

Charge-induced structural changes in Al_{12}C clusters

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The structures of Al_{12}C and Al_{12}C^- clusters are studied by using the density functional theory. We find that the charging on the icosahedral Al_{12}C cluster drives the carbon atom from the center of the cluster to its surface. The optimized ground state structure of Al_{12}C^- cluster has a low symmetry, in agreement with experimental observation.

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I. INTRODUCTION

The structure and stability of atomic clusters have been widely studied in last decade. One of the reasons for this is that the physical and chemical properties of small clusters are very different from that of their bulk phases, meanwhile it is expected that materials assembled from finite-sized clusters may have special properties. Since the discovery of C_{60} molecule,¹ and C_{60} solid,² much attention has been paid to the stable clusters, which are expected to be the building blocks for cluster-assembled materials.

Extensive theoretical studies have been carried out in this field.^{3–11} One typical example is the Al cluster,^{6,12,13} a subject of many theoretical and experimental studies. Since the valence electrons of Al atom are free-electron like, the stability of small Al_n clusters can be explained by the Jellium model^{14,15} which was originally developed to elucidate the shell structure of alkali metal clusters.¹⁴ For instance, in an Al_{13} cluster which has 39 electrons, one more electron is needed to fill up the shell. Thus the anion of the Al_{13} cluster^{4,16–19} is characterized by a closed electronic shell with a significant gap between the highest occupied molecular orbit (HOMO) and the lowest unoccupied molecular orbit (LUMO), which was confirmed by experiments.¹³ Calculations based on density functional theory (DFT) show that the structure of the Al_{13}^- cluster is icosahedral, while the structure of the neutral Al_{13} cluster is a distorted icosahedron, due to Jahn-Teller effects.

Although Al_{13}^- cluster, with its closed electronic shell, is very stable, it cannot be used for assembling new materials due to its charge. It was proposed that if one Al atom in the cluster was substituted by a tetravalent atom,^{4,9,12} such as C, Si, Ge, and Sn, the doped Al_{12}X ($\text{X}=\text{C}, \text{Si}, \text{Ge}, \text{and Sn}$) cluster would have 40 electrons and achieve a closed electronic shell without any net charge. DFT calculation has confirmed that the structures of Al_{12}X clusters are icosahedral-like, with a HOMO-LUMO gap around 1.0–2.0 eV. Among these tetravalent atom substituted clusters, Al_{12}C has the largest HOMO-LUMO gap and the largest binding energy.^{4,12} Therefore, the Al_{12}C has been extensively studied. It was predicted by various theoretical methods that the carbon atom should be located at the center of the icosahedron, and the binding energy for such a structure is higher (~0.5 eV) than other structures. In an icosahedron, the dis-

tance from the center to the vertex is about 5% shorter than the distance between vertexes. With the small carbon atom at the center of the icosahedron, the stability is enhanced, which has been demonstrated by *ab initio* molecular dynamics simulations at temperatures up to 1000 K.⁷

Recently,¹² the structures of the Al_{12}X clusters were experimentally studied by photoelectron spectra (PES). Based on the well-understood PES of the icosahedral Al_{13}^- cluster,¹² one could deduce that the structure of the Al_{12}C^- cluster is nonicosahedral, since its photoelectron spectrum is quite different from that of the Al_{13}^- cluster. However, because of the extra-electron on Al_{12}C^- , the geometrical structure of Al_{12}C^- is not necessarily the same as that of the neutral and icosahedral Al_{12}C cluster, as predicted by theoretical calculations. It is important for interpreting the experimental spectra and for verifying previous theoretical results that whether there is a structural difference between Al_{12}C and Al_{12}C^- . In this paper, we present DFT results on the atomic structures of the Al_{12}C and Al_{12}C^- clusters, which confirm that the structure of the Al_{12}C cluster is icosahedral-like, in agreement with previous studies, and the structure of Al_{12}C^- is nonicosahedral, in agreement with the PES experiments.

