact structures. Moreover, the binding between two cage-type clusters has been studied. The cages were found to be bound by van der Waals-type interactions without any geometric deformation, indicating a strong stability of the cages. Recently, the structures and stabilities of the alkali and alkaline earth metals encapsulated in perhydrogenated silicon fullerene  $Si_{20}H_{20}$  have been reported.<sup>23</sup>  $X@Si_{20}H_{20}$  complexes ( $X = Li^{0/+}, Na^{0/+}, K^{0/+}, Be^{0/2+}, Mg^{0/2+}, Ca^{0/2+}$ ) were found to have a minimum-energy endohedral structure. However, these studies only characterized local minima for endohedral structures with  $I_h$  and  $C_{5v}$  symmetries. The  $I_h$  symmetrical  $Na@Si_{20}H_{20}$  and  $K@Si_{20}H_{20}$  are found to be local minima, while the  $I_h$  symmetrical  $Li@Si_{20}H_{20}$  presents three imaginary frequencies and tends to a  $C_{5v}$  symmetry with a displacement of the alkali from the center of the cage. The encapsulation of halide anions into the dodecahedral cage  $Si_{20}H_{20}$  have shown that  $F^-$  is the anion with the largest binding energy, and the insertion of the bromide anion does not alter the structure of the cage.<sup>24</sup>

Here, we investigate for the first time the possibility to form alkali-encapsulating Si clusters  $A@Si_n$  with  $n=10-20$ .

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No covalent A–Si interaction is expected but we are interested in the possibility of stabilizing the cage with the expected transfer of one electron from A to  $\text{Si}_n$ . However, as our previous studies<sup>25–28</sup> have shown that the lowest-energy isomers for very small  $\text{ASi}_n$  clusters ( $n \leq 6$ ) keep the frame of the corresponding  $\text{Si}_n$  unchanged with the alkali atom adsorbed at the surface, we will also consider here the surface-bound alkali clusters for comparison. So we will report the geometries and properties of two types of alkali-doped silicon clusters: (1) structure in which the alkali atom is encapsulated within a silicon cage (labeled as  $c\text{-A@Si}_n$ ) and (2) structures in which the alkali atom is adsorbed at the  $\text{Si}_n$  surface (labeled as  $s\text{-ASi}_n$ ). The latter is the most stable for very small clusters, while the former could be competitive for larger size similar to transition metal-doped clusters. Details of the calculations are introduced in Sec. II. In Sec. III, we present the structures and energetics for both  $c\text{-A@Si}_n$  and  $s\text{-ASi}_n$ -type clusters, while the electronic properties and the bonding nature are discussed in Sec. IV.

## II. METHOD

The calculations have been performed in the framework of the density functional theory using the hybrid B3LYP functional which involves Becke's three-parameter exchange functional.<sup>29</sup> The Gaussian basis set used was 6-31+G(*d*), which is  $(17s11p1d)/[5s4p1d]$ ,  $(11s5p1d)/[4s3p1d]$ ,  $(17s11p1d)/[5s4p1d]$ , and  $(23s17p1d)/[6s5p1d]$  on silicon, lithium, sodium, and potassium atoms, respectively. The use of B3LYP and 6-31+G(*d*) basis set has been validated in our previous theoretical works on silicon-sodium in the sense that it provided theoretical results in good agreement with the experimental data concerning the ionization potential.<sup>25</sup> Calculations were carried out with the GAUSSIAN 98 program package<sup>30</sup> and Q-CHEM 3.0 package.<sup>31</sup> Pre- and postprocessing operations were performed with the graphical interface GABEDIT.<sup>32</sup> Only the singlet or doublet spin multiplicities have been considered since it has been already demonstrated in previous works<sup>25,26,28</sup> that for small alkali-doped silicon clusters, they are more stable than higher spin multiplicities.

In the optimization process of cluster geometries, a number of endohedral  $c\text{-A@Si}_n$  structures where the alkali atom A is trapped inside a  $\text{Si}_n$  cage-like structure were tested for each size. We have initiated the geometry optimization process from the previous structures found with a transition metal atom.<sup>11–22</sup> We have also tested new structures starting from some symmetric geometries. However, it was found that often the symmetry was broken during the quenching. All optimizations were carried on without symmetry constraints ( $C_1$  symmetry group). Harmonic frequency analysis was performed to guaranty that the optimized structures are local minima. For each stable structure, the atomic charges have been estimated through a natural population analysis (NPA).<sup>33,34</sup> Furthermore, the static dipolar polarizability  $\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$  have been calculated.

