

Exohedral Bonding Nature of Si Atom on the Ba@Si₂₈ Cluster; *Ab Initio* Study

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First-principle electronic structure is studied for the Si₂₈ and Ba@Si₂₈ clusters, which are components of the clusters in silicon clathrate II. We obtain the geometrically optimized relaxed cage structures of the clusters and the exohedral binding nature of single Si atom on the Ba@Si₂₈ clusters. The hollow Si₂₈ cluster relaxes into the Si₂₄ like cluster in the clathrate I having four exohedral Si atoms outside the hexagon in the Si₂₄ cluster. The hexagons on the Ba@Si₂₈ cluster are deformed into a chair type with relaxation. The exohedral Si atom is the most stable at the edge center near the top that meets three pentagons. We have found for the first time that the exohedral Si atom forms the three-center covalent bond between the two caged Si atoms.

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1. Introduction

The silicon clathrates have drawn much attention as expanded phases of the diamond structured Si crystal. The clathrates have begun to exhibit new physical properties such as superconductivity or thermoelectricity. There have been three types of the silicon or germanium clathrates;¹⁻⁶⁾ the clathrate I which has simple cubic lattice with Si₄₆, the clathrate II which has face-centered cubic lattice with Si₃₄ or simple cubic lattice with Si₁₃₆, and the clathrate III Ge₁₀₀ with simple cubic lattice. They have been synthesized from group IV elements such as Si, Ge, and Sn atoms or their mixtures with group III elements only when the alkali or heavy alkaline-earth metal atoms or iodine atoms⁶⁾ coexist.

The clathrate I is composed of two pentagonal dodecahedral Si₂₀ clusters and six tetrakaidecahedra (12 pentagonal and 2 hexagonal faces) Si₂₄ clusters. The full occupation of the cages leads to a stoichiometric compound M₈@Si₄₆. The clathrate II is composed of the 16 pentagonal dodecahedral Si₂₀ clusters and 8 hexakaidecahedral (12 pentagonal and four hexagonal faces) Si₂₈ clusters. The clathrate III has composition Ba₂₄@Ge₁₀₀ and is characterized as the interconnection of Ba-containing Ge₂₀ dodecahedra.⁵⁾ Figure 1 shows the shapes of the Si₂₀, Si₂₄, and Si₂₈ clusters. These clusters connect to each other, forming common faces between them, and form clathrates that are similar to the structures of zeolites and different from the structures of fullerenes in which van der Waals interaction connects carbon clusters. The solute atoms are encapsulated in these silicon clusters of the clathrates. Here we call these endohedral clusters. The atoms seem to act as templates for the formation of the clusters which seem to act as precursors for the growth of the clathrates. There remains a question whether the clathrates is crystallized forming tetrahedral radial bonds of the Si atoms on the top positions of the clusters or direct touching of the caged clusters.

There have been a few studies on the analysis of the electronic structure for these caged clusters with *ab initio* methods. This is because the clustering of the silicon atoms

forms closed packed aggregates with directional bonding and does not form hollow cage structures. This is different from the clusters of carbon atoms that form cage or hollow structures such as C₆₀ fullerenes or nanotubes. Jarrold and Constant have shown experimentally the Si clusters less than 27 atoms to grow into closed-packed prolate shapes with aspect ratio of about three and the larger clusters to grow into more spherical shapes.⁷⁾ The cage formation of the Si clusters has been realized by the encapsulization of the metal atoms and predicted theoretically by alloying of directional bonding atoms such as nitrogen⁸⁾ or carbon atoms into the frame of the Si clusters. Jackson *et al.*⁹⁾ have clarified the electronic structures of the caged Zr@Si₂₀ cluster with an *ab initio* analysis using the linear combination of atomic orbital method, predicting that the endohedral Zr atom to have a strong binding with the cage Si atoms.