II. CALCULATION DETAILS

Our calculations are based on the density functional theory^{20,21} with the spin-polarized generalized gradient approximation (GGA),^{22,23} as implemented in the Vienna *ab initio* Simulation Package (VASP).^{24,25} The wave functions are expanded in a plane wave basis with an energy cutoff of 286 eV. The atomic positions are optimized by conjugated gradient method with the energy convergence up to 0.005 eV. We use a large super cell with a lattice constant 14 Å, to make the interaction between the cluster and its periodic images negligible. The Vanderbilt ultrasoft pseudopotential²⁶ is used to describe the interaction between the core and valence electrons. Only the Γ point is used in the summation of the Brillouin zone of the simulation cell.

To test the accuracy of the theoretical method and the pseudopotentials, we have calculated the interatomic distance in the dimer Al_2 and AlC . The results are 2.49 Å for Al_2 and 1.96 Å for AlC , in good agreement with the experimental values^{27,28} of 2.47 Å and 1.96 Å. The calculated lattice constants for fcc-Al and diamond C solid are 4.05 Å and

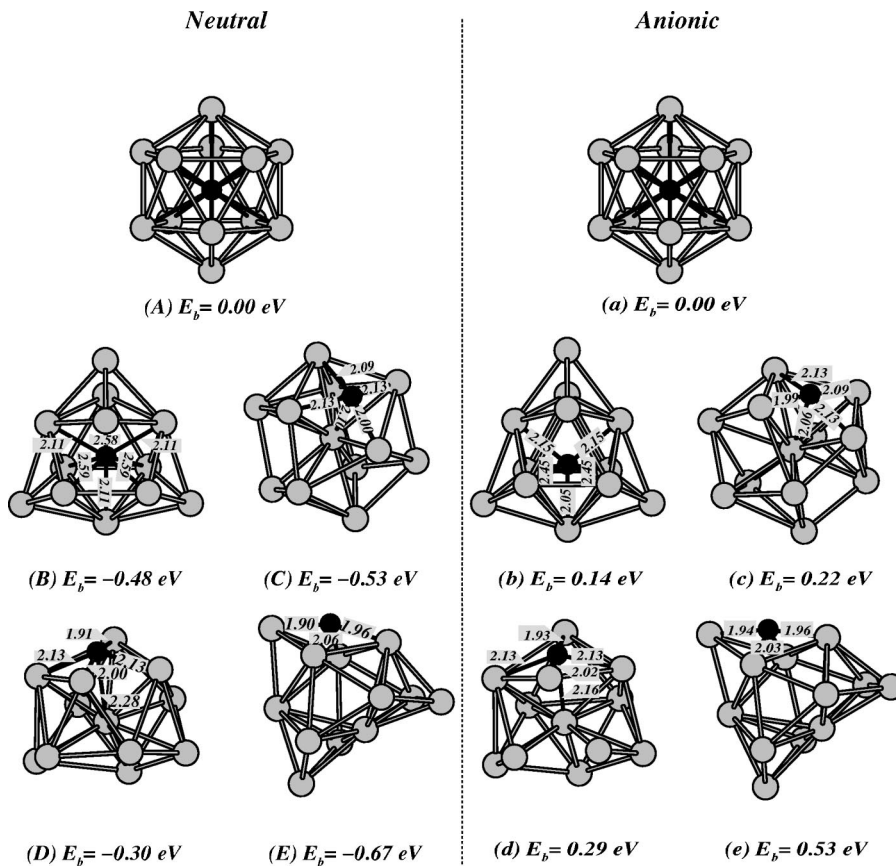


FIG. 1. Schematic structures obtained for the Al_{12}C and Al_{12}C^- clusters. The gray dots for Al atoms, and black dots for carbon atoms. Structure A, B, C, D, E are for the neutral clusters, and structure a, b, c, d, e are for the corresponding charged clusters. The binding energy of structure A and structure a is set as the reference energy for the neutral and charged cluster, respectively. The numbers in the figure show the distance (in Å) between the carbon atom and its neighbors.