## III. RESULTS

### A. Alkali-doped cage-like silicon clusters $c\text{-A@Si}_n$

The optimized geometries of the  $c\text{-Li@Si}_n$  cage-like silicon clusters, together with the energies of isomers relative to that of the lowest-energy cage structure and the spatial symmetries, are shown in Fig. 1 for  $n=10$ – $20$ . No cages were found to be stable for  $n$  lower than 10. For  $n=10$ , two isomers are found to be stable. The lowest one, formed of eight faces, is of  $D_{4d}$  symmetry. The Si–Li distances are 2.41 Å along the molecular axis and 2.30 Å for the other ones. The Si–Si distances are 2.52 Å between nearest neighbors. The second isomer lies 0.89 eV above the lowest one and is formed by two superimposed twisted  $\text{Si}_5$  planar pentagons surrounding the lithium atom. For  $c\text{-Li@Si}_{12}$ , the lowest-energy isomer is built from two superimposed deformed  $\text{Si}_6$  hexagons surrounding the lithium atom resulting in a  $C_i$  symmetry. The Si–Li distances are 2.36 Å for the nearest neighbors. In the lowest-energy isomer for  $n=14$ , the lithium atom is encapsulated in a  $\text{Si}_n$  structure composed of two nonplanar deformed  $\text{Si}_6$  hexagons between which two silicon atoms are inserted. A second isomer, lying 0.55 eV above the latter, presents a  $D_{4h}$  symmetry. For  $c\text{-Li@Si}_{15}$ , two isomers were found to be quasidegenerated. The first one is of  $C_{2v}$  symmetry, while the second one, lying 0.04 eV above, is of  $C_s$  symmetry and is composed of the  $D_{4h}$  isomer of  $c\text{-Li@Si}_{14}$  on which a Si atom is adsorbed at the surface forming three bonds with the other silicon atoms. For  $c\text{-Li@Si}_{16}$ , five isomers were found to be stable in a range of 1 eV. The lowest one is formed of eight deformed pentagons and two deformed rhombus. The smallest Si–Li distance is 2.61 Å. The second and fourth isomers, lying 0.55 and 0.94 eV, respectively, above the first one, are composed of the  $D_{4h}$  isomer of  $c\text{-Li@Si}_{14}$  with two Si atoms adsorbed at the surface. The two stable isomers for  $c\text{-Li@Si}_{18}$  are of  $C_i$  and  $C_{4h}$  symmetries, the second one being again formed from the  $D_{4h}$  isomer of  $c\text{-Li@Si}_{14}$ . For  $c\text{-Li@Si}_{20}$ , two structures were tested. The first one is that of the fullerene-like  $C_{20}$  formed of 12 pentagons. During the optimization, the latter was found to relax in a structure of  $C_1$  symmetry composed of 11 deformed pentagons and 1 trapezoid. The Si–Li distances are between 2.67 and 4.33 Å. In the second structure, the lithium atom was surrounded by a cage formed by three superimposed hexagons capped by one Si atom at the two ends. This structure was found to relax in a structure of  $C_1$  symmetry lying 0.37 eV above the first one.

We have also tried to encapsulate a sodium atom in cage-like silicon clusters. We have found stable structures for  $n \geq 14$  (Fig. 2). The stable  $c\text{-Li@Si}_n$  structures for  $n=10, 12$ , and 13 are found to be not stable with the sodium atom. During the optimization process, these structures are found to relax toward a geometry where the alkali left the cage and is finally adsorbed on the surface of a  $\text{Si}_n$  cluster. For  $c\text{-Na@Si}_{14}$ , three structures are found to be stable. The first two ones are quasisimilar to the lowest-energy isomer of  $c\text{-Li@Si}_{14}$ , where the alkali atom is encapsulated in a  $\text{Si}_n$  structure composed of two deformed  $\text{Si}_6$  hexagons between which two silicon atoms are inserted. The third isomer, lying 1.14 eV above the first one, is similar to the  $D_{4h}$  isomer of

