

The Structure and Stability of Cluster-Assembled Solid Al_{12}Si : A First Principle Study

by

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ABSTRACT

We have proposed a possible crystal structure for the cluster-assembled solid Al_{12}Si and its properties have been studied by first principles methods. We find that Al_{12}Si clusters can be condensed as a van der Waals solid with a small cohesive energy of 1.06 eV, and there is an energy gap of 1.4 eV which indicates that Al_{12}Si solid can be a semiconductor. The stability of Al_{12}Si solid is confirmed by performing *ab-initio* molecular-dynamics simulations.

Key-words: Stability; Cluster-assembled; Al_{12}Si .

PACS numbers: 36.40-c; 6150Lt; 71.15Mb+Pd

The atomic cluster, as an intermediate state between solid phase and atom, has many unique properties. Recently there is growing interest on the research to assemble those atomic clusters to solid, which adds a new dimension for the materials scientists to synthesize novel materials[1]. Generally to synthesize a cluster-assembled solid, stable cluster, as the building block of the solid, is necessary, and also the interaction between the clusters should be much smaller than the interaction in the cluster. Otherwise when the clusters are brought together, the structure of cluster would coalesce to form another phase. Moreover, since the cluster is not completely spherical-like, the geometric effects can play a crucial role on the formation of the cluster-assembled solid, as shown by previous studies [2].

Based on the first principles calculations, it was found that Al_{12}C cluster has a high stability[3], recent studies showed that it may be condensed as van der Waals solid[2]. As a matter of fact, both Al_{12}Si and Al_{12}C clusters have a large binding energy comparing to Al_{13} cluster[3,4], the binding energy of Al_{12}Si cluster is only about ~ 1 eV smaller than that of Al_{12}C cluster, and the gap between the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) for Al_{12}C and Al_{12}Si is very close. On the other hand, since in an icosahedron the center to vertex distance is about 5% shorter than the vertex to vertex distance, from the geometrical point of view the carbon atom is a little bit smaller to fill the space at the center of the icosahedron, while silicon atom can do a better job to optimize the bonds in the icosahedron. Therefore Al_{12}Si cluster should also have a high stability, although its stability may not be as high as Al_{12}C cluster. It could be another candidate for the building blocks of a van der Waals solid.

Since Al_{12}Si cluster has a large HOMO-LUMO gap, it was expected to be condensed as a van der Waals solid with fcc-like structure and its properties and stability were studied by Seitsonen et al.[5]. They found a very short Al-Al bond length between clusters, its bond energy was even larger than that in the Al bulk. So obviously fcc-like Al_{12}Si solid would not be stable, since the structure of icosahedral Al_{12}Si cluster would coalesce. As we discussed in our previous paper[2], this instability comes from the non-spherical effects of icosahedral cluster. Based on the recent simulation on cluster dimer (two icosahedral clusters, each of them contains 13 atoms)[6], we had proposed a crystal structure for the cluster-assembled solid Al_{12}C . Actually, this structure is *NaCl-like*, if we think *Na* and

Cl here are two cubic boxes which contains an icosahedraon with 13 atom and these two boxes are different only in alternated orientation of 90 degrees. The 13 atoms in the box and their relative orientation of the two boxes are shown in Fig. 1. Although recently it was shown that fcc-like Al_{12}C solid to be unstable[7], we found that Al_{12}C clusters can be condensed as van der Waals solid with this *NaCl-like* structure. The cohesive energy is only about 1.1 eV and the HOMO-LUMO gap of Al_{12}C cluster almost remains in the solid.

In this report, we present the results on the properties of Al_{12}Si solid with *NaCl-like* structure. We find that the Al_{12}Si clusters could be condensed as van der Waals solid, its stability is also testified by *ab-initio* molecular-dynamics method.