3.57 Å, respectively, in favorable comparison with the experimental results²⁹ of 4.05 Å and 3.57 Å.

III. RESULTS AND DISCUSSIONS

We first re-examined the structure of Al_{13} cluster by conjugated gradient (CG)³⁰ and simulated annealing methods. The initial configurations include some high symmetric structures, such as I_h , O_h , D_{5h} , and D_{3h} . Many initial structures with low symmetry are also constructed with the atomic positions randomly displaced. None of the optimized structures obtained is more stable than the distorted icosahedral structure. Thus the present results confirm that Al_{13} cluster with a structure of distorted icosahedron (I_h) has the largest binding energy, as previously reported.^{3,4,31}

An extensive search also shows that Al_{12}C cluster prefers an icosahedral structure. To find out the most stable structure for Al_{12}C , we have used the same procedure as in searching the ground state structure of Al_{13} . The obtained Al_{12}C structures with larger binding energies are shown in Figs. 1(a)–1(e). The structure with carbon atom at the center of the icosahedron is the most stable, all other isomer structures have binding energies about 0.3–0.6 eV smaller. Only the largest binding energy structure has a very high symmetry, with C–Al distance of 2.5 Å. While all other isomers have very low symmetries.

In most of the isomers, the carbon atom stays on the surface of the cluster, as shown in Fig. 1, which has about 4–9 neighboring Al atoms, in contrast to the 12 neighboring Al atoms in the icosahedral structure. The C–Al distance is

shorter in the former, ranging from 2.4 Å to 2.0 Å. A significant HOMO-LUMO gap has been found for all the obtained structures of Al_{12}C cluster (see Table I). In the icosahedral cluster with carbon atom located at the center [Fig. 1(a)], we find a gap of 2.0 eV, in close agreement with previously reported value.⁴ However, the gap in all other isomers is reduced to 0.5–1.3 eV, suggesting a corresponding reduction in stability.

Introducing an extra electron to the Al_{12}C cluster drives the carbon atom from the cluster center to the surface. To determine the ground state structure of Al_{12}C^- , we have optimized the atomic structure of Al_{12}C^- with many different initial configurations, including all the isomer structures of the neutral Al_{12}C cluster. The structures with the larger binding energies are also shown in Figs. 1(a)–1(e), and these structures are very similar to those optimized for the neutral Al_{12}C , with only small variations in bond angles and bond lengths. However, the relative stability among the structures for the anionic Al_{12}C^- is quite different from that of the neutral cluster. Although the icosahedral structure, which is the most stable neutral cluster, is still an isomer, a few other structures with much lower symmetry are found with larger binding energies. For all the structures shown in Figs. 1(a)–1(e), the binding energies are quite close, only with small difference around 0.5 eV. Generally, structures with the carbon atom located at the cluster center are lower in binding energy than those with the carbon atom on the cluster surface. This is in sharp contrast to the neutral cluster, in which the carbon atom prefers to be at the center. Thus the charging pushes the carbon atom to the cluster surface. In fact, the

TABLE I. Calculated properties of Al_n and $\text{Al}_m\text{C}(\text{Al}_m\text{C}^-)$ clusters ($n=2, 13$; $m=1, 4, 12$). E_{bin} (eV) is the total binding energies of the cluster, E_{gap} (eV) is the HOMO-LUMO gap, N is the number of nearest neighbors of the C atom in $\text{Al}_m\text{C}(\text{Al}_m\text{C}^-)$ clusters, while in the structure of Al_{13} it indicates the number of neighbors for the central Al atom. R (Å) is the distance between the carbon atom and its neighbors.