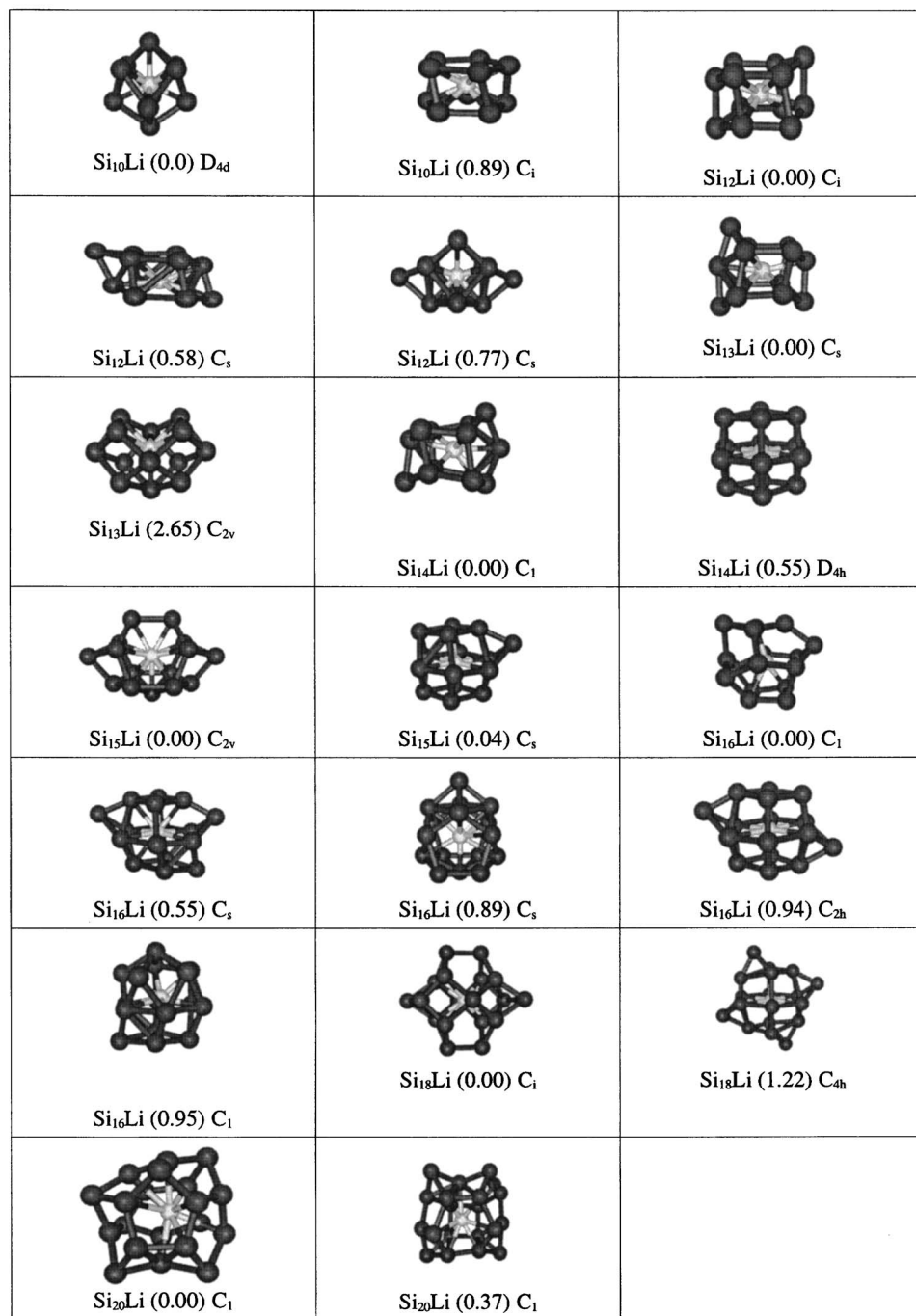


FIG. 1. Optimized geometries of *c*-Li@Si<sub>*n*</sub> cages (*n*=10–20). The relative energies (in eV) are given in parentheses for each size as well the spatial symmetry.

*c*-Li@Si<sub>14</sub>, but the symmetry is reduced to S<sub>2</sub> due to steric effects. The alkali-silicon distances are between 2.66 and 2.87 Å in the case of sodium and so slightly higher than those in the case of lithium (2.58 and 2.84 Å). Thus, the substitution of the lithium atom by a sodium atom does not considerably modify the cage. For *c*-Na@Si<sub>16</sub>, the structure of the lowest-energy isomer is the second one of *c*-Li@Si<sub>16</sub>, the first one being found not to be stable probably because the cage is too small to insert a sodium atom. The smallest Si–Na distance is 2.69 Å. One can note that the isomer formed from the S<sub>2</sub> isomer of *c*-Na@Si<sub>14</sub> plus two Si atoms adsorbed at the surface is only 0.16 eV above the lowest-energy isomer. In the case of the *c*-Li@Si<sub>16</sub>, the difference between the two similar isomers was 0.39 eV. For

*c*-Na@Si<sub>20</sub>, we tested the two structures previously investigated for *c*-Li@Si<sub>20</sub>, but only the structure formed of 12 pentagons was found to be stable. The relaxed geometry is of C<sub>1</sub> symmetry and composed of 12 deformed pentagons. The Si–Na distances are in the 2.82–4.20 Å range. We have also tried to encapsulate a potassium atom in a Si<sub>20</sub> fullerene-like cage formed by 12 pentagons. The structure was found to relax in a slightly deformed geometry with 12 slightly deformed pentagons (Fig. 2). The Si–K distances are found to be in a smaller range (3.00–3.84 Å) than those for *c*-Li@Si<sub>20</sub> (2.67–4.33 Å) and for *c*-Na@Si<sub>20</sub> (2.82–4.20 Å), and so the *c*-K@Si<sub>20</sub> cage is more spherical.