Our calculations are based on *ab-initio* molecular-dynamics method[8]. In this scheme, the local density approximation to density functional theory[9] is used. We use the form of exchange-correlation functional proposed by Ceperley and Alder and parameterized by Perdew and Zunger[10]. At the fixed atomic distances, the energy functional is minimized by conjugated gradient method. The minimization of the energy functional is also performed in a dynamical scheme which allows simultaneous relaxation for electronic and ionic degrees of freedom in Al_{12}Si solid. The first principles norm-conserving pseudopotentials of Bachelet-Hamann-Schluter type[11] with s and p non-locality are used in all the calculations, which is proved to have a high precision for silicon and aluminum in cluster and in condensed phase[12,13]. We expand the Kohn-Sham orbitals into plane waves with an energy cutoff of 16 Ry and use only the $k=0$ point in the Brillouin zone.

First, we have calculated the equilibrium structure for the isolated Al_{12}Si cluster. Since our method is based on the plane wave expansion, it is necessary to use the periodical boundary condition. To erase the interaction between the cluster and its images, one need to use a big unit cell. The test shows that a fcc-like unit cell with lattice constant of 33 a.u. is enough to make the interaction negligible. By calculating the binding energies at various Al-Si distances, we have found that the equilibrium Al-Si distance is 4.89 a.u., which is the same with the result obtained by Seitsonen et al.[5], but it is smaller than the previous results obtained by other *ab-initio* methods with localized basis function[3,14]. We have obtained a binding energy of 44.7 eV, again which is very close Seitsonen's results. For comparison, the results for Al_{12}Si and Al_{12}C clusters are listed in table. I. We can see from the table. I, it seems that the calculations based on atomic orbitals gives

systematically larger atomic distances comparing to the results from pseudopotentials. But the difference of bond lengths between Al_{12}Si cluster and Al_{12}C cluster is consistent with the pseudopotential's results. It is also worth to note that, the binding energies of Al_{12}Si cluster and Al_{12}C cluster are very close in various calculations. Since the atomic size of silicon atom is larger than carbon atom, the obtained Al-Si bond length is also larger than the Al-C bond length.

In Fig. 2, the contour plot of charge density of Al_{12}Si cluster is shown. It is clear that the overlap of charge density between the cluster and its images is very small. And also it is interesting to note that, the charge density is not spherical-like, especially along one axis direction, the charge density has a tendency to move inwards to the center, and on other axis direction, it has a tendency to move outwards from the center. Similar results are also obtained for Al_{12}C cluster[2]. So if we assemble these clusters into a solid with two 90 degrees alternated icosahedraon (*NaCl-like*), this *inwards* and *outwards* features can be well matched, which can bring clusters closer without significantly distorting the electronic structures of the clusters. Since fcc-like structure is constructed from only one kind of icosahedron, this *inwards* and *outwards* features can not be well matched, this may be one of the important reasons to explain why fcc-like structure of Al_{12}Si solid is unstable. This also suggests that the geometric effects may play an important role in the formation of cluster-assembled solid.

To calculate the total energy of Al_{12}Si solid with *NaCl-like* structure, we have used a super-cell which contains four Al_{12}Si clusters. At first, by changing the lattice constant with rigid clusters, we can obtain the total energies for the solid. Then we have performed calculations with fixed lattice constant but changing the interatomic distances in the cluster. We have not found any significant relaxation of atomic distances in the cluster. The cohesive energies, defined by the total energy minus the sum of the total energies of the isolated clusters, are shown in Fig. 3. We find an energy minimum at lattice constant of 32.5 a.u., which indicates that a solid might be formed at this lattice constant. We get a cohesive energy of 1.06 eV, which is much smaller than the binding energy (3.39 eV) in bulk[15] and also much smaller than the binding energy (3.42 eV/atom) in Al_{12}Si cluster[3]. This suggests that Al_{12}Si clusters are condensed as a van der Waals solids. While in the Seitsonen's calculations for fcc-like structure, the obtained cohesive energy was about 6.1 eV, i.e., ~ 1.0 eV per additional formed Al-Al bond. This energy was

about 0.3 eV more than the energy per bond in Al metal, which implied that the bonds formed between clusters are metallic-like. In fact, at the energy minimum of fcc-like structure, the length of additional Al-Al bond between clusters is only 4.93 a.u., whereas the intracluster Al-Al bond length is 5.14 a.u., so it is not surprise that the structure was completely changed when ions were allowed to move, as shown in Seitsonen's calculation.