In a previous paper we have clarified the stabilities, electronic structure, bonding nature, and charge transfer in the Ba@Si₂₀ and Si₂₀ clusters.¹⁰⁾ The caged Si₂₀ cluster with *I_h* symmetry was stable at cage radius with 5.959 a.u., although it collapsed into a prolate shape with relaxation. The endohedral *I_h* Ba@Si₂₀ cluster was stable with cage radius 6.313 a.u. that was found to be the sum of the Goldschmidt radii of the Ba and Si atoms. The endohedral Ba atom expands the radius of the caged Si₂₀ cluster by 5.94%. The Ba@Si₂₀ cluster relaxed into *C_i* symmetry from the *I_h* symmetry. The wavefunction of the s electrons of Ba pseudoatom expanded over the cage atoms of the cluster and there was no charge transfer from the central Ba atom to the cage Si atoms. Each cage Si atom was found to form sp₃ bonds from valence density map calculated with HOMO level.

It is essential for us to study the stabilities of the relaxed structures of the clusters in the clathrates. In the present paper we clarify the optimized equilibrium structure of the Si₂₈ and endohedral Ba@Si₂₈ clusters and the bonding nature from the charge densities around the externally attached single Si atom on the cluster with an *ab initio* electronic structure analysis. We call this external Si atom exohedral Si atom.

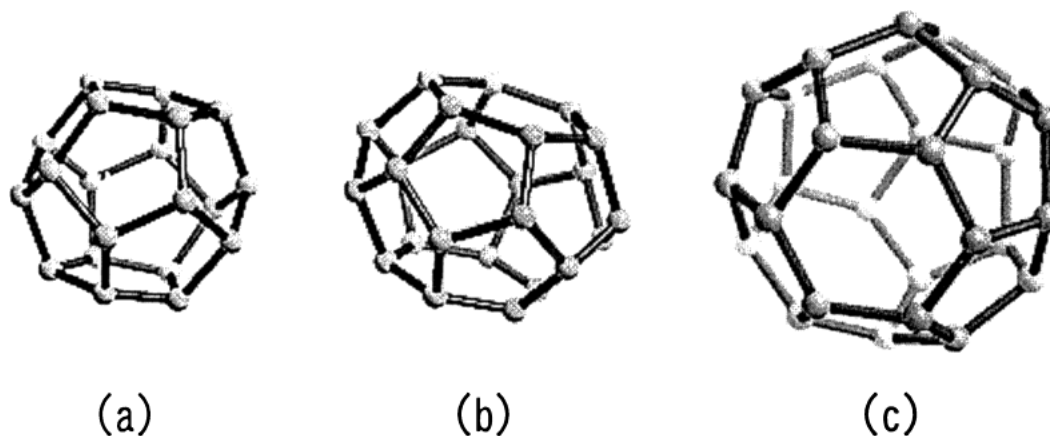


Fig. 1 The clusters appeared in clathrates I, II, and III; (a) Si₂₀, (b) Si₂₄, and (c) Si₂₈.

2. Computational Details

In our *ab initio* study the electronic structures are calculated within the frame of the local-density approximation (LDA). The electron-ion interactions are described by norm-conserving pseudopotentials in the Keinan-Bylander form.¹¹⁾ Both the pseudowavefunctions and the pseudopotentials for the Si and Ba pseudoatoms are calculated using the method given by Hamann.¹²⁾ The pseudopotential parameter are $6s^25p^65d^0$ for Ba pseudoatom with $r_{6s}^c = 2.41$ a.u. and $r_{5p}^c = 1.20$ a.u. and $3s^23p^23d^0$ for Si pseudoatom with $r_{3s}^c = 1.746$ a.u. and $r_{3p}^c = 2.122$ a.u. For both the atoms, the $l = 0$ channels are chosen to be the local parts of the pseudopotentials and nonbound states are used for the atoms. The details are given in Ref. 8). The exchange and correlation energies for pseudoatoms and crystals are evaluated with the parameterization given by Perdew and Zunger.¹³⁾ The single-particle orbitals are expanded in a plane-wave basis set at Γ point with an energy cutoff of 15 Rydberg (Ry) for the total energy calculations and 16 Ry for the geometry optimizations. We have confirmed these energies of the cut-off are sufficient to evaluate the binding nature of these clusters: we extrapolated the binding energies derived from the cut-off energies less than the 16 Ry to the higher energies, predicted the binding decrease to be at most $0.05 \text{ eV} \cdot \text{atom}^{-1}$ for the infinite cut-off energies, and have found the cut-off energies chosen to be sufficient for the present purpose of the analysis. The periodic boundary condition is applied for the rhombohedral primitive supercell of which lattice constant is 40.8 a.u. (22 nm). The mesh size of FFT has been chosen to be 2^5 , since no appreciable change of the total energies have been observed. The size of the supercell has been tested by calculating the binding energies of the exohedral Si atom on the Ba@Si₂₈ cluster and confirmed the energies to be independent of the equivalent positions on the cluster. The Kohn-Sham equations are solved by direct inversion in the iterative subspace (DIIS) method.^{14,15)} The positions of the atoms in the clusters have been relaxed with LDA and converged until the maximum magnitude of the forces is the order of 10^{-3} Ry/a.u.