Some energetic properties of alkali-encapsulated silicon cage clusters are given in Table I for the lowest-energy struc-



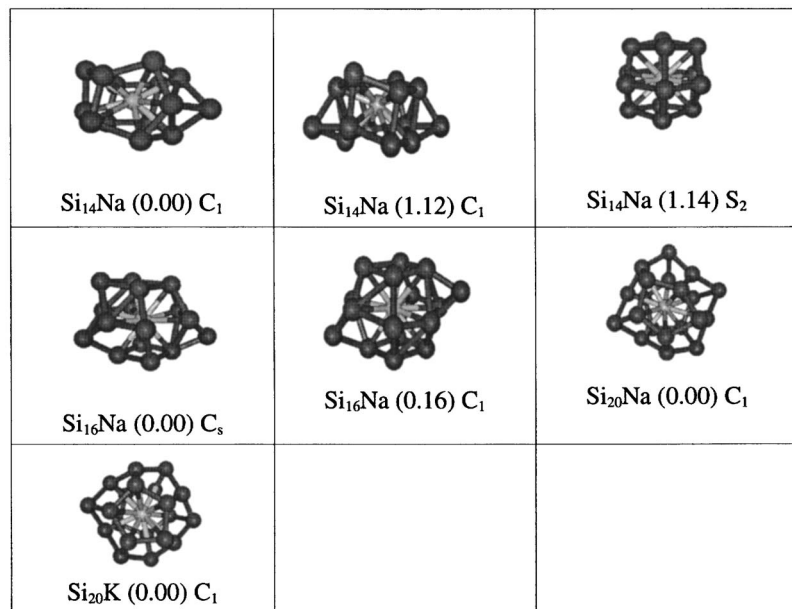


FIG. 2. Optimized geometries of *c*-Na@Si<sub>14</sub>, *c*-Na@Si<sub>16</sub>, *c*-Na@Si<sub>20</sub>, and *c*-K@Si<sub>20</sub>. The relative energies (in eV) are given in parentheses as well the spatial symmetry.

ture for each size. The cohesive energy for *c*-Li@Si<sub>*n*</sub>, calculated as  $E_c = -(E(\text{LiSi}_n) - nE(\text{Si}) - E(\text{Li})) / (n+1)$ , is found to increase slightly with *n* from 2.90 to 3.16 eV so that the clusters continue to gain energy as their growth proceeds. The second-order difference in energy, calculated as  $\Delta E = E(n+1) + E(n-1) - 2E(n)$ , is positive for *n*=14, indicating a larger stability for this size. Both the vertical ionization potential and the vertical electron affinity increase with the atomic number of the encapsulated alkali. The vertical ionization potential is in the 6.3–7.1 eV range for the three species. The vertical electron affinity is in the 2.8–3.3 eV range. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap decreases with size from 2.49 eV for *c*-Li@Si<sub>10</sub> to 1.43 eV for *c*-Li@Si<sub>20</sub>. It also decreases with the atomic number of the

encapsulated alkali (from 1.43 to 1.11 eV for *c*-Li@Si<sub>20</sub> and *c*-K@Si<sub>20</sub>). The static dipolar polarizability  $\alpha$  is found to increase with size from 46.78 to 96.64 Å<sup>3</sup> for *c*-Li@Si<sub>10</sub> and *c*-Li@Si<sub>20</sub>. Interestingly,  $\alpha$  was not found to depend on the encapsulated alkali. For *n*=20,  $\alpha$  increases very slightly from lithium to potassium (values are 96.64, 98.72, and 103.47 Å<sup>3</sup> for lithium, sodium, and potassium, respectively). In fact,  $\alpha$  is related to the electronic charge transfer from the alkali to the Si<sub>*n*</sub> cage. From the natural population analysis, the transferred charge is the same (0.55 a.u.) for the three alkalis. Besides, the volume of the cage is quasi-identical for the three species even if a deformation is observed, i.e., *c*-K@Si<sub>20</sub> being more spheric than *c*-Li@Si<sub>20</sub>. All that results in an average  $\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) / 3$  similar for the three alkalis.

TABLE I. Properties of the lowest-energy *c*-alkali@Si<sub>*n*</sub> cage-type structures: cohesive energies ( $E_c$ ), second-order difference in energy ( $\Delta E$ ), vertical ionization potential ( $\text{IP}_v$ ) and electron affinities ( $\text{EA}_v$ ), and the HOMO-LUMO gaps. Energies are given in eV. Atomic charges  $q_{\text{NPA}}$  on the alkali atom (in a.u.) and polarizabilities  $\alpha$  (in Å<sup>3</sup>) are also given.