However, at the energy minimum of Al_{12}Si solid in *NaCl-like* structure, Al-Al distance between clusters is about 9.9 a.u., which is almost twice the Al-Al distance in the cluster. Therefore the inter-cluster bonding can not be metallic-like, different from what was found in fcc-like structure. In Fig. 4, we show the charge density of Al_{12}Si solid. Comparing with charge density of an isolated Al_{12}Si cluster shown in Fig. 2, the charge density of Al_{12}Si cluster in the solid is almost the same with the charge density of the isolated cluster. The *inwards* and *outwards* features in the charge density also exist in solid and they are well matched in the present crystal structure. Fig. 5 shows the charge density along a line from one silicon to its nearest silicon atom, the highest peak is associated to the pseudo-charge of atomic silicon, the second peak at $R \sim 4.16$ a.u. is the charge density at the middle point of Al-Al bond in the cluster. We can see that, at the lattice constant of 32.5 a.u., the overlap is very small and it is only about one fifteenth of the Al-Al bond charge in the cluster. So it also suggests that the Al_{12}Si clusters are condensed as a van der Waals solid. In Fig. 5, we have also shown the results for the lattice constant of 28 a.u., at which a positive cohesive energy is obtained (see Fig. 3). Comparing the results for two lattice constants, the similar features can be observed, but clearly there is more charge piled up at interior region between the clusters, the overlap increased 3~4 times. Since the electronic structures of Al_{12}Si cluster remain almost the same in the solid at lattice constant of 28 a.u., the larger overlap of charge density leads to more repulsive interaction. That's why a positive cohesive energy is obtained. In fact, we can expect that at even smaller lattice constant, the strong interaction between clusters will change the electronic structure of Al_{12}Si cluster, and other kind of bonds, like metallic bonds, can be formed for Al atoms between the clusters, then the atomic structure will be also changed, the meta-stable phase of cluster-assembled solid Al_{12}Si will be disappeared.

Fig. 6 shows the electronic density of states for the isolated Al_{12}Si cluster and Al_{12}Si solid, which is obtained by Lorentz expansion of Kohn-Sham eigen values. We can see that, the basic features of the density states for cluster and solid are the same. In the

cluster, we have got a HOMO-LUMO gap of 1.95 eV which is in agreement with previous calculations[3,14]. As expected for the van der Waals solid, the dispersion is found to be very small, and we have got a large gap up to 1.41 eV for the Al_{12}Si solid, which is close to values obtained for C_{60} solid[16] and Al_{12}C solid[2]. This large gap suggests that Al_{12}Si solid would behave like a semiconductor, and the real gap can be expected to be larger than the present theoretical value since it is well known that the LDA always underestimates the energy gap.

As stated above, we have performed the total energy calculations by changing the atomic distances of Al_{12}Si cluster at the lattice constant of 32.5 a.u., and no visible changes on the atomic structure of Al_{12}Si clusters have been observed after they are condensed to the solid. To further check the stability of Al_{12}Si solid, we have let ions move by performing *ab-initio* molecular-dynamics simulation. Started at the lattice constant of 32.5 a.u., our dynamical simulation lasts for 6000 steps (~ 0.85 ps). Contrary to what was observed in fcc-like Al_{12}Si solid, we find that the ions only vibrate around the equilibrium positions, amplitudes of vibration are very small, the average temperature is only about 1 K, which strongly indicates that the present structure of Al_{12}Si solid could be stable. Since the Al_{12}Si cluster is observed to keep almost icosahedral structure up to high temperature[17], It is interesting to study how the temperature affects the stability of Al_{12}Si solid, i.e., at how high temperature, the structure of Al_{12}Si solid will be destroyed and consequently a new structure is formed.

