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ELECTRONIC STRUCTURE OF CLUSTER-ASSEMBLED $Al_{12}C$ (Si) SOLID*

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The electronic structures of the cluster-assembled solid $Al_{12}C$ (Si) are studied by the *ab initio* method. We find that $Al_{12}C$ (Si) can solidify into a van der Waals solid. The electronic band structures show very weak dispersion. The main features in the electronic structure of cluster are retained in the solid, and an energy gap up to about 1.5 eV is observed for $Al_{12}C$ and $Al_{12}Si$ solids.

Keywords: electronic structure, cluster-assembled solid
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Recently there has been growing interest in clusters and cluster-assembled solids. This kind of research can add a new dimension for material scientists in synthesizing novel materials.[1] It is now possible not only to make specific clusters in the gas phase, but also to assemble them into solids not found in nature. Since there are quite big differences between the properties of clusters and those of atoms, we may presume with good reason that the cluster-assembled materials have unusual properties much different from those in atomic solid phases. The well-known example is C_{60} cluster and C_{60} solid.

Generally, the clusters should have very high stability to obtain the cluster-assembled materials, otherwise the structure of clusters would coalesce when bringing them together.[2] In most cases, the interaction between clusters should be very weak compared with the interaction within clusters, so the main features of the electronic structures of the clusters can retain in the cluster-assembled solid. For instance, the atoms in C_{60} are covalently bonded,[3] while the interaction between the molecules is van der Waals-like. A few years ago, based on first principle calculations,[4,5] the icosahedral $Al_{12}C$ and $Al_{12}Si$ clusters are found to be very stable with an energy gap up to about 2 eV.[6] It was suggested that they could be good candidates for the cluster-assembled solid. Although there were some studies which confirmed the high stability of those icosahedral clusters, a few trials, which were based on the hypothesis of fcc-like crystal structure, failed to predict a stable $Al_{12}C$ (Si) solid.[7,8] In fact, in fcc-like $Al_{12}Si$ solid[8] the Al-Al distance between clusters was found to be very short, its binding energy being even larger than that in Al bulk. Similarly, in fcc-like $Al_{12}C$ solid,[7] it was found that the total energy increased monotonically with the decrease of the lattice constant, and there was no local minimum, which is necessary for the formation of a meta-stable phase.

Recently, based on *ab initio* calculations, it has been shown why the fcc-like structure is not stable for those kinds of cluster-assembled solids and it has also been proved that $Al_{12}C$ (Si) solid could be stable with the so-called NaCl-like structure,[9] if we consider here Na and Cl as two cubic boxes, each containing a 13- atom icosahedron in alternated orientation of 90 degrees. The relative position of the two 13-atom clusters in the $Al_{12}C$(Si) solid is shown in Fig.1.

In this paper, we present the electronic structures of the cluster-assembled $Al_{12}C$ and $Al_{12}Si$ solids. By calculating the charge density for different lattice constant, we show how the interaction between clusters can be changed from van der Waals-like to metallic-like, which would make the $Al_{12}C$ (Si) solid with NaCl-like structure unstable. The band structures of $Al_{12}C$ and $Al_{12}Si$ solids are found to be weakly dispersive. The energy gap for both solids is observed to be ~1.5 eV.

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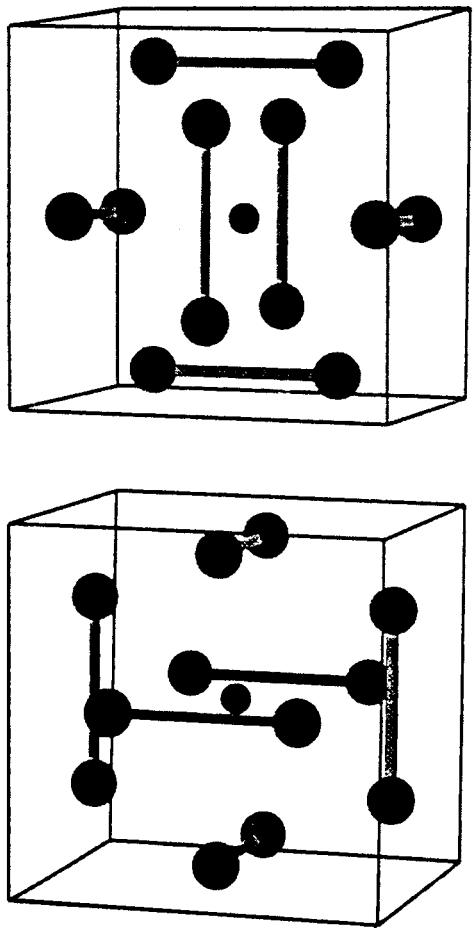