<i>n</i>	$E_c$	$\Delta E$	$\text{IP}_v$	$\text{EA}_v$	Gap	$q_{\text{NPA}}$	$\alpha$
<i>c</i> -Li@Si <sub><i>n</i></sub>							
10	2.90		7.11	2.75	2.49	0.22	46.78
12	2.99		7.10	3.22	2.41	0.58	60.91
13	3.01	−0.33	6.71	2.99	1.95	0.52	64.27
14	3.05	0.73	6.62	3.00	1.54	0.58	68.95
15	3.04	−0.02	6.88	3.24	1.60	0.58	73.83
16	3.04		6.23	2.71	1.47	0.49	77.37
18	3.10		6.73	3.24	1.99	0.50	86.85
20	3.16		6.29	2.79	1.43	0.55	96.64
<i>c</i> -Na@Si <sub><i>n</i></sub>							
14	2.88		6.75	3.17	1.39	0.61	71.97
16	2.88		6.71	3.13	1.20	0.51	75.58
20	3.09		6.32	2.94	1.35	0.55	98.72
<i>c</i> -K@Si <sub><i>n</i></sub>							
20	3.20		6.60	3.30	1.11	0.55	103.47

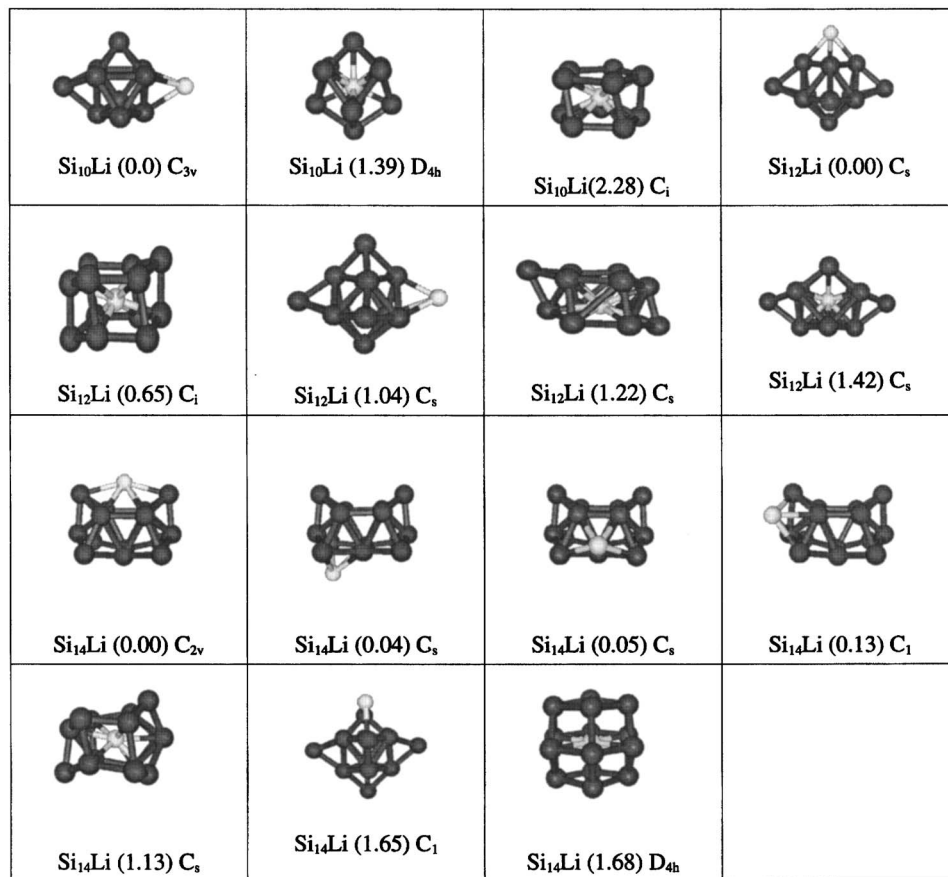


FIG. 3. Geometries of the lowest-energy isomers of both surface-bound lithium and cage-type structures for Si<sub>n</sub>Li ( $n=10, 12,$  and  $14$ ). Relative energies (in eV) are given.

## B. Surface-bound alkali clusters $s\text{-ASi}_n$

In our previous studies,<sup>23–26</sup> we have shown that the lowest-energy isomers for very small ASi<sub>n</sub> clusters ( $n \leq 6$ ) keep the frame of the corresponding Si<sub>n</sub> unchanged and the alkali atom is adsorbed at the surface. Consequently, we present here an investigation of such surface-bound alkali  $s\text{-ASi}_n$  for  $n=10, 12,$  and  $14$  to determine their energy relative to that of the cage-like structures. Our goal is not to make a global search for the lowest-energy isomer with a global optimization procedure of the potential energy surface but only to give information on the relative energy of cage-like structures as compared to structures which probably compete the lowest isomers.