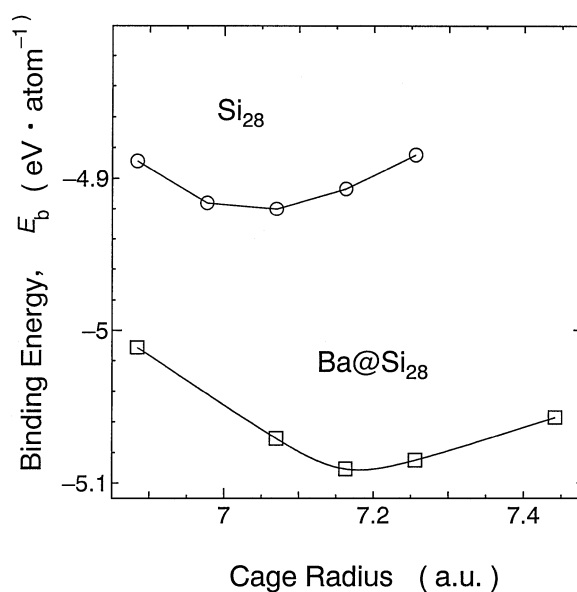


Fig. 2 Variation of the LDA binding energies E_b of Si₂₈ and Ba@Si₂₈ clusters as a function of cage radius, calculated with the geometry conserving condition.

3. Results and Discussion

3.1 Binding energy

The LDA binding energies E_b of the Si₂₈ and Ba@Si₂₈ clusters have been calculated with a geometry conserving condition. Here we define the energies to be the difference between the total energy of the cluster and those of the isolated atoms calculated with the same electron correlation approximation. The atom positions of the clusters are obtained by the crystal structure of the clathrate II. Figure 2 shows the variation of the LDA binding energies as a function of the cage radius. For the Si₂₈ cluster, the cage radius at the energy minimum is 7.04 a.u. and the radius for the Ba@Si₂₈ cluster is 7.14 a.u. expanding by about 1.9% from that of Si₂₈ cluster. For the I_h Ba@Si₂₀ cluster, on the other hand, the radius at energy minimum was 5.949 a.u. and expanded by 5.94% from that of I_h Si₂₀ cluster.⁹⁾ The interatomic distance of the Si atoms on the I_h Ba@Si₂₀ cluster was 4.252 a.u.⁹⁾ which was smaller than 4.44 a.u. in the diamond structured Si crystal. The interatomic distance of the Si atoms on the

Ba@Si₂₈ cluster in Fig. 2 is 4.258 a.u. for hexagonal rings and 4.263 a.u. for pentagonal rings which are almost the same as those in the *I_h* Ba@Si₂₀ cluster. Although the interatomic distances of both the Ba@Si₂₀ and Ba@Si₂₈ clusters are almost the same, their degrees of expansions from their hollow structures are different each other. This is because there is a sufficient space in the larger Ba@Si₂₈ cluster than Ba@Si₂₀ cluster.