In conclusion, from the results obtained by first principles calculation and *ab-initio* molecular-dynamics simulation, we find that Al_{12}Si clusters are condensed as a van der Waals solid, with a small cohesive energy of 1.06 eV. The fact that the Al_{12}Si solid is stable with the *NaCl-like* structure, instead of fcc-like structure, indicates that the geometric effects can play a crucial role on the cluster-assembled solid. The obtained results show that the Al_{12}Si solid might be another interesting solid, like C_{60} and Al_{12}C solid.

Acknowledgment: X.G.G is thankful to The Third World Academy of Science and CNPq (Brazil) for the hospitality at the CBPF. Thanks are also to Dr. J.A. Helayel-Neto for providing all the facilities that made my stay at CBPF very profitable. This work is partially supported by NNSF of China, and the research developed jointly with National center of supercomputation at the Federal University do Rio Grande of Sul(UFRS)and the center of supercomputation at the Federal University of Rio de Janerio(UFRJ).

Figure Captions

Fig. 1 The structure of two Al_{12}Si clusters with alternated 90 degrees of orientation, and also it shows the relative orientation of Al_{12}Si clusters in solid phase. Big balls for Al atoms and small balls for C atoms.

Fig. 2 The contour map of charge density for an isolated Al_{12}Si cluster.

Fig. 3 The cohesive energies for *NaCl-like* Al_{12}Si solid as function of lattice constant. The solid line is a guide for the eye.

Fig. 4 The contour map of charge density of Al_{12}Si solid.

Fig. 5 The charge density along a line between two nearest silicon atom in Al_{12}Si solid, where R is equal to half of the lattice constant.

Fig. 6 The electronic density of states for Al_{12}C cluster (solid line) and for Al_{12}C solid (dash line).