Clusters		GGA					Ref.		
		N	R			E_{bin}	E_{gap}	R	E_{bin}
Al ₂			2.48			1.87		2.47 ^a	
AlC			1.96			4.00		1.955 ^b	
Al ₄ C		4	1.91	1.92	2 × 2.13	14.50		2.04 ^c	
Al ₄ C [−]		4	2 × 1.94 × 2 × 2.03			17.69		1.99 ^d	
Al ₁₃		12	6 × 2.65 6 × 2.70			34.85		2.8 ^e	35.97
Al ₁₂ C	A	12	3 × 2.53 9 × 2.54			38.83	1.96		
	B	9	3 × 2.11 2 × 2.58 4 × 2.59			38.35	1.34		
	C	5	2.00	2.09	2.10 2 × 2.13	38.30	0.94		
	D	5	1.91	2.00	2 × 2.13 2.28	38.53	1.17		
	E	4	1.90	1.96	2 × 2.06	38.16	0.52		
Al ₁₂ C [−]	a	12	12 × 2.55			40.90			
	b	7	2.05 2 × 2.15 4 × 2.45			41.04			
	c	5	1.99	2.06	2.09 2 × 2.13	41.12			
	d	5	1.93	2.02	2 × 2.13 2.16	41.19			
	e	4	1.94	1.96	2 × 2.03	41.43			

^aReference 27.

^bReference 28.

^cReference 32.

^dReference 34.

^eReference 4.

structure of Al_{12}C^- cluster had been reported by a few authors,³² however, all the previous results³² showed that carbon atom is inside the cluster, while we have shown that carbon atom should be on the surface of the cluster.

It should be noted that, for the neutral Al_{12}C cluster, the binding energy difference between the icosahedral structure and structure E (Fig. 1) is as large as ~ 0.7 eV. But in the anionic cluster, the energy ordering is reversed, with structure E more stable. In order to understand if this is really a charging effect and how much charge is needed to change the relative stability between the structure E and the icosahedral structure, we have calculated the binding energies for the two structures with different charging states, which are shown in Fig. 2. These two structures have comparable binding energies when ~ 0.75 electrons is added onto the Al_{12}C cluster. The more charged the cluster is, the more stable the structure E will be. It confirms that in the charged cluster carbon atom prefers to stay on the cluster surface.

The local bonding environment around the carbon atom in the ground state and various isomers are very much different. In the icosahedral [Fig. 1(A), Fig. 1(a)] structure, carbon atom has 12 neighbors, while in all other structures there are fewer neighbors. As shown in Table I, the binding energy can be qualitatively correlated with the number of neighbors of the carbon atom. However, the correlation is reversed for the charged cluster: the fewer neighbors the carbon atom has, the larger the binding energy will be. This observation can be qualitatively understood by the competition between metallic and covalent bonding of carbon atom. In the neutral cluster,

the metallic bonding between C and Al atom dominate due to shell closing with 40 electrons, and localized covalent bond is unfavorable. In this case, the binding energies increases with the number of neighboring Al atoms. When the cluster is negatively charged, the shell closing effect does not exist any more, and local covalent bonds can be formed around carbon atom. In such a case, the carbon atom should bond with only four neighboring Al atoms, in the most favorable structure. It has been shown previously that the Al_4C cluster is planar,^{32,33} and our calculations also produce a planar structure for Al_4C and Al_4C^- . The local structure around the carbon atom in Al_{12}C^- also favors a planer structure, very

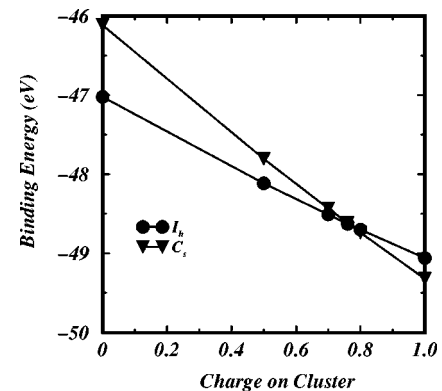


FIG. 2. Binding energies of Al_{12}C as a function of charges for icosahedral structure a and structure e. Structure e becomes a stable structure when the cluster is charged by around 0.75 electrons.

