Guest Atom Displacements in Silicon Cluster $\text{Na}_2@\text{Si}_{50}\text{H}_{44}$

Hiroyuki Takenaka* and Kazuo Tsumuraya

Department of Mechanical Science and System Engineering, School of Science and Engineering, Meiji University,
 Kawasaki 214-8571, Japan

We present the displacements of the guest sodium atoms in double caged $\text{Na}_2@\text{Si}_{50}\text{H}_{44}$ cluster. The cluster consists of a piece of clathrate II consisting of two adjacent Si_{28} cages filled with guest sodium atoms, being hydrogenated in order to terminate the dangling bonds. Although in a single $\text{Si}_{28}\text{H}_{28}$ cage the endohedral sodium atom locates at the center, the sodium atoms in each of the double cage cluster displace about 0.06 nm away from each center of the cages to form a dimer between the endohedral sodium atoms. The displacements are attributed to the formation of covalent bond between the endohedral sodium atoms and the ionic bonding between the sodium atoms and the cage silicon atoms.

(Received October 17, 2005; Accepted November 10, 2005; Published January 15, 2006)

Keywords: silicon clathrate, silicon cluster, endohedral atom, density functional calculation, guest atom displacement, covalent bond, ionic bond

1. Introduction

Group 14 clathrates have been synthesized when the cages contain specific endohedral atoms of which electronegative differences are large from host atoms. The endohedral atoms are alkali metallic, alkaline earth metallic, Te or I atoms.¹⁻⁴⁾ The clathrates are expanded phases of diamond type silicon crystal. So the band gaps are greater than that of the latter. When the clathrates contain alkali metallic or alkaline earth metallic atoms, they become metallic because of the increased valence electron density released from the endohedral atoms. Then the endohedral atoms give rise to rattling motions in the encapsulated cages. So the clathrates have low thermal conductivity. The clathrates may be used for thermo-electronic devices when they give large thermo-electric power and high electric conductivity.

Several types of structures of the silicon clathrates have been found. They consist of mainly Si_{20} , Si_{24} , Si_{28} , and distorted Si_{20} cages. The clathrate I consists of Si_{20} cages with dodecahedra (denoted 5^{12} ; 12 pentagons) and Si_{24} cages with tetrakaidecahedra ($5^{12}6^2$; 12 pentagons and two hexagons), the II consists of the Si_{20} cages and Si_{28} cages with hexakaidecahedra ($5^{12}6^4$) and the III consists of the Si_{20} cages and distorted Si_{20} dodecahedra. Among these, the clathrate II is composed of the largest Si_{28} cages and the smallest Si_{20} cages. So, the clathrate II may have the lowest thermal conductivity caused by the rattling motion in the Si_{28} cages. The symmetry is $Fd\bar{3}m$ space group with origin at center $\bar{3}m$. The clathrate contains 34 Si atoms per rhombohedral unit cell consisting of two Si_{28} cages and four Si_{20} cages. The structure is composed of 136 Si atoms in simple cubic lattice containing eight Si_{28} cages and 16 Si_{20} cages. The Si_{28} cages are connected tetrahedrally just like carbon atoms in the diamond crystal and the adjacent Si_{28} cages joint each other at the common hexagonal rings. The Si_{20} cages fill the remained room connecting each other. Figure 1 shows this situation.

Cros *et al.*⁵⁾ have reported that the lattice constants of the $\text{Na}_x@\text{Si}_{136}$ clathrate II are constant up to around $x = 10$ and

Fig. 1 (a) The coordination of connected Si_{20} cages around Si_{28} cages in clathrate II. The Si_{28} cages are white. Removing the shaded Si_{20} cages gives the tetrahedrally connected Si_{28} cages shown in (b). The central shaded Si_{28} cage is connected on the four hexagonal rings forming giant tetrahedral bonds.

