

## Electronic and Structural Properties of Si<sub>20</sub> and C<sub>20</sub> Based Solids

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Cluster-based solids often show not only geometrical but also electronic hierarchy. Dodecahedral clusters Si<sub>20</sub> and C<sub>20</sub> proposed previously based on the *sp*<sup>3</sup> model potential are found to form energetically stable body-centered-cubic type lattice with additional atoms: (Si<sub>3</sub>Si<sub>20</sub>)<sub>2</sub> = Si<sub>46</sub> and C<sub>46</sub>. Although all the atoms in this lattice are tetrahedrally coordinated, their electronic structure is considerably different from that of the diamond-lattice phases. In the case of Si<sub>46</sub>, for example, the fundamental gap is found to be wider than that of diamond Si. Due to these interesting electronic features and to a wide variety of potential modifications, they are important future materials to be studied.

### 1. INTRODUCTION

Based on the tetrahedral model potential for *sp*<sup>3</sup> atoms, we investigated the geometry of the group-IV element clusters more than a decade ago [1]. Since the pentagon angle (108°) is very close to the ideal angle of *sp*<sup>3</sup> hybridized bonds, not only the six-membered-ring but also the five-membered-ring based structures were obtained as optimized cluster geometries. Among them, the 20-atom dodecahedral-cage clusters corresponding to Si<sub>20</sub>, C<sub>20</sub>, and Ge<sub>20</sub> (Fig. 1) is found to be one of energetically highly preferable geometries. Moreover, its distribution of interatomic distances shows very good correspondence to that in amorphous bulk materials observed experimentally. Also the electronic structure in a lower valence band energy region of five-membered clusters (Si<sub>5</sub> and Si<sub>20</sub>) studied in the density-functional formalism shows good accord with the characteristic features of amorphous material [2]. Based on these correspondences,

five-membered ring and dodecahedral cage units are expected to be present in amorphous phase of group-IV elements.

Recently, this 20-atom cage cluster is being studied rather intensively especially for C<sub>20</sub>, since C<sub>20</sub> was rediscovered as the smallest possible fullerene-cage cluster having no hexagons. More interestingly, new superconducting Si-based materials discovered recently [3] has been pointed out to be essentially the body-centered cubic (bcc) lattice of the Si<sub>20</sub> dodecahedra [4].

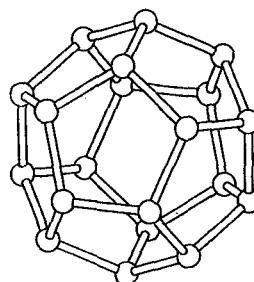


Figure 1. Si<sub>20</sub>, C<sub>20</sub>, and Ge<sub>20</sub>.

This new class of superconducting Si-network materials contains alkali (Na or K) and alkaline-earth (Ba) atoms incorporated inside the cage-type network, and the ideal stoichiometry for the Na and Ba codoped case is  $\text{Na}_2\text{Ba}_6\text{Si}_{46}$ . Although there are two kinds of polyhedral units corresponding to  $\text{Si}_{20}$  and  $\text{Si}_{24}$  cage structures, only  $\text{Si}_{20}$  units do not share their atoms with others and are considered to be a basic building unit of this lattice. As mentioned above, these  $\text{Si}_{20}$  dodecahedra form the bcc-type lattice, with  $90^\circ$  rotation of the cube-center-site  $\text{Si}_{20}$ , doubling the unit-cell size to give the simple-cubic lattice. This rotational ordering makes half the distorted tetrahedral interstitial sites (three sites per  $\text{Si}_{20}$ ) surrounded by four dangling bonds of  $\text{Si}_{20}$  cages. These sites are then occupied by additional Si atoms:  $(\text{Si}_3 \text{Si}_{20})_2 = \text{Si}_{46}$  (Fig. 2). Due to the Si-Si bonds between  $\text{Si}_{20}$  cages (8 bonds per  $\text{Si}_{20}$ ) and to those between the  $\text{Si}_{20}$  cage and the additional Si atoms (12 bonds per  $\text{Si}_{20}$ ), all the Si atoms are tetrahedrally coordinated. In addition, Ba and Na atoms occupy remaining interstitial sites and  $\text{Si}_{20}$ -cage center sites, respectively. Then, the stoichiometry is  $(\text{Ba}_3\text{Si}_3 \text{Na}@\text{Si}_{20})_2 = \text{Na}_2\text{Ba}_6\text{Si}_{46}$ . (Here, A@B means the endohedral complex, i.e. cage B with A inside).

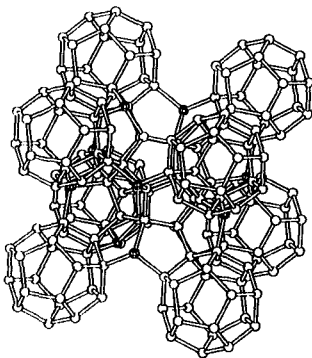


Figure 2.  $(\text{Si}_3\text{Si}_{20})_2 = \text{Si}_{46}$  lattice.

## 2. GEOMETRICAL STRUCTURE

Since all the Si atoms in  $\text{Na}_2\text{Ba}_6\text{Si}_{46}$  are tetrahedrally coordinated, the  $\text{Si}_{46}$  lattice itself may be stable without metal atoms. The structural optimization within the framework of the density functional theory has been performed and actually  $\text{Si}_{46}$  is found to correspond to the energy-minimum geometry. The cohesive energy per atom is found to be only slightly smaller (0.09 eV per atom) than the diamond-lattice Si. In the  $\text{Si}_{46}$  lattice, there are three kinds of Si atoms, 8 atoms having only intra and intercage bonds, remaining 12 atoms on the cage having bonds with interstitial-site atoms, and 3 interstitial-site atoms (per  $\text{Si}_{20}$ ). Accordingly, there are four kinds of Si-Si bonds. At the optimized lattice geometry, the bond lengths obtained are 2.356 Å (48 bonds), 2.392 Å (12 bonds), 2.338 Å (8 bonds), and 2.383 Å (24 bonds), giving 2.366 Å as an average, which is only 0.6 % longer than the diamond lattice. This smallness of the bond-length deviations ensures the energetical stability of this lattice.