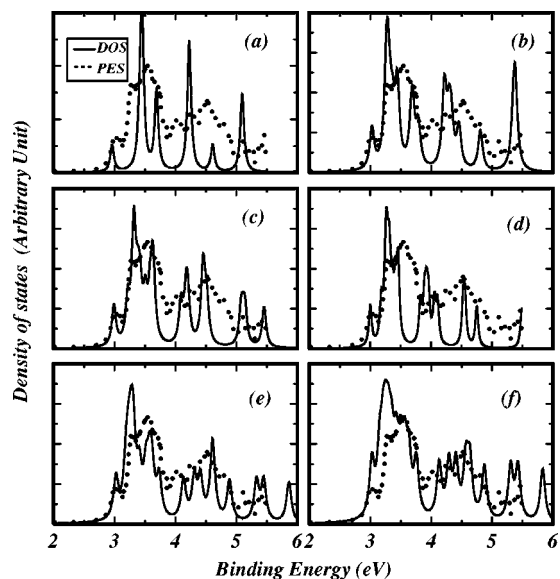


FIG. 3. Calculated electronic density of states (DOS) for the obtained structures of the Al_{12}C^- cluster. The experimental PES (Ref. 12) is also shown (dotted lines) for the comparison. A good agreement between DOS and PES can be observed in panel (e).

similar to the structure of the isolated Al_4C cluster, with similar bond lengths between the carbon atom and the neighboring Al atoms (see Table I).

Comparing the electronic density of states (DOS) and the photoelectron spectra (PES) (Ref. 12) confirms that the Al_{12}C^- cluster has the structure e. We have calculated the DOS by expanding the eigenvalues with Lorentz form. Both the calculated DOS and the measured PES are shown in Fig. 3. For better comparison, we have shifted DOS to align up the first peak, which is due to the extra electron in the anionic cluster. As shown in Fig. 3(a), the DOS for the icosahedral Al_{12}C^- is clearly different from the experimental PES, both in the peak positions and widths. Structure b [Fig. 3(b)] has a few peaks around 3.5 eV, which are not observed in the experimental PES. While the DOS of structure c, d, e [Figs. 3(c)–3(e)] are in better agreement with experimental PES, although there are some differences in 4.0–5.0 eV region. For structure c and structure d, the calculated DOS is much sharper, as compared with the PES. Overall, the best agreement between the calculated DOS and the experimental

PES in this region is found for structure e. Based on this qualitative comparison, we can exclude the high symmetrical structure of icosahedron and conclude that the most possible structure of the Al_{12}C^- cluster should be structure e, which is indeed the most stable structure in terms of binding energy.

We have also studied the thermal stability of structure e by performing molecular dynamics simulation at about 1000 K with a time step 1.0 fs. Structure e is quite stable during the simulation for 4 ps. Although the energy difference between structure e and other structures is not very large, we have not found structural transition to other isomers. Figure 3(f) shows the calculated DOS averaged from the simulated trajectory. The agreement between theoretical DOS and experimental PES is reasonably good.

IV. SUMMARY

Motivated by recent experimental observation, in which the structure of the Al_{12}C^- cluster was found to have a much lower symmetry than that of the icosahedral structure, we have studied the neutral and negatively charged Al_{12}C cluster, by using the density functional theory. Our results confirm that the neutral Al_{12}C has an icosahedral structure. With an extensive search of the Al_{12}C^- structure, a few structures are found with higher binding energies than that for the icosahedral structure. These structures are of low symmetry, and with fewer neighboring Al atoms around the carbon atom than that was found in the icosahedral structure. In the most stable structure found in the present studies, the carbon atom is located at the surface of the anionic cluster with four neighboring Al atoms and with bond lengths similar to those in the Al_4C or Al_4C^- clusters. The distance between the carbon atom and its nearest neighbor is much shorter (30%) than that in the icosahedral structure.

In conclusion, the structure of the anionic Al_{12}C^- is quite different from the structure of the neutral Al_{12}C cluster, which is confirmed by the good agreement between the PES and calculated DOS, indicating a significant structural effect induced by the charge added to the Al_{12}C cluster.

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