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Neutral and negatively charged $Al_{12}X$ (X=Si, Ge, Sn, Pb) clusters studied from first principles

S. F. Li[1,2] and X. G. Gong[1]

[1]*Surface Physics Laboratory, Department of Physics, Fudan University, Shanghai 200433, People's Republic of China*

[2]*School of Physics and Engineering, Zhengzhou University, Zhengzhou-450052, People's Republic of China*

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First-principles calculations have been performed to study the ground states of both neutral and anionic $Al_{12}X$ (X=Si, Ge, Sn, Pb) clusters. We find that both neutral and charged $Al_{12}Si$ cluster prefer icosahedral structure, in agreement with previous calculations. However, each of $Al_{12}X$ (X=Ge, Sn, Pb), either neutral or anionic clusters, shows symmetry of C_{5v} with atom X located on the cluster surface, contrary to the conclusion from the previous experimental work [Phys. Rev. B **65**, 153404 (2002)].

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The structure and stability of atomic clusters have been extensively studied in past decades. One of the reasons is that the physical and chemical properties of small clusters are very different from that of their bulk phases, so it is expected that cluster-assembled materials may show unique properties. Fullerenes[1] and their subsequent bulk synthesis[2] are typical examples in this area.

Extensive theoretical studies have been carried out to examine electronically stable metal clusters in this field.[3–18] One typical example is Al cluster,[6,12,17,18] which has been the subject of many theoretical and experimental studies. Since the valence electrons of Al are free-electron-like, the stability of small Al_n clusters has been explained by the jellium model.[14,15] The anion of the Al_{13} cluster, having 40 valence electrons, is characterized by a closed electronic shell with a significant gap between the highest-occupied and the lowest-unoccupied molecular orbitals (HOMO-LUMO),[4,16–20] which was confirmed by experiments.[17,18,13] Calculations based on density functional theory (DFT) show that the structure of the Al_{13}^- cluster is icosahedral-like, while the structure of the neutral Al_{13} cluster looks like a distorted icosahedron, due to Jahn-Teller effects. However, because of the Coulomb repulsion, the charged cluster Al_{13}^- cannot be used to assemble new materials despite high symmetry and high stability.

Some effort has been made to study neutral icosahedral clusters by substituting a tetravalent atom, such as C, Si, Ge, or Sn for one Al atom in Al_{13},[3–10] such doped $Al_{12}X$ (X=C, Si, Ge, Sn) clusters would have 40 valence electrons forming a closed electronic shell without any net charge. Previous DFT calculations[4,9,20] have indicated that the structures of $Al_{12}X$ (X=C, Si, Ge) clusters are icosahedral-like with large HOMO-LUMO gaps, whereas $Al_{12}Sn$ cluster has been predicated to have a structure, in which the Sn atom replaces a surface atom instead of the central atom of Al_{13}.[9] To our knowledge, no theoretical calculations for $Al_{12}Pb$ have been reported yet so far.

Recently, Li and Wang[12] predicated that $Al_{12}C^-$ cluster should have low symmetry rather than I_h high symmetry, which has been confirmed by our latest DFT calculations.[20] Meanwhile, based on the comparison between the photoelectron spectra (PES) of $Al_{12}X^-$ and Al_{13}^-, Li and Wang[12] argued that the anionic $Al_{12}X^-$ (X=Ge, Sn, Pb) clusters would have I_h symmetry with X located at the center of the clusters. However, from the available calculated results for $Al_{12}X$ (X=C, Si, Ge, Sn),[4,9,20] it seems that, with the size of X atom increasing, the tetravalent atom X will prefer occupying a position on the surface of $Al_{12}X$ cluster. Therefore, it is important and interesting to interpret the experimental spectra and to verify whether $Al_{12}X^-$(X=Ge, Sn, Pb) clusters are indeed I_h symmetry. In this paper, present theoretical results show that both $Al_{12}Si$ and its anion are icosahedral-like, in agreement with previous studies. While for both the neutral and anionic $Al_{12}X$ (X=Ge, Sn, Pb) clusters, our results confirm that the tetravalent atoms X are the favorite to locate on the cluster surface, the symmetry of the structure is therefore lowered to C_{5v} rather than I_h as derived from the experimental work.[12]

Present calculations are based on the density functional theory (DFT) (Ref. 21) with the spin-polarized generalized gradient approximations (GGA),[22,23] as implemented in the Vienna *ab initio* simulation package (VASP).[24] The wave functions are expanded in a plane wave basis with an energy cutoff of 241 eV. The interaction of valence electrons with the core is described with PAW method.[25] The atomic positions are optimized by conjugated gradient (CG) method[26] with the energy convergence up to 0.001 eV. We use a simple cubic supercell with the size of 15 Å to make the interactions between the cluster and its periodic images negligible. Only the Γ point is used for the summation of the Brillouin zone.

