

## ***Ab-initio* structural optimization of icosahedral silicon clusters**

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The properties of clusters changes depending on the number of atom in the clusters. Aluminum and Lithium have been known to take icosahedral 13 atom clusters as low energy structures. Since the silicon atoms, on the other hand, have a directional bonding in the crystalline state, the bonding character in the clusters is different from that in the metal clusters. Recently, Bahel et al. have estimated the cohesive energies of a  $Si_{12}$  icosahedral and an atom centered  $Si_{13}$  icosahedral clusters with the tight binding method using empirical parameters. We calculate, for the first time, the forces acting on atoms of the icosahedral  $Si_{12}$  cluster using the first principle norm conserving pseudopotential method with the planewave basis set and the supercell calculation. We show the forces acting on the atoms at equilibrium positions of the silicon 12 icosahedral cluster which are derived from the symmetry conserving conditions.

### **1. INTRODUCTION**

Microclusters play an important role in nanostructure materials. Despite demanding of the materials for industry, detailed properties of microcluster remain unknown. A key of understanding the materials is an atomic level understanding. One of the interesting topics for them is physical properties of the clusters with the first principle calculations.

For the clusters the ratios of the surface area to the volume are quite high comparing with the surface on the bulks, although for bulks the ratio is zero. The atoms in the bulk state are energetically stabler than those on the surface. This is because the atoms on the surface of the clusters have fewer number of coordinated atoms and the electronic structures of the surface atoms are different from those in the bulks.

Among the clusters, the icosahedral clusters have an interesting nature in bonding, since the ratio is the highest among the icosahedrons, the face-centered cubic (fcc) or the hexagonal closed packed (hcp) clusters; the icosahedral structure has the most compact structure and is closest to sphere. It has been found that for simple metals such as Al and Li

the icosahedral 13 atom clusters are energetically stabler than the other two types of geometries.<sup>4) 6)</sup> This is because those elements have no directional bondings. Those atoms tend to take a closed packing structure like the icosahedral structures. Bauschlicher et al.<sup>4)</sup> have shown with configuration interaction calculation that thirteen-aluminum-cluster prefers to take the icosahedron as the lowest energy structure compared to hcp, fcc and planar structures of  $Al_{13}$ . Pacchioni et al.<sup>6)</sup> have found with the same method the icosahedral  $Li_{13}$  cluster to be stabler than either the fcc or hcp  $Li_{13}$  clusters.

Semiconductors, on the other hand, have a directional bonding in the bulk state. These elements seem to have the directional bonding even in the clusters. Thus, the electronic structures of the icosahedral semiconductor cluster are different from those of the simple metal clusters. There has been no experimental report on the existence of icosahedral silicon structures. Recently Bahel et al.<sup>5)</sup>, however, have predicted the existence of the  $Si_{12}$  icosahedral cluster by using a tight-binding method, which uses empirical parameters obtained from extended Hückel method. They predicted the cage diameter to be 0.5

nm with little Jahn-Teller effect.

In a previous paper<sup>18)</sup>, our *ab-initio* calculations have predicted the difference of the electronic structure between the icosahedral Si<sub>12</sub> cluster and the atom centered Si<sub>13</sub> cluster. We have calculated the total energies of the clusters with the symmetry conserving (I<sub>h</sub>) conditions. The total energy of the Si<sub>12</sub> cluster is lower than that of the Si<sub>13</sub> cluster by 0.64 eV / atom. The Si<sub>13</sub> cluster has the double minima in total energy curve. The charge densities of icosahedral faces on the Si<sub>12</sub> cluster are higher than those on the Si<sub>13</sub> cluster. The center atom of the Si<sub>13</sub> cluster has weakened the surface bonding through decreasing the densities of the two center bonds on the surface. We have discussed the difference of the bonding nature between the silicon and the lithium icosahedral. Figure 1 shows the total energy of the icosahedral Si<sub>12</sub> and Si<sub>13</sub> clusters as a function of cage radius with holding the symmetry conserving conditions. Figure 2 shows the shapes of the icosahedral Si<sub>12</sub> cluster. The icosahedral clusters belong to I<sub>h</sub> point group symmetry. Those clusters possess twenty equilateral triangles on the icosahedral faces. There has been, however, no study on the structures of the fully relaxed structure of the Si<sub>12</sub> and Si<sub>13</sub> clusters.

In the present paper we calculate, for the first time, the forces acting on atoms of the icosahedral Si<sub>12</sub> cluster using the first principle norm conserving pseudopotential method with the planewave basis set and the super calculation. We calculate the force acting on the atoms at equilibrium positions derived from the symmetry conserving conditions.

In Section 2, we give details of the computational method. The results and discussion are presented in Section 3. We conclude the paper in Section 4.