Fig.1. The unit cell of $Al_{12}C$ (Si) solid, the stable structure of a Lennard-Jones cluster dimer with two icosahedral clusters rotated 90 degrees relative to the c_2 axis. The two boxes are drawn for the eyes. Big balls for Al and small balls for C (Si).

The calculations are based upon the density functional theory[10] with the local density approximation,[11] and the Kohn-Sham orbital is expanded into plane waves with energy cutoff of 35 Ry for $Al_{12}C$ solid and 14 Ry for $Al_{12}Si$ solid to express the electronic density. We only treat the valence electrons explicitly and use Bachlet-Hamann-Schluter type pseudopotential[12] to describe the interaction between the valence electrons and ionic cores. The conventional unit cell is very complicated, containing eight $Al_{12}C$ (Si) clusters, i.e., 104 atoms per unit cell.[13] However, the conventional unit cell forms a fcc-structure, and there are two $Al_{12}C$ (Si) clusters in a primitive unit cell, as shown in Fig.1. We use only two special K-points for the self-consistent calculation of charge density. With the converged potentials, eigenvalues at other K-points can be obtained accordingly.

The equilibrium lattice constants for $Al_{12}C$ (Si) solid have been studied by the density functional theory.[9] We have replotted the cohesive energy vs lattice constant curves in Fig.2. The cohesive energies for the $Al_{12}C$ and $Al_{12}Si$ solids, defined as the total energy minus the sum of the total energies of isolated clusters, are very small. Contrary to what was found in the fcc-like structure of $Al_{12}C$,[7] we find an energy minimum at lattice constant of 30.8 and 32.5 a.u. for $Al_{12}C$ and $Al_{12}Si$ solids, respectively. For both solids, the cohesive energies are very small, they are only ~1eV, which is much smaller than the binding energy of 3.39 eV[14] in the bulk, but close to the cohesive energy in C_{60} solid.[15] These results suggest $Al_{12}C$ (Si) clusters be condensed as van der Waals solids, as discussed in our previous paper.[6,9]

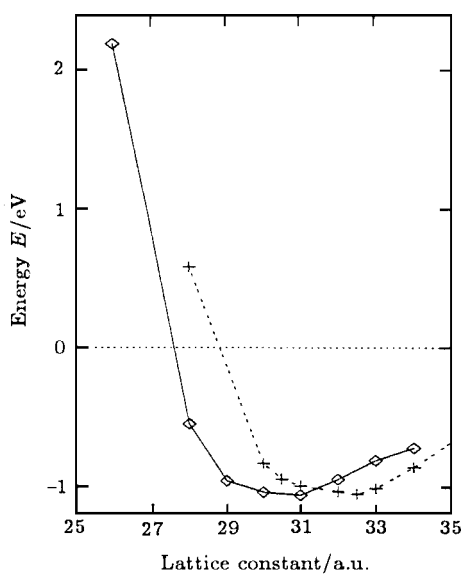

Fig.2. Cohesive energies for $Al_{12}C$ solid (solid line) and $Al_{12}Si$ solid as functions of lattice constant.