3.2 Relaxed structures

We have relaxed the atom positions of the Si₂₈ cluster shown in Fig. 1(c). The optimized structures are shown in Fig. 3. Although there have been four hexagons on the surface of the Si₂₈ cluster (Fig. 1), the relaxed structure has only single hexagon on the surface; located at the bottom position of the cluster in Fig. 3. This implies that the Si clusters tend to form pentagons in their equilibrium structures, which is contrary to the carbon clusters in which carbon atoms tend to form hexagons such as carbon nanotubes. The figure shows a single hexagonal ring at the upper part of the cluster attaching four exohedral Si atoms above the ring. This can be seen as a Si₂₄ cluster attaching four exohedral Si atoms which is the cluster appeared in the clathrate I. This indicates this S₂₄ cluster to be more stable than the hollow Si₂₈ cluster even when the Si₂₄ cluster is free of the endohedral atom.

Figure 4 shows the relaxed structure of the Ba@Si₂₈ cluster containing endohedral Ba atom. The hexagons on the cluster deforms from the regular shape to a chair type that appears in the diamond structured silicon crystal.

3.3 Exohedral bonding of Si atom

In order to investigate the most stable endohedral position of a single Si atom around the Ba@Si₂₈ cluster, we have traced the trajectory of the atoms of the Ba@Si₂₈ clusters including the endohedral Si atom. The equation of motion of atoms has been modified so as to introduce a breaking to the velocities of the atoms. Initially we have placed a Si atom at the ontop site of the atom at which three pentagons meet on the cluster. This is because the electronic bonding of the Si atoms is expected to have sp³ bonding character in this Ba@Si₂₈ cluster. The Si atom has however moved into an edge center near from the ontop site of the cluster. The other

edge centers have been unstable comparing with this edge center.

Figure 5 shows the electronic charge density on the plane of the Ba@Si₂₈ cluster that intercepts the exohedral Si atom and the two cage Si atoms. The three atoms forming a triangle are shown at the upper left part in Fig. 5. The plane does not intercept the centers of the atoms except the three atoms. The charge distribution is high at the center of the triangle, constructing a three-center bond with two atoms in the cluster. The similar distribution has been observed between the exohedral atom and two atoms on the B₁₂ icosahedral cluster¹⁶⁾ and has been called the three-center covalent bond. There is a difference between them: the present three-center covalent bond is formed among the exohedral atom and the two cage atoms, although for the B₁₂ cluster, it is formed on the three cage atoms.

For the Ba@Si₂₀ cluster, the exohedral Si atom was also stable at the center of edge on the cluster.¹⁰⁾ However, the

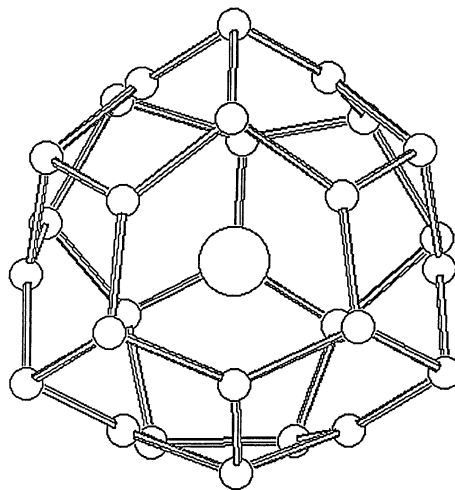


Fig. 4 Structure of the geometry optimized Ba@Si₂₈ cluster.

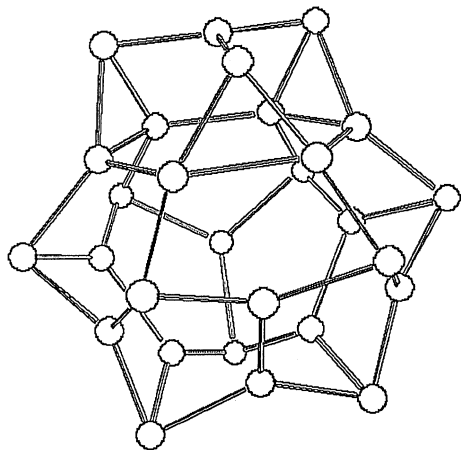


Fig. 3 Structure of the geometry optimized Si₂₈ cluster.