## 2. COMPUTATIONAL METHOD

Although we use the periodic cells to clarify the band structures in the crystals, we can use the cells for the cluster calculations, if the size of the cells is large enough and the interactions between the clusters are negligible. Andreoni et al.<sup>1)</sup> calculated the electronic structures of silicon thirteen-atom and

sixteen-atom clusters with a cut off energy of 11 Ry and with a fcc supercell size of 40 a.u. Kohn-Sham equation<sup>12)</sup> is expanded in planewaves at  $\Gamma$  points based on their works<sup>1)7)</sup>. In order to justify the present calculation, we have evaluated the effects of the cut-off energy and the supercell size in the total energies of the system.

We calculate the total energies with the Kohn-Sham total-energy functional form<sup>12)15)</sup>. In solving the Kohn-Sham equation, the system requires the number of 9985 planewaves for the cell size to diagonalize the matrix. We can use a Car-Parrinello<sup>3)</sup> iterative minimization method to reduce this memory size. This is an iterative minimization method that gives both the eigenvalues and the eigenvectors. The method solves a constrained molecular dynamics equation of motion given by

$$\mu \ddot{\psi}_i = -H\psi_i + \sum_j \Lambda_{ij} \psi_j, \quad (1)$$

for the electronic states, where  $\mu$  is a fictitious mass of wavefunction  $\psi_i$ ,  $H$  the Kohn-Sham Hamiltonian, and  $\Lambda_{ij}$  the Lagrange multiplier.

William and Soler<sup>13)14)</sup> have proposed a suggestion that the second order equation of motion can be replaced to a first order one given by

$$\mu \dot{\psi}_i = -H\psi_i + \sum_j \Lambda_{ij} \psi_j. \quad (2)$$

This is a steepest descent method. Convergence of the first order equation method has been found to be faster than that of the second order equation. We use the steepest descent method for electronic system and the first principle norm conserving pseudopotential for valence electrons proposed by Hamman et al.<sup>8)</sup> and Bachelet et al<sup>9)</sup>. We use the exchange-correlation-energy functional obtained by Perdew and Zunger<sup>10)</sup> from the electron gas data of Ceperley and Alder<sup>11)</sup> by Monte Carlo simulation. We use Hellman-Feynman theorem to obtain interatomic forces.

## 3. RESULTS AND DISCUSSIONS

We calculate the force acting on the atoms at equilibrium positions determined with the symmetry conserving condition. Table 1 shows the forces of

atoms at the first step. There are inversion symmetries of the forces between atom 1 and 12, atom 2 and 11, atom 3 and 10, atom 4 and 9, and atom 6 and 7. No symmetry exists between atom 5 and 8 since only z force component of atom 5 is different from those of the other atoms. In order to clarify the force directions of the atoms, we show the coordinates of the initial positions of the atoms, which have been the equilibrium positions with symmetry conserving relaxations. The magnitudes of the forces is a multiple of the coordinates of the atoms except for atom 5. All atoms expand to the outward from the equilibrium with symmetry conserving condition. The force vector between atom 5 and 8, however, is tilted by one degree from the inversion symmetry direction. This is attributed to the Jahn Teller effect of the icosahedral symmetry  $Si_{12}$  cluster, although Bahel et al.<sup>5)</sup> intend that the cluster has little the Jahn-Teller effect with the empirical tight binding method.

#### 4. CONCLUSIONS

Our ab-initio calculations have clarified the atomic forces acting on the equilibrium positions which are calculated with symmetry conserving relaxations. All atoms are found to move to the outward with inversion symmetry except for a single atom. The magnitude of the force of the atom is tilted from the inversion symmetry direction by one degree. This can be explained by the Jahn-Teller effect of the icosahedral silicon cluster.

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#### References

1) U. Röthlisberger, W. Andreoni, and P. Giannozzi, *J. Chem. Phys.* **96**, 1248 (1992); W. Andreoni, in *The Chemical Physics and Atomic and Molecular Clusters*, edited by G. Scoles (North-Holland, The