increase with increasing the sodium content x . This means that the sodium atoms are encapsulated in the larger Si_{28} cages preferentially. The increase of the lattice constants is due to the encapsulation of the endohedral sodium atoms into the smaller Si_{20} cages. This indicates that the Si_{28} cage has sufficient room to accommodate the endohedral sodium atom. Demkov *et al.*⁶⁾ have found from their density functional calculations on clathrate $\text{Na}_4@\text{Si}_{136}$ that the guest sodium atoms move away from the center of the Si_{28} cages by 0.017 nm and the site symmetry was reduced from T_d to C_{3v} . They discussed the displacements were due to a Jahn–Teller distortion. Brunet *et al.*⁷⁾ have measured the displacements using extended X-ray absorption fine structure (EXAFS). They observed the displacements by 0.09 ± 0.02 nm for the

*Graduate Student, Meiji University

full occupation of the endohedral sodium atoms. They discussed the displacements to be attributed to Peierls or Jahn–Teller effect. Libotte *et al.*⁸⁾ have calculated the displacements of the endohedral sodium atoms. They found the displacements to be 0.0456 nm from the density functional calculation and 0.091 nm from a tight-binding calculation. Tournus *et al.*⁹⁾ have reported the guest displacements of the endohedral sodium atoms from the EXAFS measurements. The displacements were 0.1 nm in the Si_{28} cages of the clathrate $\text{Na}_2@\text{Si}_{34}$ and 0.2 nm in the clathrate $\text{Na}_6@\text{Si}_{34}$. They also calculated the displacements as 0.065 nm from supercell calculation of the two adjacent Si_{28} cages with $\text{Na}_2@\text{Si}_{50}\text{H}_{44}$ cluster using the density functional calculation.

No origin of the guest atom displacements however has been presented in the earlier papers. The present paper evaluates the guest atom displacements in the finite double caged Si_{28} cluster which is extracted from the clathrate II using the density functional calculation. We present the origin of the guest displacements in the cluster.

2. Computational details

We calculate the electronic states of the hydrogenated clusters using molecular orbitals based on a linear combination of atomic orbitals. We use a frozen core approximation for constructions of the molecular orbitals: the atomic orbitals are assigned $3s^1$ for Na atoms, $3s^2 3p^2$ for Si atoms, and $1s^1$ for H atoms. We adopt two Slater-type functions for each orbital and the generalized gradient functional of Perdew, Burke, and Ernzerhof¹⁰⁾ for the exchange correlation functionals. All atoms are relaxed for the maximum magnitude of the forces to decrease less than 4.3598×10^{-20} J/nm (10^{-3} H/Å).

The initial coordinates of the $\text{Na}_2@\text{Si}_{50}$ cluster are obtained from the coordinates of the clathrate II in simple cubic lattice, in which there are two adjacent Si_{28} cages containing two endohedral Na atoms. We terminate the dangling bonds of the three coordinated Si atoms on the cages with hydrogen atoms, which results in similar bonding states as in the crystalline state with the cluster. This termination allows the size of the cluster to shrink and allows the interatomic Si–Si distances to decrease to those in the clathrate. In this work, we use the ADF package¹¹⁾ to calculate the electronic states.

3. Results

First we calculate a stable position of the sodium atom in the single caged Si_{28} cluster hydrogen terminated, *i.e.* $\text{Na}@\text{Si}_{28}\text{H}_{28}$. When we have relaxed all the atom positions of the cluster, the endohedral sodium atom has remained at the center of the cage. Next, we calculate the cohesive energies of the cluster by displacing the sodium atom from the center of the cage. The directions are to the center of a hexagonal ring, to the center of the pentagonal ring, and to a silicon atom between them by fixing all the atom positions. The energies have been minimum at the center of the Si_{28} cage for the three cases.

Next, we calculate the stable positions of the sodium atoms

Fig. 2 The displacements of endohedral Na atoms in the $\text{Na}_2@\text{Si}_{50}\text{H}_{44}$ cluster. Each endohedral Na atom in the Si_{28} cages displaces by 0.0632 nm from the center of the cages to other side of Na atom, *i.e.* toward the center of the joint hexagonal ring.