The structures for Si<sub>10</sub>, Si<sub>12</sub>, and Si<sub>14</sub> have been extensively studied from theory and seem to be now firmly established. Si<sub>10</sub> adopts a compact tetracapped trigonal prism of C<sub>3v</sub> symmetry,<sup>35–38</sup> while Si<sub>12</sub> presents a compact hexacapped trigonal prism of C<sub>2v</sub> symmetry.<sup>37–39</sup> The lowest minimum structure for Si<sub>14</sub> has been found recently<sup>39</sup> as constituted by a deformed hexagon bonded to two adjacent pentagons. For the three sizes, we have studied the stability of the  $s\text{-LiSi}_n$  structures in which the lithium atom was adsorbed on all possible sites of the lowest minimum geometry for Si<sub>n</sub>. The lowest-energy isomers found are compared to cage-like structures in Fig. 3. For all sizes, the  $s\text{-LiSi}_n$  structures in which the alkali atom is attached at a bridge site are found to be more stable than  $c\text{-Li@Si}_n$  structures by 1.39, 0.65, and 1.13 eV for  $n=10, 12,$  and  $14$ , respectively. For  $s\text{-LiSi}_{10}$ , the Li atom is found to be bound at the only free

face of the prism similarly to the lowest-energy structure of NaSi<sub>10</sub> found by Wei *et al.*<sup>40</sup> The structure keeps the C<sub>3v</sub> symmetry and the Si–Li distances are 2.70 Å. For  $n=12$ , the lithium atom is capped over four atoms with distances between Li and Si in the 2.55–2.81 Å range. For  $s\text{-LiSi}_{14}$ , four isomers can be constructed with the Li atom attached at a bridge site. These four structures were found to be quasidegenerated. In the lowest-energy one, the Li atom is capped over the six atoms of a deformed hexagonal site. The Si–Li distances are 2.73 and 2.75 Å.

The cohesive energies of  $s\text{-LiSi}_n$  structures are plotted in Fig. 4 together with those of  $c\text{-Li@Si}_n$  structures. For  $s\text{-LiSi}_n$

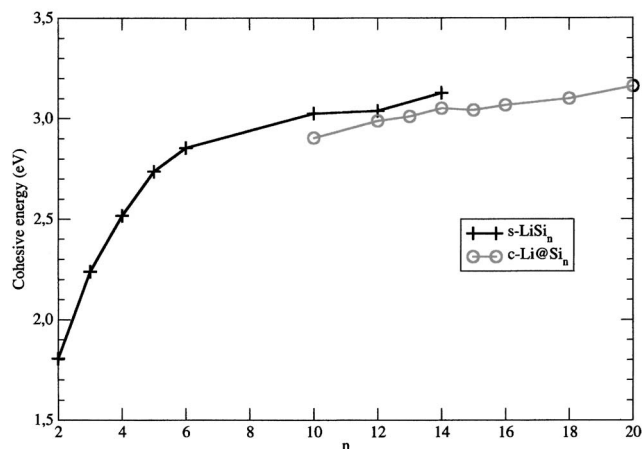


FIG. 4. Cohesive energies of both  $s\text{-LiSi}_n$  and  $c\text{-Li@Si}_n$  clusters.

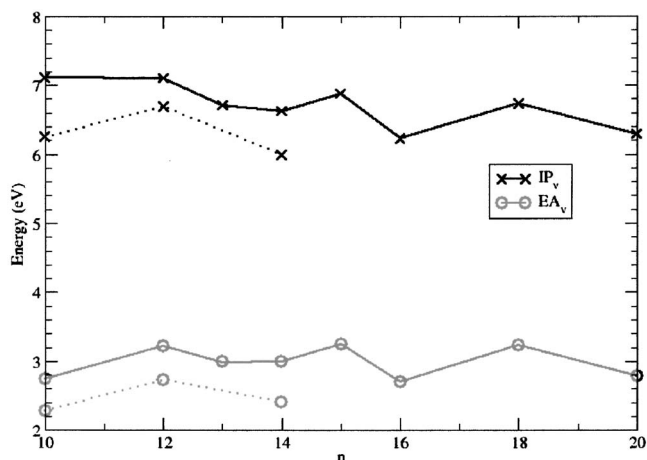


FIG. 5. Vertical ionization potentials and electron affinities of both  $s\text{-LiSi}_n$  (dotted lines) and  $c\text{-Li@Si}_n$  (full lines) clusters.