Netherlands, 1990), p159; W. Andreoni, Giorgio Pastore, Roberto Car, Michele Parrinello, and Paolo Giannozzi, in *Proceedings of the XIX International Conference on the Physics of Semiconductor*, Warsaw, 1988, Vol. 2., edited by W. Zawadski (1989), p1759; Pietro Ballone, Wanda Andreoni, Roberto Car, and Michele Parrinello, *Phys. Rev. Lett.*, **60**, 271 (1988); Wanda Andreoni, Giorgio Pastore, Roberto Car, Michele Parrinello, Paolo Giannozzi, NATO ASI Series B: edited by M. A. Abram and M. Jaros ( Plenum, N. Y., 1989 ) Vol. 189, p129  
 2) Haruki Eguchi, Kazuo Tsumuraya, Kenji Ninomiya, and Takashi Kuriki, Submitted to *Phys. Rev. B*.  
 3) R. Car and M. Parrinello, *Phys. Rev. Lett.*, **55**, 2471 (1985)  
 4) Charles W. Bauschlichlicher, Jr. and Lars G. M. Pettersson, *J. Chem. Phys.* **87**, 2198 (1987)  
 5) Atul Bahel and Mushti V. Ramakrishna, *Phys. Rev. B* **51**, 13849 (1995)  
 6) Gianfranco Pacchioni and Jaroslav Koutecky, *J. Chem. Phys.* **81**, 3588 (1984)  
 7) P. A. Serena, A. Baratoff, and J. M. Soler, *Phys. Rev. B* **48**, 2046 (1993)  
 8) D. R. Hamman, M. Schlüter, and C. Chiang, *Phys. Rev. Lett.* **43**, 1494 (1979)  
 9) G. B. Bachelet, D. R. Hamann, and M. Schlüter, *Phys. Rev. B* **26**, 4199 (1982)  
 10) J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981)  
 11) D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.*, **45**, 566 (1980)  
 12) W. Kohn and L. J. Sham, *Phys. Rev.* **140**, 1133A (1965)  
 13) A. Williams and J. Soler, *Bull. Am. Soc.* **32**, 562 (1987)  
 14) M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias and J. D. Joannopoulos, *Review of Modern Physics*, **64**, 1045 (1992)  
 15) P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, 864A (1964)

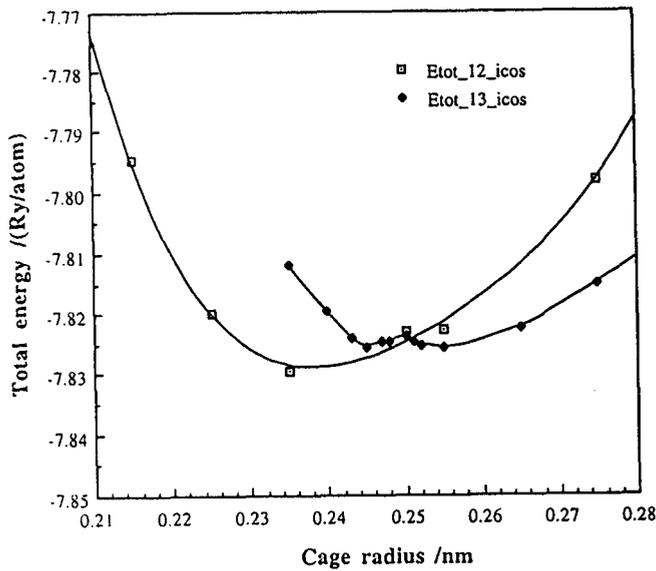


FIG. 1 The changes of the total energies of the  $Si_{12}$  cluster as a function of cage radius.

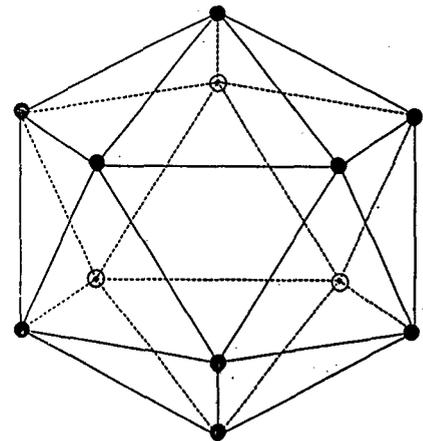


FIG. 2 Schematic drawings of the icosahedral  $Si_{12}$  cluster with  $I_h$  point group: The icosahedral  $Si_{12}$  cluster which has a 1-5-5-1 layered structure

atomic position	x coordinate	y coordinate	z coordinate	IF1 (absolute value)
1	0.000	2.136	1.338	2.520
2	1.320	0.000	2.148	2.521
3	1.858	1.290	0.000	2.262
4	1.858	-1.290	0.000	2.262
5	0.000	2.136	-1.192	1.886
6	-1.320	0.000	2.148	2.521
7	1.320	0.000	-2.148	2.521
8	0.000	-2.136	1.338	2.520
9	-1.858	1.290	0.000	2.262
10	-1.858	-1.290	0.000	2.262
11	-1.320	0.000	-2.148	2.521
12	0.000	-2.136	-1.338	2.520

TABLE 1. Force x,y and z components for the atomic positions

atomic position	x coordinate	y coordinate	z coordinate
1	0.000	3.778	2.335
2	2.335	0.000	3.778
3	3.778	2.335	0.000
4	3.778	-2.335	0.000
5	0.000	3.778	-2.335
6	-2.335	0.000	3.778
7	2.335	0.000	-3.778
8	0.000	-3.778	2.335
9	-3.778	2.335	0.000
10	-3.778	-2.335	0.000
11	-2.335	0.000	-3.778
12	0.000	-3.778	-2.335

TABLE 2 x, y and z coordinates for the atomic positions