Fig. 3 The calculated total density of states of $\text{Na}_2@\text{Si}_{50}\text{H}_{44}$ cluster. We show convolution of energy levels broadened using gaussian functions with $\sigma = 0.1090 \times 10^{-19}$ J (0.0025H). The atomic orbital $3s^1$ of an isolated sodium atom splits into the molecular orbitals with the bonding HOMO state, the antibonding unoccupied LUMO state just above the HOMO, and the unoccupied antibonding states far above the LUMO state.

in the relaxed $\text{Na}_2@\text{Si}_{50}\text{H}_{44}$ cluster, which is the double caged Si_{28} cluster. During the relaxation, the positions of the endohedral sodium atoms have moved by 0.0632 nm from the relaxed central positions in the cages toward the center of the hexagonal ring as shown in Fig. 2. The guest atoms have displaced symmetrically with respect to the ring surface. The displacements are comparable with those 0.065 nm by Tournus *et al.*⁹⁾

We have plotted the density of states in Fig. 3 in which the eigenvalues of the molecular orbitals are broadened with gaussian functions. The eigenvalue -4.4121×10^{-19} J (-0.1012H) of the $3s$ atomic orbital of the isolated Na atom splits into the molecular eigenvalues. The bonding HOMO state is -6.2380×10^{-19} J (-0.1431H , A1.g16) and the antibonding states are -6.1037×10^{-19} J (-0.1399H ,

Fig. 4 The projected electron charge densities drawn with the eigenfunction of the HOMO level. (a) the density profile on the plane of joint hexagonal Si ring between the two Si_{28} cages of the cluster. (b) the density profile on the plane which intercepts both the endohedral two sodium atoms and one of silicon atom of the joint hexagonal ring. The lowest contour line corresponds to 10^{-10} . Each contour corresponds to 12 logarithmic levels between the lowest and unity. The blue lines are higher densities than the green ones.

LUMO, A2.u15), $-0.2757 \times 10^{-19} \text{ J}$ (-0.0063H , A1.g23), $0.0467 \times 10^{-19} \text{ J}$ (0.0011H , A2.u24). There is a large forbidden gap just below the HOMO state. If the cluster contains no endohedral atom, the cluster is an insulator. The HOMO–LUMO gap is only $0.1343 \times 10^{-19} \text{ J}$. Thus the cluster is easy to be removed the electrons leading to the ionized $+2$ state. The position of the HOMO state in the DOS is almost the same as in the clathrate II indicating that the overall electronic structure is similar to that of the clathrate II.¹²⁾

We have shown that bonding state of the sodium atoms corresponded to HOMO in Fig. 3. So, we calculate the charge density profiles using the HOMO level. The charge density on the plane of the joint hexagonal silicon ring is shown in Fig. 4(a). The each double circle on the outermost hexagon corresponds to the intersections of the H–H bonds, where one of the hydrogen on the Si_{28} cage and the other is on the other

Fig. 5 The difference charge density profile between the self consistent charge density and the overlapped isolated atom densities. The intersection plane is the same as in Fig. 4(b).

Si_{28} cage. The inner six rectangles correspond to the covalent bonds between the hexagonal silicon ring. The silicon atoms locate between the rectangular regions. There is a finite charge density region which is circle shaped at inner of the hexagon. Figure 4(b) shows the charge density of the HOMO state which intercepts the two endohedral sodium atoms and one of the silicon atom in the hexagonal ring. There is also a finite HOMO charge density region between the two endohedral sodium atoms, indicating a covalent bonding formed between the $3s^1$ electrons of each Na atom.

We have shown the guest atom displacements in Fig. 2. The sodium atoms in each of the double cage cluster have displaced 0.06 nm away from each center of the cages to form dimer between the sodium atoms. The projected charge densities of the HOMO level which corresponds to $3s$ state of the sodium atoms showing the covalent bonding between the endohedral atoms. The displacements may be also caused by the interaction between the sodium atoms and the frame silicon atoms. To check this we calculate the difference charge density profile between the self-consistent charge density and the overlapped isolated atom densities. The density is shown in Fig. 5 with a logarithmic scale. Thus the blank region corresponds to negative charge. The regions around the endohedral sodium atoms are negative which indicates that the valence electrons have transferred from the sodium atoms to the frame silicon atoms.

