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Cohesive Mechanism and Structure of Cluster-Assembled Solid $Al_{12}C$

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Abstract

We have proposed a possible crystal structure for the cluster-assembled solid $Al_{12}C$, and its electronic structures and stability have been studied in the framework of the density functional theory and *ab-initio* molecular-dynamics. We find that $Al_{12}C$ clusters are condensed by van der Waals force, with a very small cohesive energy of 1.1 eV. A significant energy gap exists in solid, which suggests that it can be a novel semiconductor. The combined steepest descent calculations show that upon the formation of solid, the relaxation of atomic distances of the $Al_{12}C$ cluster is very small. The stability of the $Al_{12}C$ solid is also confirmed by a dynamical simulation at low temperature.

Key-words: Cluster-assembled $Al_{12}C$.

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In the past decades, a great deal of efforts have been devoted to the synthesizing and the fundamental understanding of new materials in atomic dimension[1]. With the discovery of C_{60} molecule and its solid phase[2], an enormous interest in the study of cluster and cluster-assembled materials has been aroused. Since the properties of clusters are quite different from that of atoms, it is reasonable to expect that the cluster-assembled materials have unusual properties, which would be quite different from that in atomic solid phase, like what observed in solid C_{60}[3]. To obtain the cluster-assembled materials, a high stability of the clusters is usually essential, otherwise the clusters would coalesce when bringing them together, and the merits for synthesizing the cluster-assembled materials would be lost, it is also necessary to have smaller interaction between clusters as compared to the interaction in the cluster itself.

Recently, from the total energy and electronic structure calculations[4], it had been found that the stability of Al_{13} cluster can be significantly enhanced by doping with a tetravalent carbon atom. Since there exists about 2 eV gap between the highest occupied molecular orbitals(HOMO) and the lowest unoccupied molecular orbitals(LUMO), the interaction between $Al_{12}C$ cluster can be expected to be small. Therefor the $Al_{12}C$ cluster is suggested to be a good candidate to form a cluster-assembled solid. In fact, the high stability of $Al_{12}C$ cluster was confirmed by a few recent studies[5,6]. Seitsonen et al.[6] studied the dynamical stability of $Al_{12}C$ cluster by Car-Parrinello method, and they found that, even above 900 K, the structure of $Al_{12}C$ cluster remains icosahedral-like, which indicates that the $Al_{12}C$ cluster is indeed stable. Moreover, Kawai et al.[5] have studied the interaction between two $Al_{12}C$ clusters by Car-Parrinello method, they found that the structure of $Al_{12}C$ clusters remains unchanged. However no successful studies for the cluster-assembled $Al_{12}C$ solid have been made. Seitsonen et al.[6] studied the properties of $Al_{12}C$ solid with fcc-like structure, but they found that the total energies increased monotonically with the decreasing of the lattice constant, and there is no local minimum which is necessary for the formation of a meta-stable phase.

In this letter, based on the recent simulation on the cluster dimer and cluster- assembled solid[7], we propose a crystal structure for the $Al_{12}C$ solid. In the total energy calculations, we have obtained a minimum at lattice constant of 30.8 a.u., and we do find that the interaction between the clusters in $Al_{12}C$ solid is very weak, and the cohesive energy is very small. By performing the combined steepest descent on the ions and electrons, and dynamical simulation at low temperature, we show that $Al_{12}C$ solid is a stable van der Waals solid.

As discussed by Khannan and Jena, the geometric effects are important in the cluster-assembled materials[8]. In the icosahedral $Al_{12}C$ cluster, although 12 aluminum atoms are homogeneously distributed on a spherical surface, it can not be rotational invariant like a rare-gas atom. It is well known that, even in the icosahedral fullerene of C_{60}, which has a smoother surface since it contains 60 carbon atoms on the surface, various phases with different rotational order have been observed at low temperature[9]. Obviously, the relative orientation of clusters may play an important role in the formation of a solid from the icosahedral $Al_{12}C$ clusters.