In Fig.3, we show the charge density along the line connecting the two neighboring silicon atoms in $Al_{12}Si$ solid with different lattice constants, corresponding to 32.5, 28.0 and 27.0 a.u., respectively. The highest peak close to the core of the Si atom is associated with the pseudo-charge of atomic silicon, the small second peak at about $R \sim 4.1$ a.u. is the charge density at the middle point of the Al-Al bond in the cluster. The overlap of charge density between two clusters is very small. This validates the formation of a van der Waals solid. Comparing the results at lattice constant of 32.5 a.u. with that at the lattice constant of 28.0 a.u., some similar features can be observed clearly at the equilibrium lattice constant of 28.0 a.u., and there is more charge piled up in the

interior region between two clusters. Since the electronic density is not redistributed for lattice constant of 28.0 a.u., the large overlap of charge density leads to more repulsive interaction. We observed a positive energy at the lattice constant of 28.0 a.u., as shown in Fig.2. Figure 3 shows also the charge density at the lattice constant of 27.0 a.u. We can see that, besides more charge in the interior region, the peak at $R \sim 4.1$ a.u., which corresponds to the Al—Al bond charge in the clusters, disappears at the lattice constant of 27.0 a.u. The main features of electronic structures of $Al_{12}C$ (Si) clusters are changed, and the redistribution of charge density happens. This suggests that if the cluster-assembled solid is compressed significantly, the basic features of the electronic structures can be changed, the pressure-induced phase transition from the meta-stable phase of the cluster-assembled solid to other more stable phases could occur. Consequently the structure of clusters could be destroyed.

In Figs.4(a) and 4(b), we show the contour plots of the charge density at different lattice constants. We can see clearly how the charge density redistributed in the contouns by changing the lattice constant. The depletion of charge density between two Al atoms can also be observed in Fig.4(b). The charge density in the cluster is removed away to form metallic bonds between clusters, and the van der Waals interaction does not exist any more. After the formation of the metallic bonds between clusters, as observed in the previous calculation,[7,8] the cluster-assembled solids $Al_{12}Si$ and $Al_{12}C$ could become unstable and the other phases of compounds might be formed.

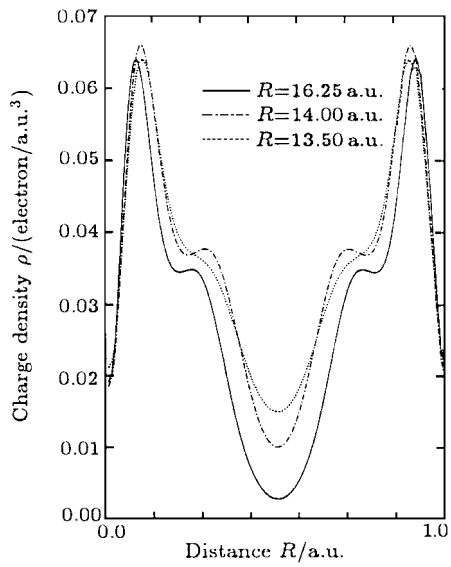

Fig.3. The charge density along a line between two nearest silicon atoms in $Al_{12}Si$ solid, where R is equal to half of the lattice constant.