To test the accuracy of the plane wave basis set and the PAW potential used in our code VASP,[24] we have optimized the bond lengths of X_2 (X=Al, Si, Ge, Sn, Pb) dimmers and the lattice constants of their bulk counterparts, respectively. For Al, Si, Ge, Sn, Pb dimmers, the obtained bond lengths are 2.49, 2.22, 2.38, 2.76, and 2.92 Å, in good agreement with experimental values of 2.47, 2.24, 2.44, 2.76, and 2.93 Å, respectively.[27] The calculated lattice constants for Al, Si, Ge, Sn, Pb solids are 4.05, 5.47, 5.79, 6.63, and 4.98 Å, which are also in close agreement with experimental values of 4.05, 5.43, 5.66, 6.49, and 4.95 Å,[28] respectively.

In order to find the ground state structure, we have constructed and selected about 20 initial geometries for each $Al_{12}X$ (X=Si, Ge, Sn, Pb), on which the extensive optimizations are performed. We have also performed simulated annealing with initial temperature at 700 K.

For the neutral clusters, the extensive search shows that $Al_{12}Si$ cluster prefers icosahedral structure with Si located at

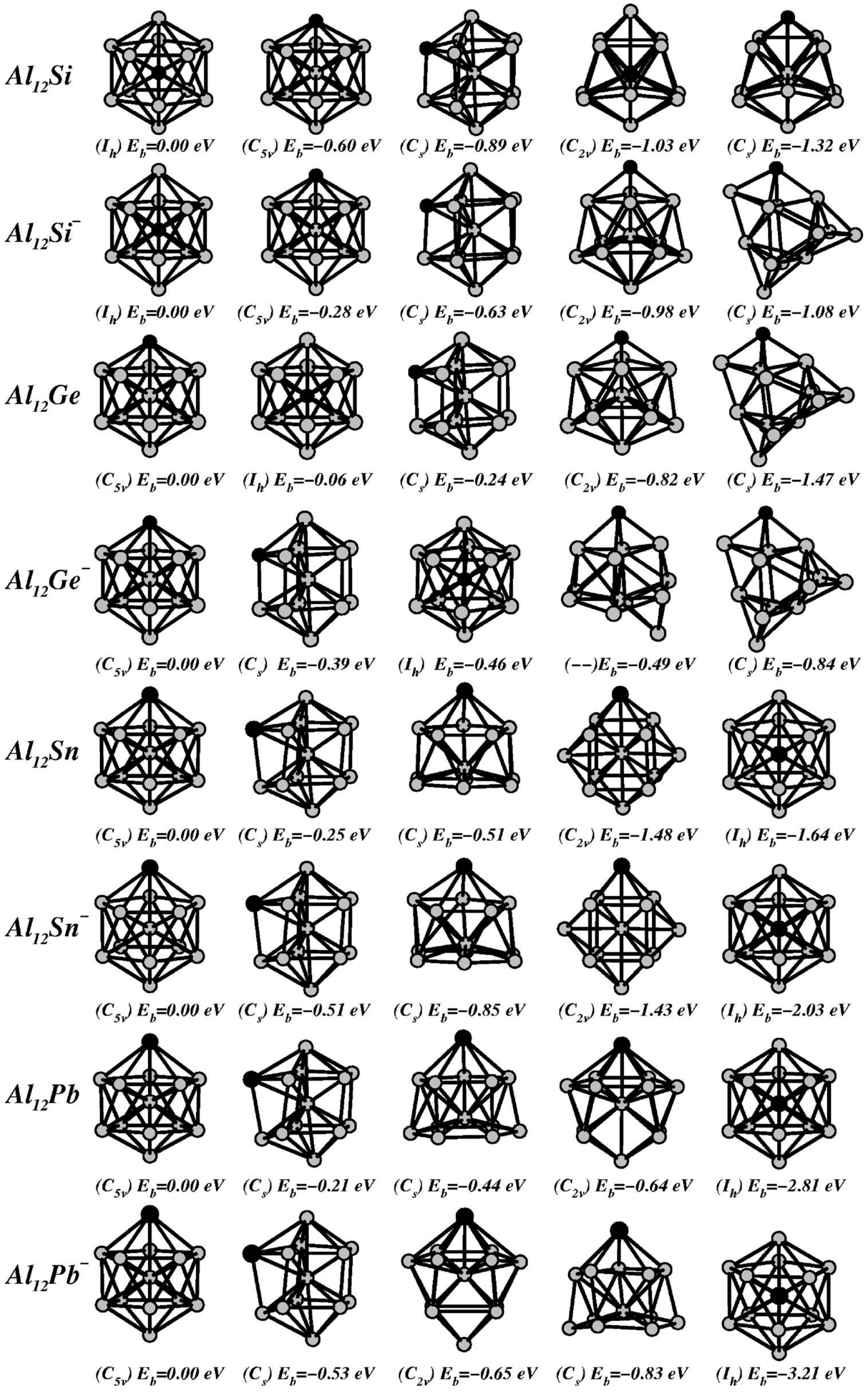

FIG. 1. Schematic showing of structures for the $Al_{12}X$ and $Al_{12}X^-$ (X=Si, Ge, Sn, Pb) clusters. The gray dots for Al atoms, and black dots for X atoms. The binding energies for the most stable structures of $Al_{12}X$ and $Al_{12}X^-$ are set as the reference energy, respectively.

the cluster center and $Al_{12}X$ (X=Ge, Sn, Pb) clusters favorite C_{5v} symmetry, with X atoms sitting at the cluster surface, as shown in Fig. 1 and Table I. In the present work, the structures of $Al_{12}X$ (X=Si, Ge, Sn, Pb) clusters have been studied by CG[26] method, with many initial configurations including the structures of both high and low symmetry, which is similar to what have been performed in our previous work for $Al_{12}C$.