The recent simulations on the cluster dimer (two icosahedral 13-atom clusters) and cluster-assembled solid with the Leonard-Jones potential show that[7], the relative cluster orientation is very important for the stability of the cluster dimer. If we put 12 surface atoms of a body-center icosahedron on the six faces of a cubic box, the most stable structure for a cluster dimer is with two cubic boxes in alternated orientation of 90 degrees, as shown in Fig. 1. In fact, only in this configuration, the mass centers of two icosahedron can approach more closely than any other isomers which have higher energies, as confirmed by the charge density shown below. This suggests that, when the clusters are brought together, they should be properly arranged according to their geometric shape. In fact, the intuitive fcc-like structure, which is the lowest energy structure for the atomic van der Waals solid, was proved to be unstable for cluster-assembled $Al_{12}C$ solid. So, we have tried to design a structure for $Al_{12}C$ solid, in which each $Al_{12}C$ cluster is alternated 90 degrees with all its nearest neighbours. This turns out to be a cubic-like structure, each unit cell contains eight $Al_{12}C$ clusters. Actually, similar structure has been observed in AB_{13} system[10], where B_{13} has icosahedral structure, the large atom A is believed to be an electron donor to close the electronic shell of B_{13} which makes B_{13} stable[11]. To show whether this structure is stable for $Al_{12}C$ solid, we have performed first principles calculation and *ab-initio* molecular-dynamics simulation, and its stability is confirmed. With the same crystal structure, we have studied the properties of the cluster-assembled $Al_{12}Si$ solid which was proved to be unstable for fcc-like structure[12], and also the cluster-assembled solid $Al_{13}K$, which was suggested to have CsCl structure[13] but recent calculation showed that icosahedral $Al_{13}K$ cluster would not be stable in CsCl structure[14]. The results on $Al_{12}Si$ and $Al_{13}K$ solid will be published elsewhere[15].

All our calculations are based on the density functional theory with the local density approximation[16] and Car-Parrinello method[17]. The electronic density is expressed in terms of Kohn-Sham orbitals[18], which are expanded into plane waves with energy cutoff of 35Ry. Only the valence electrons are treated explicitly and their interactions with the ionic cores are described by the Bachelet-Hamann-Schluter type pseudopotentials[19] with sp non-locality for Al and also for C. The minimization of the energy functional is performed with conjugate gradient for the fixed atomic distances, also with combined the steepest descent for electrons and ions in $Al_{12}C$ solid at a lattice constant of 30.8 a.u. We have used time step of 4.0 a.u. and fictitious mass of 300 a.u for electrons in all the calculations.

At first, we have studied the isolated icosahedral $Al_{12}C$ cluster. Due to the plane wave expansion, one is forced to use periodical boundary condition. We use only the Γ point of Brilliouin zone in the k-summation. To erase the interaction between the cluster and its images, it is necessary to have a very large cell. As it was observed by Seitsonen et al.[6], we have found that a fcc-cell with the lattice constant up to 30 a.u. is enough to make the interaction between the cluster and its images negligible. This can also be confirmed by the total charge density of $Al_{12}C$ cluster, as shown in Fig. 2. By calculating the total energies at different Al-C distances, we have got the equilibrium Al-C distance of 4.69 a.u. which is equal to what was obtained in Ref.[6]. The obtained binding energy value of 45.9 eV is also comparable to 45.3 eV obtained by Seitsonen et al., and the small difference may come from different psudopotentials used for carbon. These results are also in agreement with the results of other previous *ab-initio* methods[20].