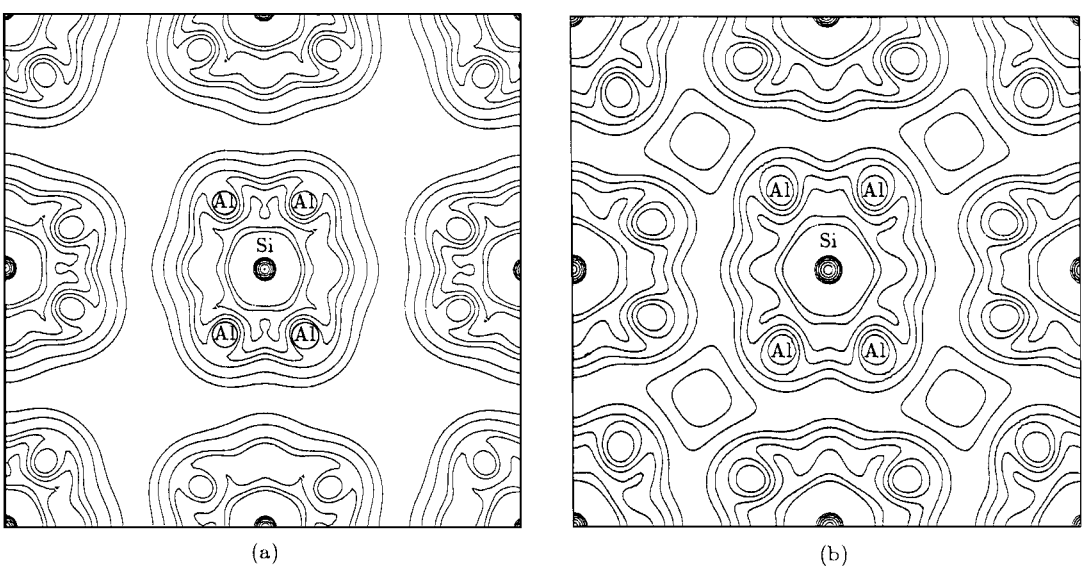

Fig.4. The contour plot of the charge density of $Al_{12}Si$. (a) for lattice constant 32.5 a.u., (b) for lattice constant 28.0 a.u.

Figure 5 shows the calculated band structures of $Al_{12}Si$ and $Al_{12}C$ solids with equilibrium lattice constants. For comparison, the degeneracy of the energy levels in $Al_{12}X$ (X=Si, C) clusters are reported. The isolated $Al_{12}X$ cluster has an icosahedral symmetry and its energy levels have up to fivefold degeneracy. The highest occupied orbit of $Al_{12}C$ (Si) clusters is fourfold and is completely occupied by eight electrons.[6] After forming a solid, the basic features of an isolated $Al_{12}C$ (Si) cluster still retain in the solid. The sequence of levels is not alternated. The energy gap between the highest occupied orbit and the lowest unoccupied orbit is about 2.0 eV in $Al_{12}X$ (X=C, Si) clusters, while this gap retains in the solid up to 1.5 eV. The top of the valence band and the bottom of the conduction band are at the Γ-point, this indicates that $Al_{12}C$ (Si) can be a direct-gap semiconductor. Being different from what is observed in C_{60} solid,[15] the transition between the valence-band top and the conduction-band bottom is optically active. It can be seen that deep levels of $Al_{12}C$ (Si) clusters have very little dispersion when the clusters form a cluster-assembled solid. However, the considerable dispersion around the Fermi energy is visible for the $Al_{12}C$ and $Al_{12}Si$ solids. Similar cases have been observed in C_{60} solid. Comparing the band structures of $Al_{12}C$ solid and $Al_{12}Si$ solid, the band gap of $Al_{12}Si$ is a little smaller than that of $Al_{12}C$, and the $Al_{12}Si$ band is less dispersive. It is interesting to note that in both $Al_{12}C$ and $Al_{12}Si$, the first Hg state above the Fermi level has a very weak band effect, while the bands above the Hg have strong band effect.