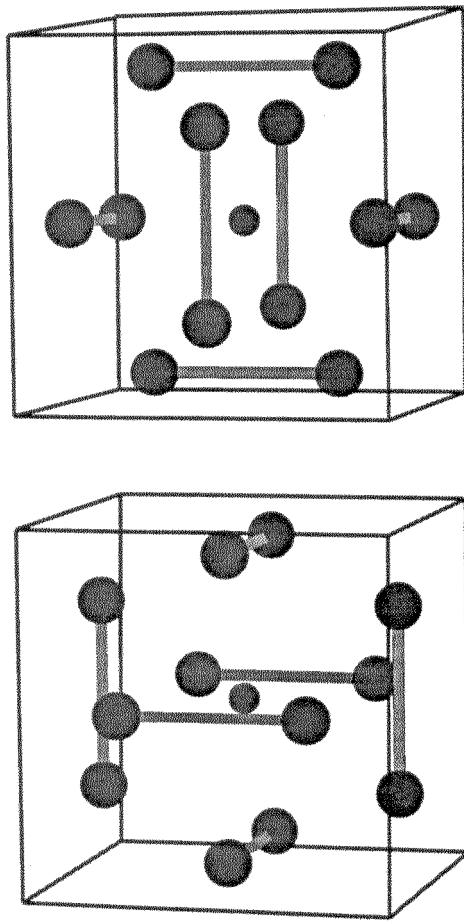


Fig. 1

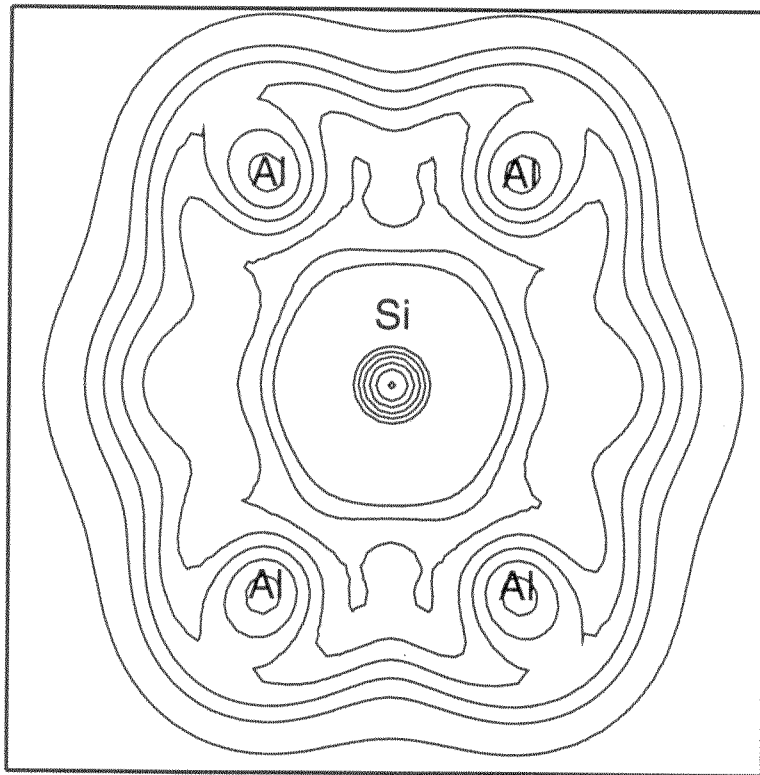


Fig. 2

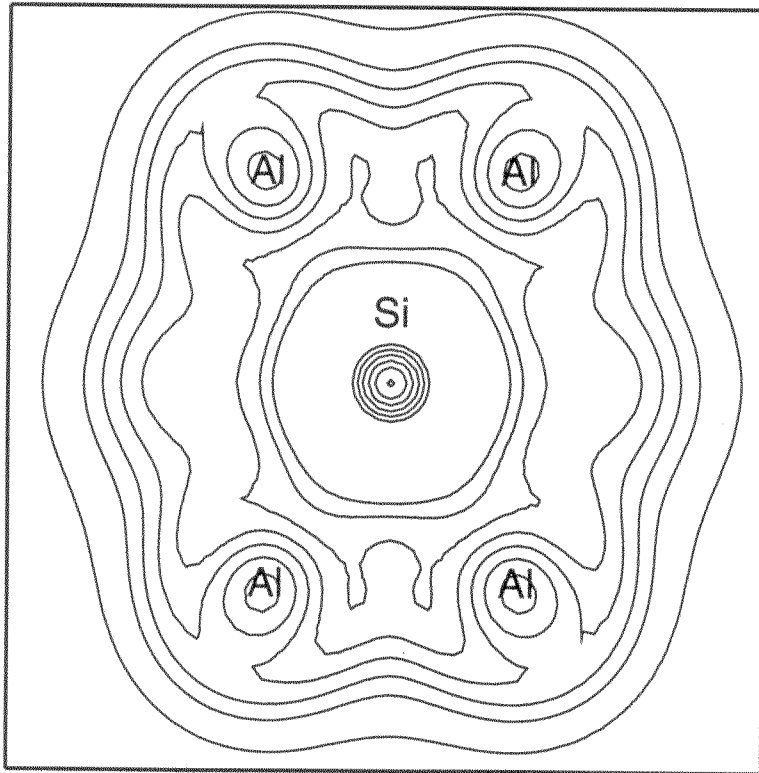


Fig. 2

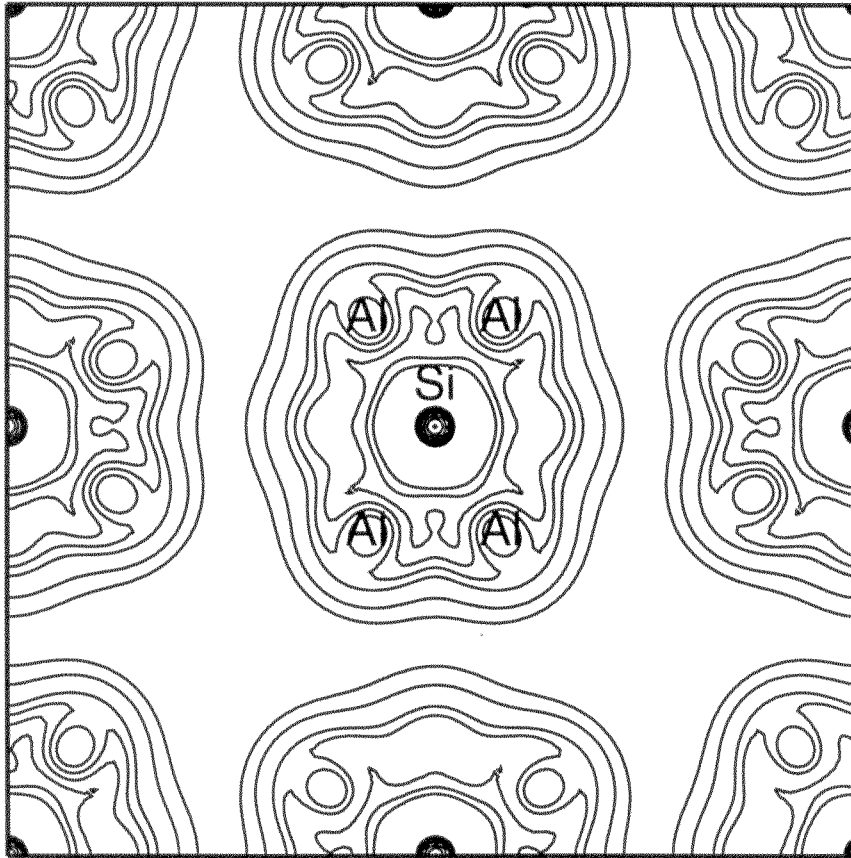


Fig. 4

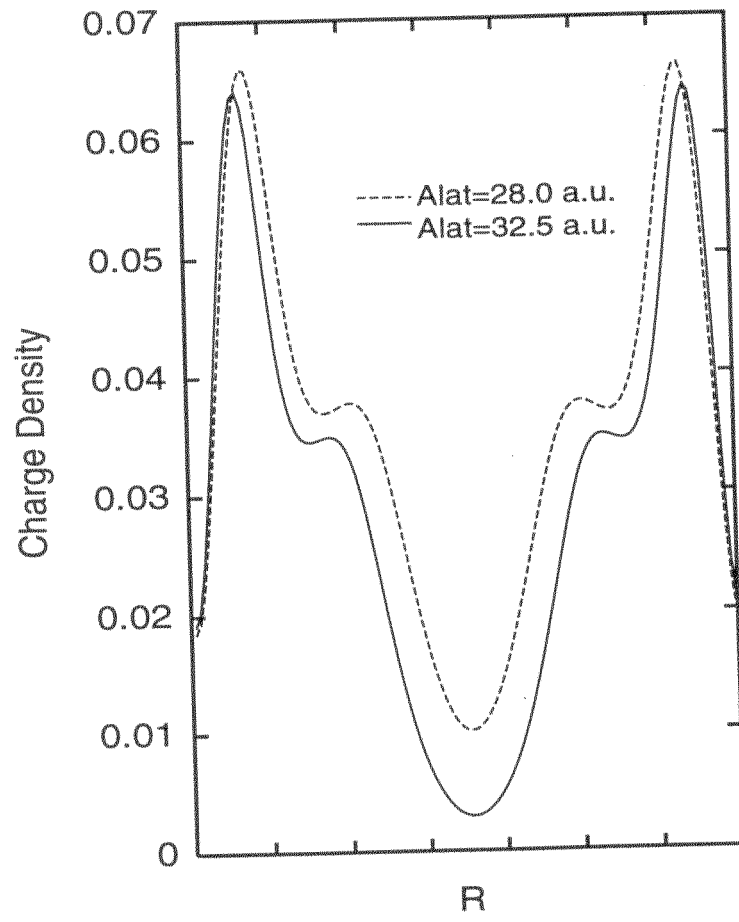


Fig. 5