As for bond-angle deviations, the associated energy cost should be much smaller due to the softness of the bond-bending distortion modes. Nevertheless, most bond angles are found to be in the range of  $105^\circ - 111^\circ$  i.e., around the ideal angle of  $109.5^\circ$ , with one exceptional angle of  $124.5^\circ$  on the hexagon.

The similar 46-atom lattice can be considered for C atoms. Actually, the  $\text{C}_{46}$  lattice is found to be stable from the density-functional calculation again with very small cohesive-energy loss (0.16 eV per atom) from diamond [5]. In the case of this  $\text{C}_{20}$  based lattice, its hardness is of high interest due to its  $sp^3$  hybridized character of C atoms as in the case of diamond, the hardest material known at present. The  $\text{C}_{46}$  lattice is actually found to be very hard. The bulk modulus of this

lattice calculated is as much as 85 % of that of diamond. This ratio is very close to the density ratio of two materials (87%).

The ring statistics for these  $\text{Si}_{46}$  and  $\text{C}_{46}$  lattices is completely different from the diamond lattice, which is a perfect six-fold ring system. In  $\text{Si}_{46}$  and  $\text{C}_{46}$  lattices, as much as 87 % rings are five-fold and only 13 % are six-fold rings. This pentagonal network character gives strong effect on the electronic structure, which is discussed in the next section.

### 3. ELECTRONIC STRUCTURE

In Fig. 3, the electronic structure of  $\text{Si}_{46}$  is shown [4]. It can be seen that the  $\text{Si}_{46}$  electronic structure possesses several features different from that of the diamond Si. First, there appears a new gap inside the valence band. Secondly, a whole valence-band width (about 11 eV) is considerably narrower than that of the diamond Si (12 eV). Thirdly, the fundamental gap between the valence-band top and the conduction-band bottom becomes wider by as much as 0.7 eV. These characteristic features are all considered to be the consequences of the difference in ring statistics pointed out in the previous section. Interestingly, the valence-band density of states has been found to show good correspondence with the  $\text{Si}_{20}$ -cluster energy-level distribution. This again confirms that the  $\text{Si}_{46}$  lattice is essentially solid  $\text{Si}_{20}$ , and the presence of the "hierarchy" in the electronic structure.

In the case of  $\text{C}_{46}$ , the electronic structure is again found to be different from that of diamond [5]. Interestingly, it is also different from that of  $\text{Si}_{46}$ . For example, a new gap does not open within the valence band of  $\text{C}_{46}$ . Such difference may be due to the different hybridization strength of  $s$  and  $p$  states in C

and Si atoms.

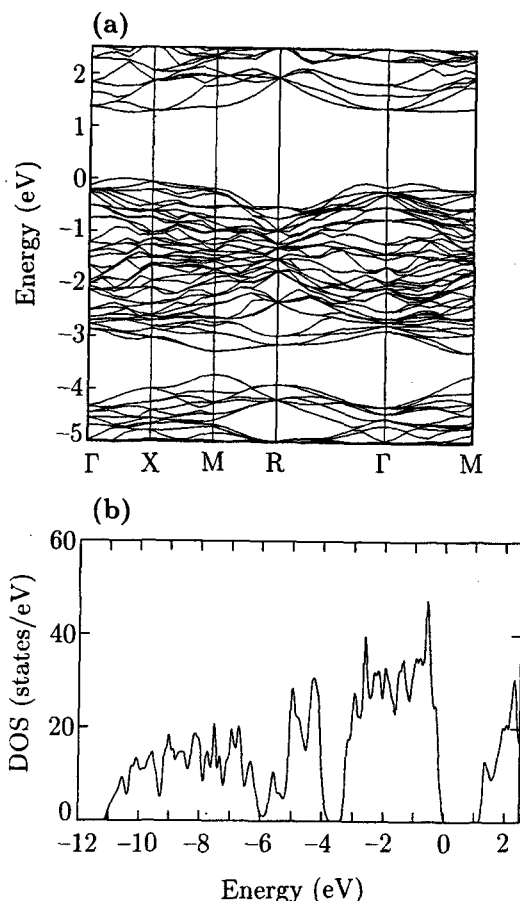


Figure 3. (a) Electronic band structure and (b) density of states of  $\text{Si}_{46}$  [4].

### 4. CONCLUDING REMARKS

Electronic properties of  $\text{Si}_{20}$  and  $\text{C}_{20}$  based solids,  $\text{Si}_{46}$  and  $\text{C}_{46}$ , are found to be considerably different from those of diamond-lattice phases. Although only metal-doped  $\text{Si}_{46}$  materials have been produced up to now, their energetical stabilities predicted theoretically suggest the possibilities of producing these dodecahedral-cage materials in a variety of ways. Metal ions realizing the  $\text{Si}_{46}$  lattice seem to play only a role of "spacers" to make competing diamond-lattice phase less preferable. Hence, rare-

gas atoms (*e.g.* Ar, Xe for Si<sub>46</sub> and Ne for C<sub>46</sub>) or some other small molecules may also act as spacers. They might be technologically very important materials with wider possibility of modification and doping than the ordinary (diamond-lattice) materials since cluster-based solids generally possess wide interstitial areas, and in this case the intracluster areas.

## REFERENCES

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