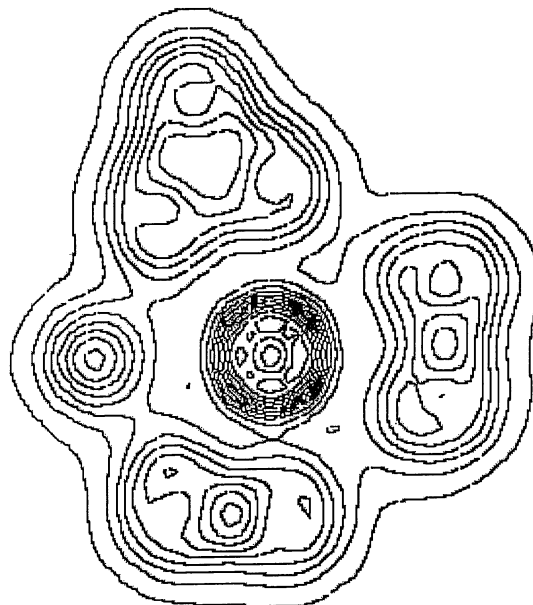


Fig. 5 The plot of the valence electron density of the geometry optimized Ba@Si₂₈ cluster on the plane containing the exohedral Si atom and two cage atoms bonded with the atom.

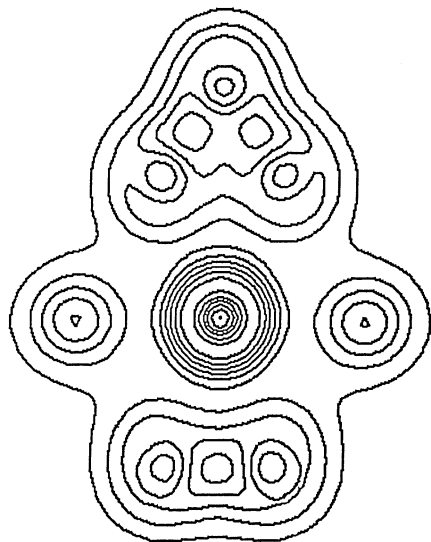


Fig. 6 The same figure as Fig. 5, but for Ba@Si₂₈ cluster and the projection plane is on the central Ba atom of the cluster and on the two cage atoms connected with the exohedral Si atom.⁹⁾

bonding forms between the exohedral Si atom and the cage atoms, forming two two-center covalent bonds as shown in Fig. 6, in which the charge density plane contains two Si–Si bonds and bisects another two Si–Si bonds perpendicular to the former bonds. The bond between the two cage atoms is broken in this case. This is different from the three-center covalent bond for the Ba@Si₂₈ cluster appeared in Fig. 5. The formation of the two-center covalent bond can be explained as follows; the minimum of the binding energy for the Ba@Si₂₀ cluster was expanded by about 6% from the hollow *I_h* Si₂₀ cluster by the inclusion of endohedral Ba atom. The presence of the exohedral Si atom breaks the two-center bonds on the cage of the cluster and form two two-center bonds between the cage atoms, since the interatomic distances on the *I_h* Ba@Si₂₀ are far expanded from the equilibrium distance on the Si₂₀ cluster. The formation of the two-center bonds weakens the bond between the cage atoms on the Ba@Si₂₀ cluster. The distance between the cage atoms forming the triangle with three-center bond was expanded to 4.989 a.u., although the other interatomic distances were 4.50 a.u.¹⁰⁾

The Ba@Si₂₈ cluster has sufficient space to fill the Ba atom and has deformed with relaxation as shown in Fig. 4. The distance between the two cage atoms forming the three-center covalent bond in the triangle has been 4.462 a.u. that is almost the same as the other edges on the cage atoms of the cluster.