To evaluate the charge transfer quantitatively, we evaluate the charge transfers of the constituent atoms. As is well known, the Mulliken's analysis depends on the basis functions used. For instance, Guerra *et al.*,¹³⁾ ADF developers, have shown that the charge transfer of carbon atom in methane is negative for double Slater-type zeta functions

although it is positive for the triple zeta with two sets of polarized functions. They showed that Voronoi or Hirshfeld analyses gave reasonable, comparable values with Bader charges. The charge transfers of the endohedral sodium atoms have been 0.335e with Voronoi analysis and 0.220e with Hirshfeld analysis. The received charges of the silicon atoms of the hexagonal ring have been $-0.075e$ for Voronoi analysis and $-0.033e$ for Hirshfeld analysis. The rest of the silicon Si atoms transfers electron as large as 0.023e for Voronoi analysis and 0.058e for Hirshfeld analysis. The electrostatic interaction exists between the sodium atoms and the frame silicon atoms, indicating the ionic bonding between them.

4. Discussion

The endohedral Na atoms in the $\text{Na}_2@Si_{50}H_{44}$ cluster have displaced from the center of the cages towards the center of the joint hexagonal ring as shown Fig. 2. We have plotted the electron charge density corresponding to the Na bonding state in this cluster. The bond charge density with respect to the Na–Na atoms has appeared. Thus, this corresponds to the covalent bond between the Na atoms. We have presented the charge transfer using Voronoi and Hirshfeld population analyses. The charge of 0.2–0.3e of the valence electron of the endohedral sodium atoms has transferred to the frame silicon atoms. The rest of the electrons contribute to the covalent band between the endohedral atoms. Although the present analysis uses the cluster model extracted from the clathrate II, both the interactions Na–Na binding and the host-guest attraction through the charge transfer may act in the clathrate II.

5. Conclusions

In this paper, we have investigated the electronic states of $\text{Na}_2@Si_{50}H_{44}$ cluster to study the origin of the displacements

of the endohedral atoms. Both the endohedral sodium atoms move by 0.0632 nm close to each other from the center of the Si_{28} cages. The charge density profile consists of the 3s molecular orbital of sodium atom has indicated the covalent bonding charge density. Both the sodium atoms have transferred electrons by 0.2–0.3e to the frame silicon atoms. The displacements in this cluster are attributed to the formation of dimer between the endohedral Na atoms and the ionic bonds between the endohedral sodium atoms and the frame atoms.

REFERENCES

- 1) C. Cros: Ph. D. Thesis, No. 205, University Bordeaux (1970).
- 2) C. Cros, E. Reny and M. Pouchard: *Mol. Cryst. Liq. Cryst.* **310** (1998) 199–204.
- 3) S. Bobev and S. C. Sevov: *J. Solid State Chem.* **153** (2000) 92–105.
- 4) K. A. Kovnir and A. V. Shevelkov: *Russian Chem. Rev.* **73** (2004) 923–938.
- 5) E. Reny, P. Gravereau, C. Cros and M. Pouchard: *J. Mater. Chem.* **8** (1998) 2839–2844.
- 6) A. A. Demkov, O. F. Sankey, K. E. Schmidt, G. B. Adama and M. O’Keeffe: *Phys. Rev. B* **50** (1994) 17001–17008.
- 7) F. Brunet, P. Melinon, A. S. Miguel, P. Keghelian, A. Perez, A. M. Flank, E. Reny, C. Cros and M. Pouchard: *Phys. Rev. B* **61** (2000) 16550–16560.
- 8) H. Libotte, J. P. Gaspard, A. Sanmiguel and P. Melinon: *Europhys. Lett.* **64** (2003) 757–762.
- 9) F. Tournus, B. Masenelli, P. Melinon, D. Connettable, X. Blase, A. M. Flank, P. Lagarde, C. Cros and M. Pouchard: *Phys. Rev. B* **69** (2004) 035208–035213.
- 10) J. P. Perdew, K. Burke and M. Ernzerhof: *Phys. Rev. Lett.* **77** (1996) 3865–3868.
- 11) G. te Velde, F. M. Bickelhaupt, S. J. A. van Gisbergen, C. F. Guerra, E. J. Baerends, J. G. Snijders and T. Ziegler: *J. Comput. Chem.* **22** (2001) 931–967.
- 12) J. C. Conesa, C. Tablero and P. Wahnou: *J. Chem. Phys.* **120** (2004) 6142–6151.
- 13) C. F. Guerra, J. Handgraaf, E. J. Baerends and F. M. Nickelhaupt: *J. Comput. Chem.* **25** (2003) 189–210.