To calculate the cohesive energy of $Al_{12}C$ solid, we have used a primitive cell with two $Al_{12}C$ clusters. By changing the lattice constant with rigid cluster, the different cohesive energies can be obtained, and its values, relative to the isolated clusters, are shown in Fig. 3. In contrary to the result of fcc-like solid, we have obtained an energy minimum at the lattice constant $\sim$30.8 a.u., which indicates that the $Al_{12}C$ solid could be formed with this lattice constant. The cohesive energy of the cluster-assembled solid $Al_{12}C$ is very small, only about 1.1 eV which is smaller than $\sim$3.5 eV/atom in the isolated $Al_{12}C$ cluster. The very small cohesive energy, which is comparable to $\sim$ 1.6 eV for C_{60} solid[3], implies that the $Al_{12}C$ clusters are condensed by rather week van der Waals force. Similar to C_{60} solid in which intra-cluster C-C distance is almost twice the inter-cluster C-C distance, the shortest Al-Al distance between different clusters in $Al_{12}C$ solid is about 9.2 a.u., it is much longer than the normal Al-Al bond in bulk aluminum, therefore it is very difficult for Al atoms from different clusters to have interaction stronger than the van der Waals interaction. These features are also visible in the contour map of the valence charge density, which is shown in Fig. 4. From this figure we can see that, the charge density of $Al_{12}C$ cluster in solid is almost the same as the charge density of the isolated cluster, and the charge density overlap between the clusters is very small leading to a stable cluster-assembled solid. It is worth to note that the charge density of $Al_{12}C$ cluster and solid, shown in Fig. 2 and Fig. 4 respectively, is not spherical-like. At one axis direction, the charge density has a tendency to move inwards to the center of carbon, and at another axis direction, the charge density has a tendency to move outwards from the center of carbon. So the neighboring clusters need to rotate 90 degrees in order to bring them closer without distorting the charge density significantly. While in fcc-like $Al_{12}C$ solid, this *inwards* and *outwards* features in charge density can not be well matched. This may be one of the reasons why fcc-like $Al_{12}C$ solid is not stable.

At the lattice constant of 30.8 a.u., which corresponds to the energy minimum in Fig. 3, we have calculated the total energies by changing Al-C distances in the cluster. We find that changes for Al-C bonds are very small. Then we have performed the combined steepest descent on ions and electrons, a very small relaxation on the structure has been observed again with the energy gaining only about 0.02 eV. These results clearly indicate that the icosahedral structure of the isolated $Al_{12}C$ cluster remains unchanged upon forming a solid, at least it is stable against steepest descent.

The electronic density of states is obtained by Lorentz expansion of Kohn-Sham eigenvalues, Fig. 5 shows the obtained results for the isolated cluster and also for the solid. We can see that, the basic features of the density of states for cluster and solid are almost the same. The small splitting of degenerate states in solid, which is generally proportional to the crystal field, confirms again the very weak interaction between the clusters in $Al_{12}C$ solid. For the isolated cluster, we have obtained a HOMO-LUMO gap up to 1.96 eV which is close to the results obtained in previous calculation by discrete variational method[4]. In the solid, we find that the change of gap due to the dispersion is small, the obtained energy gap for $Al_{12}C$ solid is 1.52 eV which is almost the same with the result obtained for C_{60} solid[3]. Since it is well known that LDA always underestimates the gap, the real gap for the $Al_{12}C$ solid will be larger than the presently obtained values. This large gap in $Al_{12}C$ solid suggests that the $Al_{12}C$ solid would behave like a semiconductor.

To further check the stability of $Al_{12}C$ solid, we have performed a molecular-dynamics simulation at a temperature of ~20 K. The simulation is started by giving a small random displacement to each of atoms at the equilibrium structure with lattice constant of 30.8 a.u. Contrary to the result of fcc-like $Al_{12}C$ (and also $Al_{12}Si$)[6,15], we find that the structure of icosahedral $Al_{12}C$ cluster remains unchanged in our observed time of 1.1 ps, the atoms move only around the equilibrium positions. In Fig. 6, the obtained pair correlation functions for C-Al and Al-Al are shown. The peaks are clearly separated, and the broadening of the peak is very small since temperature is very low. It will also be very interesting to study its dynamical properties and stability changing with temperature, and with pressure, since it may probably have another phase by applying a certain pressure as observed in a typical molecular solid[21], this work is still in progress.

In conclusion, we have proposed a possible structure for the cluster-assembled $Al_{12}C$ solid. Based on the first principles methods, its stability is confirmed by cohesive energy, steepest descent on the ions and dynamical simulation at low temperature. The very small cohesive energy and the small overlap of charge density between clusters suggest that the forces between the $Al_{12}C$ clusters in solid phase is van der Waals like. The obtained physical properties, like electronic structures, are similar to C_{60} solid, which indicates that $Al_{12}C$ solid might be another interesting cluster-assembled solid. The present studies show that the shape and geometric structure of the cluster can play an important role in synthesizing a solid, which may bring very rich structures to the cluster-assembled solid.