The exohedral Si or Al atom has been found to form the three-center bond with two cage atoms on the B₁₂ and Al₁₂ clusters with icosahedral symmetry.¹⁶⁾ However, in the case of icosahedron with thirteen atoms, B₁₃ and Al₁₃, the exohedral Si or Al atoms are stabilized at the center of the three triangle of the cage atoms which is a stable position for the rigid sphere packing on the twelve atom clusters.¹⁶⁾ From these they concluded that the B₁₃ and Al₁₃ are metallic and the B₁₂ and Al₁₂ clusters have a covalent bonding nature. If we apply this concept to the present case, this leads to the

Ba@Si₂₈ to be a covalent bonding.

The stable positions of the single exohedral Si atom imply a growth mechanism of the clathrates. Not only the Ba@Si₂₀ cluster,¹⁰⁾ but also the Ba@Si₂₈ have shown the edge center to be the most stable positions for the exohedral Si atom. This implies that the clathrates grow with direct touching of the clusters, connect each other, and form common faces between them. This is because the most stable positions of the Ba@Si₂₈ and Ba@Si₂₀ clusters are not the ontop sites on the clusters but the edge center positions in both the cases.

4. Conclusions

First-principle electronic structure calculations have been carried out for the Si₂₈ and endohedral Ba@Si₂₈ clusters, which are components of the clusters in the silicon clathrate II. We have obtained the geometrically optimized cage structures of the Si₂₈, Ba@Si₂₈, and Ba@Si₂₈ clusters with the exohedral Si atom. The hollow Si₂₈ cluster has relaxed into the Si₂₄ like cluster appeared in the clathrate I having four exohedral Si atoms outside the hexagon. The hexagons on the Ba@Si₂₈ cluster have deformed into chair type with relaxation. The exohedral Si atom has been most stable at the edge center near the top that meets three pentagons on the Ba@Si₂₈ cluster. We have found the three-center covalent bond among the exohedral Si atom and two cage atoms on the cluster.

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REFERENCES

- 1) C. Cros: PhD. Thesis, No. 205, University Bordeaux (1970).
- 2) C. Cros, E. Reny and M. Pouchard: *Mol. Cryst. Liq. Cryst.* **310** (1998) 199–204.
- 3) J. S. Kasper, E. F. Hagenmuller and C. Cros: *Science* **150** (1965) 1713–1714.
- 4) C. Cros, M. Pouchard and E. F. Hagenmuller: *J. Solid. State. Chem.* **2** (1970) 570–581.
- 5) H. Furuoka, K. Iwai, S. Yamanaka, H. Abe, K. Yoza and L. Hamings: *J. Solid State Chem.* **151** (2000) 117–121.
- 6) E. Reny, S. Yamanaka, C. Cros and M. Pouchard: *Chem. Commun.* (2000) 2505–2506.
- 7) M. F. Jarrold and V. A. Constant: *Phys. Rev. Lett.* **67** (1991) 2994–2997.
- 8) K. Jackson, G. Jungnickel and T. Frauenheim: *Chem. Phys. Lett.* **292** (1998) 235–242.
- 9) K. Jackson and B. Nellermoe: *Chem. Phys. Lett.* **254** (1996) 249–256.
- 10) T. Nagano, K. Tsumuraya, H. Eguchi and D. J. Singh: *Phys. Rev.* **B64** (2001) 155403–155414.
- 11) L. Keinman and D. M. Bylander: *Phys. Rev. Lett.* **48** (1982) 1425–1428.
- 12) D. R. Hamann: *Phys. Rev.* **B40** (1989) 2980–2987.
- 13) J. P. Perdew and A. Zunger: *Phys. Rev.* **B23** (1981) 5048–5079.
- 14) P. Pulay: *Chem. Phys. Lett.* **73** (1980) 393–398.
- 15) G. Kresse and Furthmuller: *Phys. Rev.* **B54** (1996) 11169–11186.
- 16) M. Fujimori, T. Nakata, E. Nishibori, K. Kimura, M. Tanaka and M. Sakata: *Phys. Rev. Lett.* **82** (1999) 4452–4455.