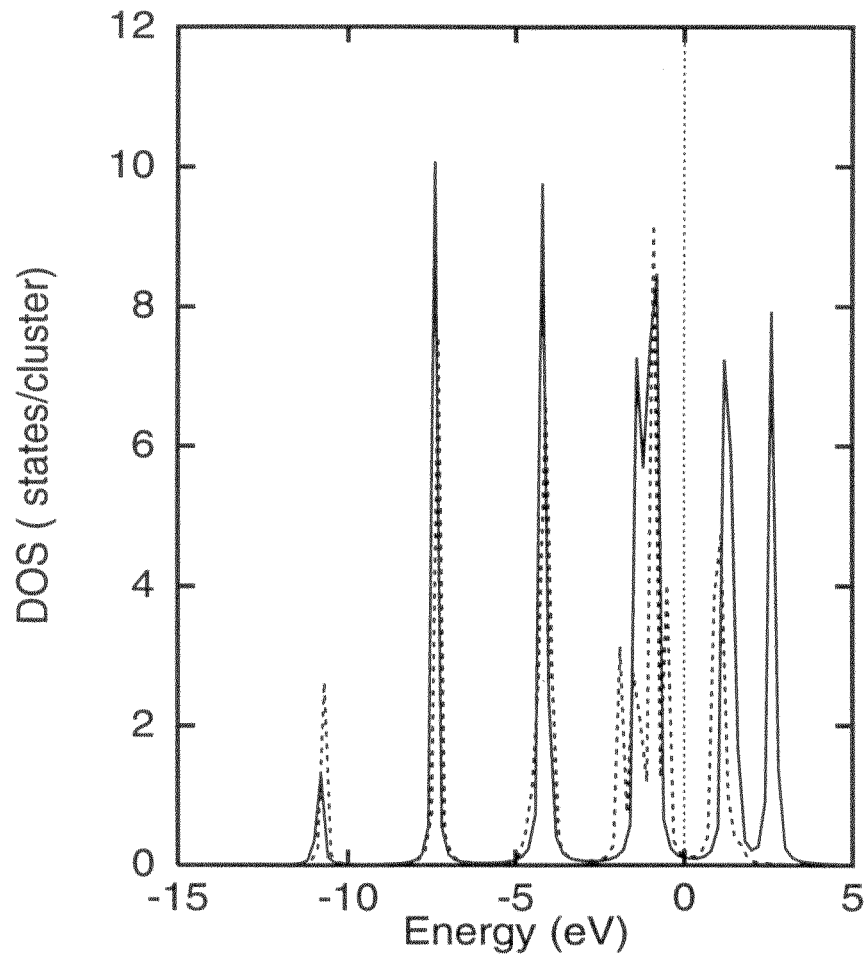


Fig. 6

Table I. Comparison of the binding energy(E_b) and the nearest neighbour distance for icosahedral $Al_{12}Si$ and $Al_{12}C$ clusters.

	$Al_{12}Si$		$Al_{12}C$	
	d(Al-Si)(a.u.)	E_b (eV)	d(Al-C) (a.u.)	E_b (eV)
Present*	4.89	44.7	4.68	45.9
Seitsonen et al. ^a	4.89	44.9	4.69	45.3
Gong and Kumar ^b	5.22	39.2	5.05	40.6
Khanna and Jena ^c	5.05	39.2	4.78	41.1

* see also Ref.[2]

^aReference [6,7]

^bReference [3]

^cReference [4]

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