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Figure Captions

Fig.1 The atomic structure of $Al_{12}C$ cluster dimer, and also it shows the relative orientation of $Al_{12}C$ 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 $Al_{12}C$ cluster.

Fig.3 The cohesive energies for $Al_{12}C$ solid. The solid line is the guide for the eye.

Fig.4 The contour map of charge density of $Al_{12}C$ solid on (001) plan.

Fig.5 The electronic density of states for $Al_{12}C$ cluster (solid line) and for $Al_{12}C$ solid (dash line).

Fig.6 The pair correlation function for $Al_{12}C$ cluster (solid line) and for $Al_{12}C$ solid (dash line).

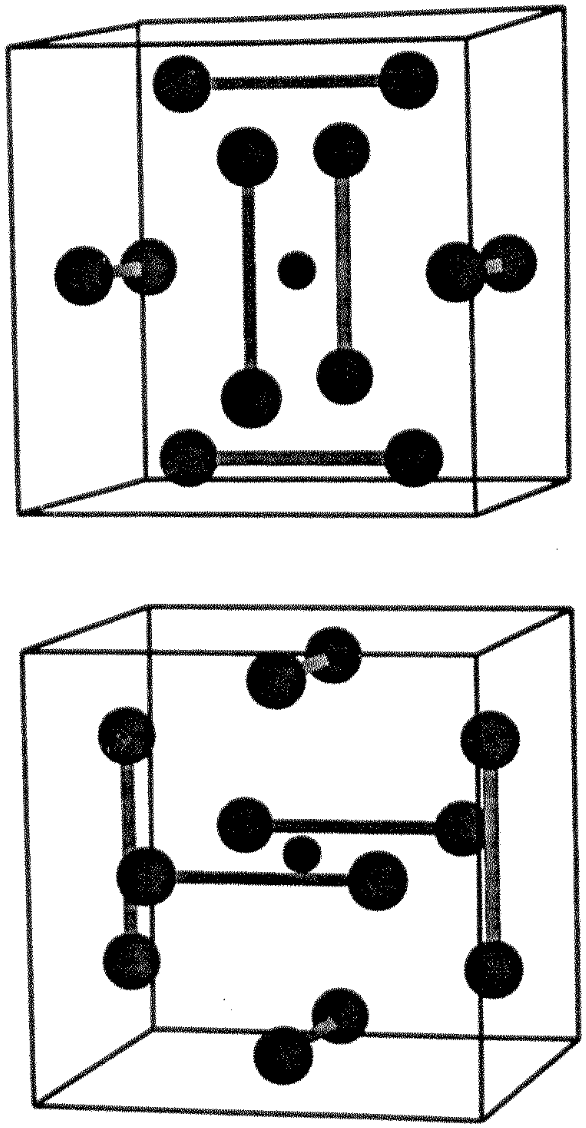


Fig. 1

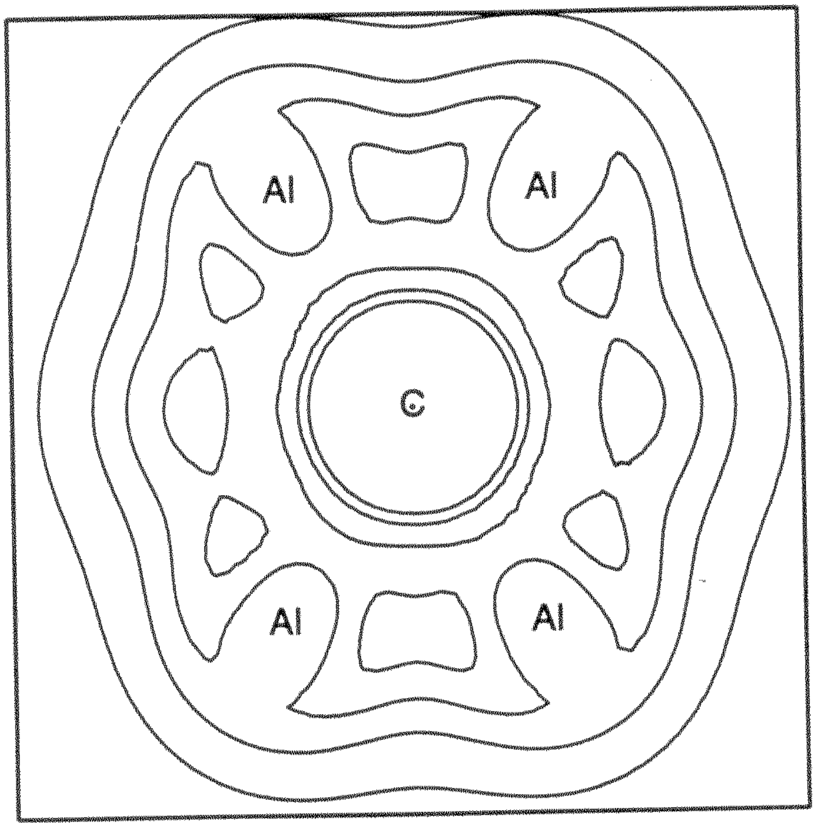


Fig. 2

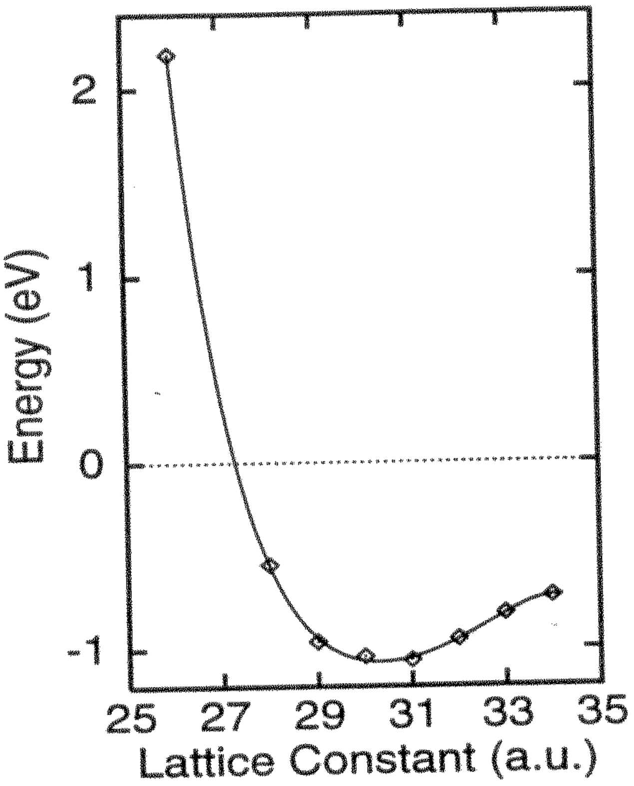


Fig. 3

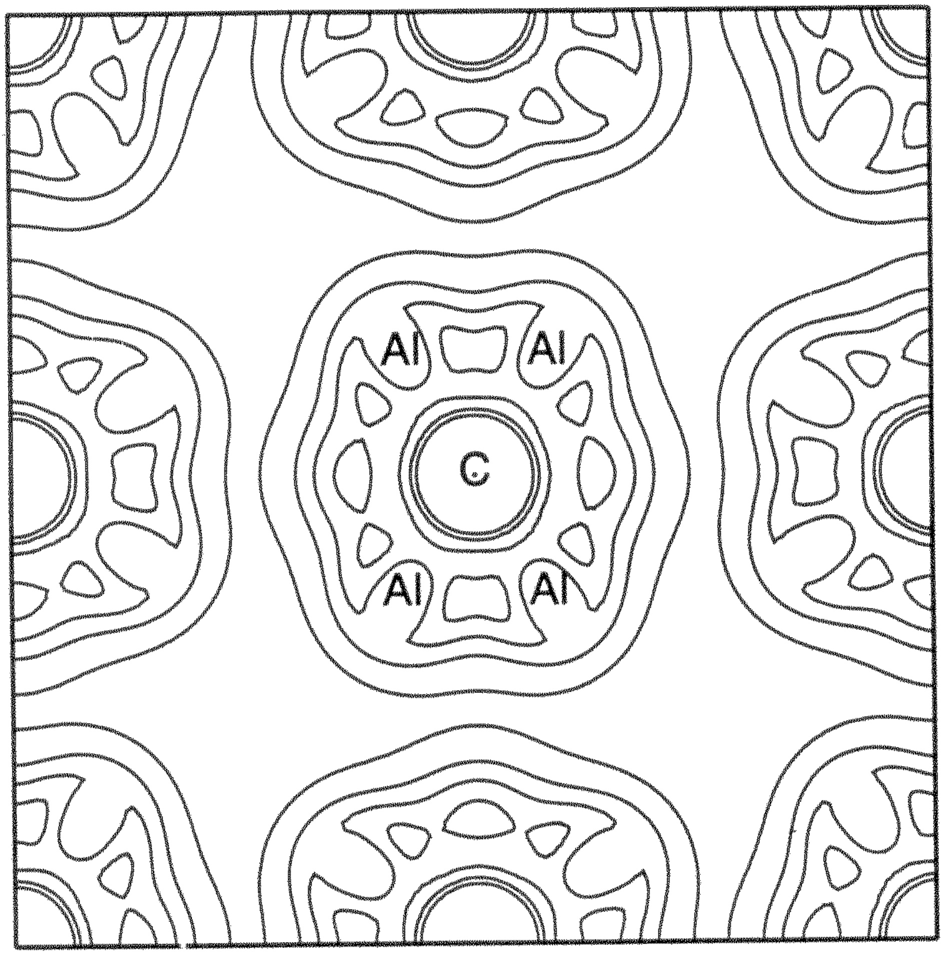
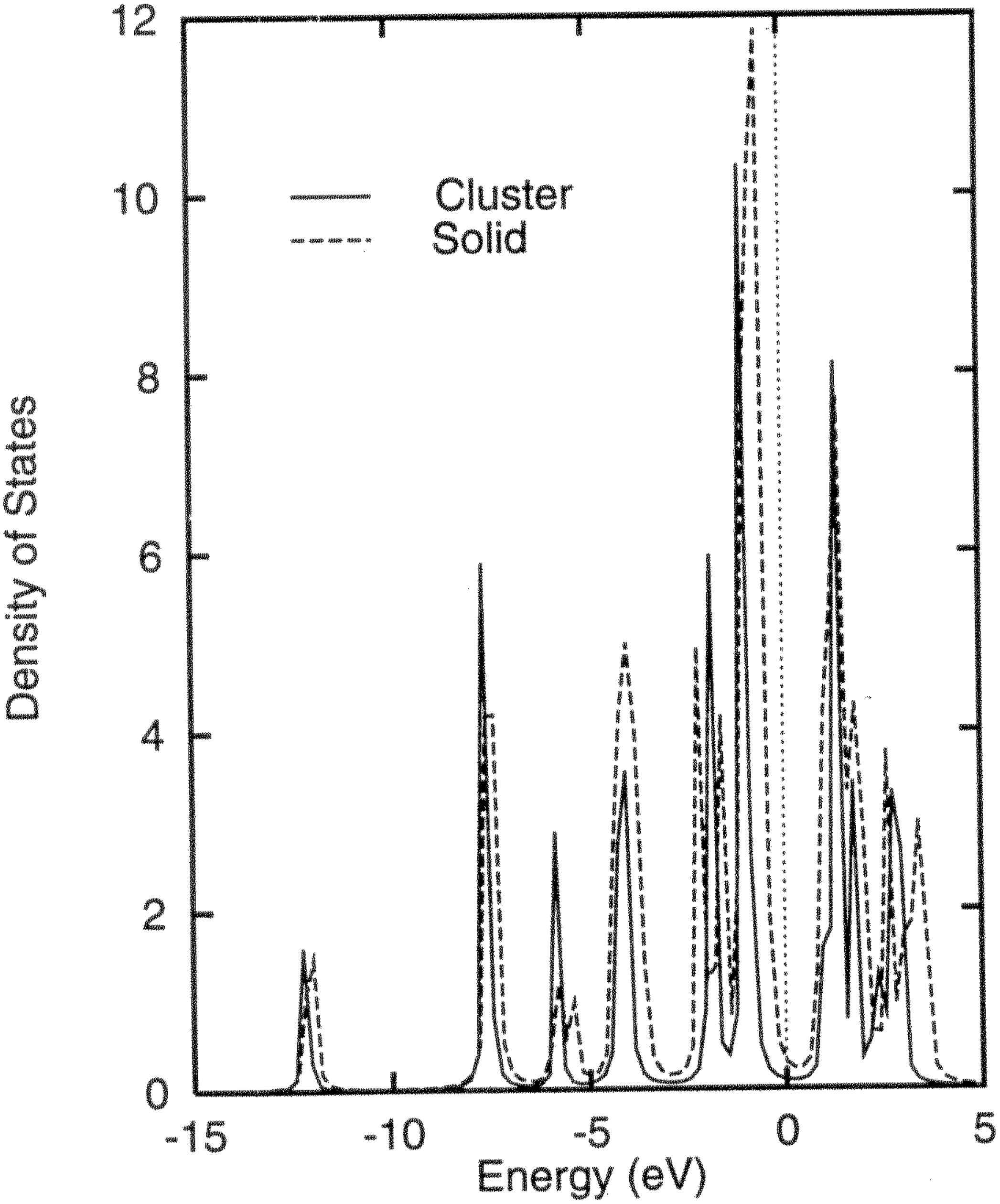