structures, we display also the values for  $n \leq 6$  obtained from our previous works. The calculations show a strong increase of the cohesive energy with the size until  $n=6$  so that the clusters continue to gain energy as their growth proceeds, then for larger  $n$  the increase becomes weaker. We have also calculated the binding energy of Li to the  $\text{Si}_n$  cluster as  $E_b = -(E(\text{Si}_n\text{Li}) - E(\text{Si}_n) - E(\text{Li}))$  for both  $s\text{-LiSi}_n$  and  $c\text{-Li@Si}_n$  structures for  $n=10, 12$ , and  $14$ . For  $s\text{-LiSi}_n$ ,  $E_b$  is found to be 1.44, 2.13, and 1.70 eV for  $n=10, 12$ , and  $14$ , respectively. For  $c\text{-Li@Si}_n$ ,  $E_b$  is found to be 0.97, 1.84, and 1.46 eV with respect to the local optimized empty cage  $\text{Si}_n$  for  $n=10, 12$ , and  $14$ , respectively, while it is found to be 0.10, 1.48, and 0.57 eV with respect to the lowest-energy isomer of  $\text{Si}_n$  for  $n=10, 12$ , and  $14$ , respectively. The small  $E_b$  values for  $c\text{-Li@Si}_{10}$  indicate that this structure is probably very difficult to produce experimentally. Both  $\text{IP}_v$  and  $\text{EA}_v$  are slightly lower for  $s\text{-LiSi}_n$  than for  $c\text{-Li@Si}_n$  but the evolutions with size are similar (Fig. 5) and unfortunately the differences between the values for the two types of structure are too small to allow an experimental characterization of the conformation of the clusters. The HOMO-LUMO gap was found to be lower for  $s\text{-LiSi}_n$  than for  $c\text{-Li@Si}_n$  by about 0.2–0.6 eV (Table II). The atomic charge on the alkali atom due to the electron transfer from the alkali atom to Si ones is higher for surface-bound alkali (about 0.8–0.9 a.u.) than for cage structures (about 0.55 a.u.) because the electron transfer is mostly unidirectional in the case of  $s\text{-LiSi}_n$  while the alkali-electron is attracted in various directions in the case of

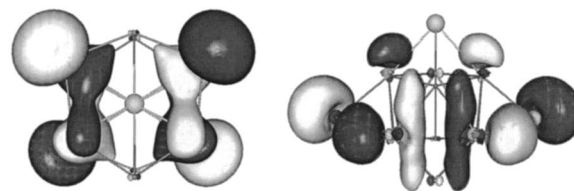


FIG. 6. HOMO of  $c\text{-Li@Si}_{12}$  and  $s\text{-LiSi}_{12}$ . Isovalue is 0.03 a.u. Li atom is represented by a clear ball.

$c\text{-Li@Si}_n$ , resulting in a smaller extracting force. However, the static dipolar polarizability is similar for the two types of structures.

#### IV. DISCUSSION

The natural population analysis indicates that there is an electron transfer from the alkali atom to the  $\text{Si}_n$  structure, the transfer being, however, higher for  $s\text{-LiSi}_n$  than for  $c\text{-Li@Si}_n$ . Besides, the HOMO, represented in Fig. 6 for both  $c\text{-Li@Si}_{12}$  and  $s\text{-LiSi}_{12}$ , is completely located on silicon atoms without any contribution from the alkali atom, confirming that one electron is transferred from the alkali atom to the  $\text{Si}_n$  structure. So the electronic structure of  $s\text{-LiSi}_n$  can be described as  $s\text{-Li}^+\text{Si}_n^-$  while that of  $c\text{-Li@Si}_n$  can be described as  $c\text{-Li}^+\text{@Si}_n^-$ . However, the localization of the transferred charge differs for the two types of structures: in the case of  $s\text{-LiSi}_n$  structure, the transferred charge is located on the nearest neighbors of the alkali atom, while it is completely delocalized on the whole cage in the case of  $c\text{-Li@Si}_n$  structure. It is illustrated in Fig. 7 for  $n=12$ : the total charge on the four nearest neighbors of Li in  $s\text{-LiSi}_{12}$  is about  $-1$  a.u. [Fig. 7(b)], while in the case of  $c\text{-Li@Si}_{12}$  the atomic charge is quasisimilar on all silicon atoms [between  $-0.11$  and  $+0.02$  a.u. (Fig. 7(a))]. Hence, the  $c\text{-Li@Si}_n$  structures are composed of one positive charge surrounded by negative ones distributed on all the surface of the cage. In Fig. 7(c), we show the isosurfaces of the difference between the total electronic charge of the  $c\text{-Li@Si}_{12}$  cluster and the total electronic charge of both bare  $\text{Si}_n$  cluster and Li atom. In  $c\text{-Li@Si}_{12}$  cluster, an excess of electronic charge is found all around the alkali and distributed in a region located between the alkali and the Si cage. An analysis of the orbitals shows covalent bondings between the Si atoms in which the alkali atom contributes very little. Only few molecular orbitals show contribution from atomic orbitals of the alkali. Hence, the stability of the  $c\text{-A@Si}_n$  structures is due to both the covalent interactions between Si atoms and the electro-