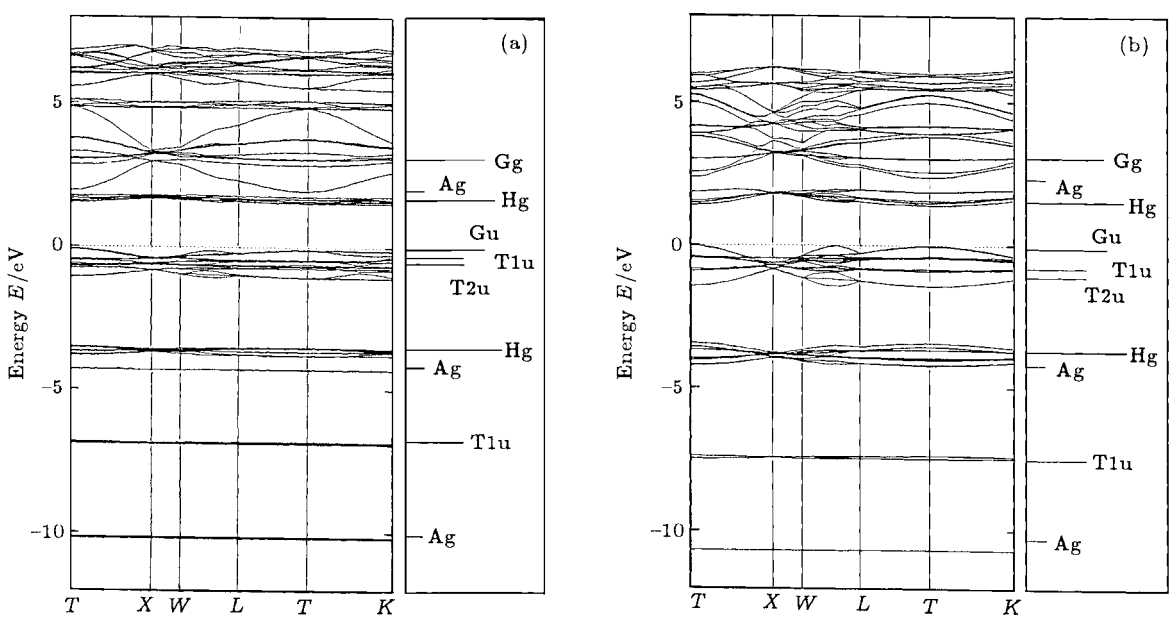

Fig.5. The band structures of $Al_{12}C$ (a) and $Al_{12}Si$ (b). The Fermi energy is shifted to zero.

Figure 6 shows the electronic density of states of the $Al_{12}C$ (Si) solid by Lorentz expansion of eigenvalues.[16] It is clear that the peaks are very sharp, reflecting the weak dispersion of the bands, and the gap up to 1.5 eV can be observed. Since the electronic structures of $Al_{12}C$ and $Al_{12}Si$ clusters are similar, a strong similarity of density of states between $Al_{12}C$ solid and $Al_{12}Si$ solids also exists.

In summary, we have performed density functional calculation on the $Al_{12}C$ (Si) solid with NaCl-like crystal structure proposed previously. We find that, around the equilibrium lattice constant, the charge density is very close to the superposition of cluster charge density. The overlap between clusters is very small, suggesting a van der Waals interaction. If the cluster-assembled solid is compressed significantly, the charge density can be redistributed, indicating a pressure-induced phase transition might occur. It is found that the band structures and the electronic density of states of $Al_{12}C$ and $Al_{12}Si$ are similar. Also, the band dispersion is very weak in both solids, and the main features of electronic structure in clusters still retain in solids. The band structures show that $Al_{12}C$ and $Al_{12}Si$ are semiconductors with a direct energy gap.

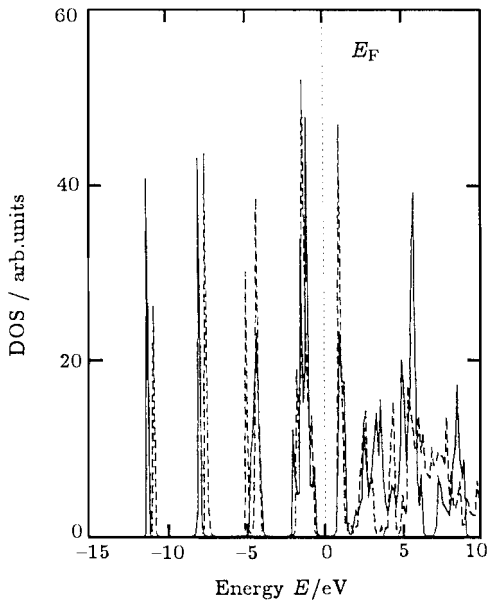

Fig.6. The electronic density of states for $Al_{12}Si$ (solid line) and $Al_{12}C$ (dashed line).

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