Fig. 4



Density of States
Energy (eV)
Cluster
Solid
0
2
4
6
8
10
12
-15
-10
-5
0
5

Fig. 5

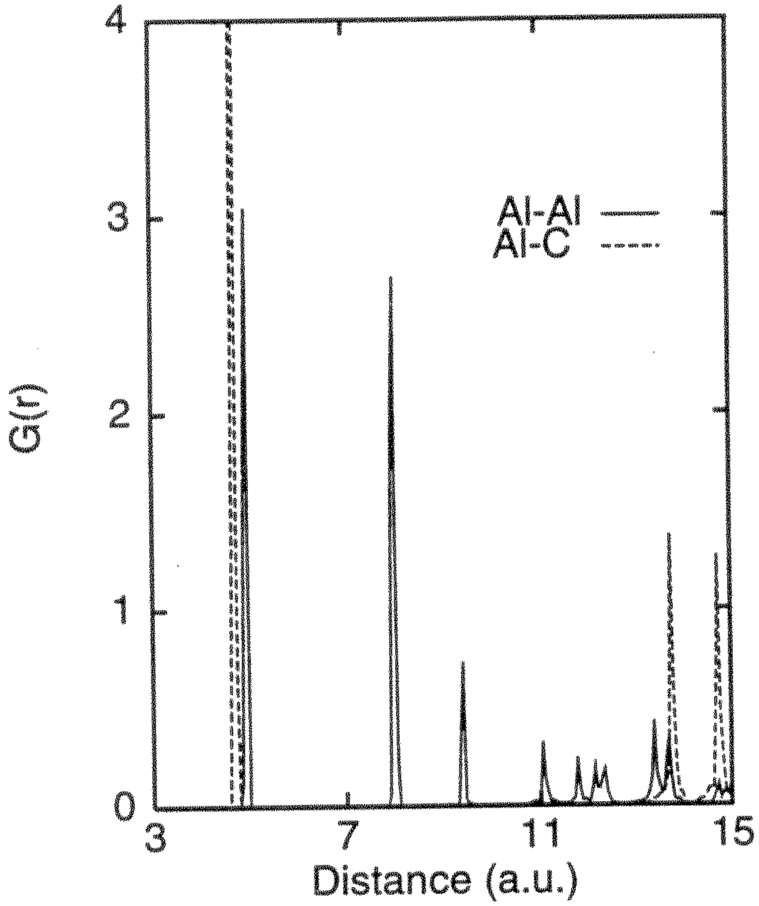


Fig. 6

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