TABLE II. Properties of the lowest-energy surface-bound alkali  $s\text{-LiSi}_n$ -type structures: cohesive energies ( $E_c$ ), vertical ionization potential ( $\text{IP}_v$ ) and electron affinities ( $\text{EA}_v$ ), and the HOMO-LUMO gaps. Energies are given in eV. Atomic charges  $q_{\text{NPA}}$  on the alkali atom (in a.u.), polarizabilities  $\alpha$  (in  $\text{\AA}^3$ ), and dipole moment  $\mu$  (in D) are also given.

$n$	$s\text{-LiSi}_n$						
	$E_c$	$\text{IP}_v$	$\text{EA}_v$	Gap	$q_{\text{NPA}}$	$\alpha$	$\mu$
10	3.02	6.25	2.28	1.86	0.81	49.81	5.55
12	3.04	6.69	2.73	2.26	0.86	58.00	5.47
14	3.13	5.99	2.41	1.23	0.81	78.61	2.67

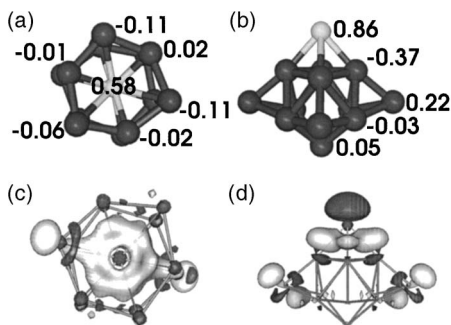


FIG. 7. Atomic charges (in a.u.) from the natural population analysis for both  $c\text{-Li@Si}_{12}$  (a) and  $s\text{-LiSi}_{12}$  (b). For  $c\text{-Li@Si}_{12}$ , only charge on atoms of the upper hexagon are given. For  $s\text{-LiSi}_{12}$ , only values for some arbitrary chosen atoms are given. Isosurfaces [(c) and (d)] of the difference between the total electronic charge of  $\text{LiSi}_{12}$  clusters and the total electronic charge of both bare  $\text{Si}_n$  cluster and Li atom are displayed. The value of the isosurface is 0.002 a.u. The excess of electronic charge on  $\text{LiSi}_{12}$  is shown in clear.

static interaction between a positive charge on the alkali atom surrounded by negative ones on silicon atoms. We also display the isosurfaces of the difference between the total electronic charge of the  $s\text{-LiSi}_{12}$  cluster and the total electronic charge of both bare  $\text{Si}_n$  cluster and Li atom in Fig. 7(d). They show a positive charge on the lithium atom and a negative one on the nearest neighbors of the alkali atom, in very good agreement with the  $q_{\text{NPA}}$  charges.

## V. CONCLUSION

We conclude that Si cage structures doped with an alkali atom are stable, the cage size depending on the dopant. For Li atom, some cages are found to be stable for  $n \geq 10$ , the size  $n=14$  seeming to be the most favorable, while for Na atom cages are found to be stable for larger size, i.e.,  $n \geq 14$ . In all cases, the alkali atom is located at the center of the cage. An important electronic charge transfer from the alkali to the Si cage is observed so that the electronic structure can be described as a positive charge located on the alkali atom surrounded by a negative one distributed in a region located between the alkali and the Si cage. The stability is due to both covalent interactions between Si atoms and the electrostatic interaction between the positive charge on the alkali atom and the negative ones on silicon atoms. For  $n=20$ , the fullerene-like  $c\text{-A@Si}_{20}$  formed of 12 pentagons encapsulating an alkali atom are found to relax in a structure of  $C_1$  symmetry composed of 11 deformed pentagons and one trapezoid for lithium atom, and 12 deformed pentagons for sodium and potassium atoms, the alkali atom being located at the center of the cage. The encapsulation of one K atom induces a very slight deformation compared to the  $I_h$  structure. We have also considered surface-bound lithium  $s\text{-LiSi}_n$  isomers in which the lithium atom is adsorbed at the surface of the  $\text{Si}_n$  cluster. To our knowledge, the present study is the first one investigating this family of isomers for  $n > 10$ . Such isomers are found to be more stable than  $c\text{-A@Si}_n$  cage for  $n=10, 12$ , and  $14$  by about 1 eV. Given this large energy difference, the experimental formation of clusters at low temperature will probably privilege the

surface-bound alkali  $s\text{-ASi}_n$  isomers. The formation of  $c\text{-A@Si}_n$  cages requires probably a high temperature and perhaps the development of particular techniques.

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