[20] All the structures for $Al_{12}X$ (X=Si, Ge, Sn, Pb) with larger binding energies are also shown in Fig. 1, and the average binding energies calculated with respect to the free atoms including the spin polarization corrections are also given in Table I.

We find that if we start with the $Al_{12}Si$ cluster, in which the Si atom is located at the center of an O_h-Al_{12} cage, the $Al_{12}Si$ will eventually relax to I_h symmetry, with binding energy of 37.44 eV and HOMO-LUMO gap of 1.97 eV, in-

TABLE I. Calculated properties of neutral and negatively charged $Al_{12}X$ (X=Si, Ge, Sn, Pb) clusters. $\bar{E}_b$ (eV), the average binding energy of $Al_{12}X$ clusters defined as $\bar{E}_b=-[E(Al_{12}X)-12E(Al)-E(X)]/13$; C and S in the bracket of symmetry label refer to center and surface site for atom X in the cluster, $\bar{R}$(Å), the average nearest bond length of X-Al, E_{gap} (eV), the HOMO-LUMO gap.

	Neutral				Anionic		
Clusters	Sym.	$\bar{R}$	$\bar{E}_b$	E_{gap}	Sym.	$\bar{R}$	$\bar{E}_b$
$Al_{12}Si$	I_h(C)	2.64	2.880	1.97	I_h(C)	2.65	3.052
	C_{5v}(S)	2.66	2.834	1.68	C_{5v}(S)	2.71	3.030
	C_s(S)	2.71	2.812	1.54	C_s(S)	2.61	3.003
	C_{2v}(C)	2.71	2.801	1.38	C_{2v}(S)	2.56	2.976
	C_s(S)	2.58	2.778	1.47	C_s(S)	2.50	2.968
$Al_{12}Ge$	C_{5v}(S)	2.75	2.796	1.62	C_{5v}(S)	2.80	2.998
	I_h(C)	2.67	2.791	1.99	C_s(S)	2.70	2.968
	C_s(S)	2.71	2.778	1.61	I_h(C)	2.80	2.962
	C_{2v}(S)	2.65	2.733	1.24	—(S)	2.63	2.960
	C_s(S)	2.57	2.683	0.45	C_s(S)	2.62	2.933
$Al_{12}Sn$	C_{5v}(S)	2.95	2.762	1.57	C_{5v}(S)	2.99	2.967
	C_s(S)	2.92	2.743	1.66	C_s(S)	2.92	2.928
	C_s(S)	2.94	2.723	1.42	C_s(S)	2.94	2.901
	C_{2v}(S)	2.88	2.648	0.89	C_{2v}(S)	2.93	2.857
	I_h(C)	2.75	2.636	1.85	I_h(C)	2.74	2.811
$Al_{12}Pb$	C_{5v}(S)	3.05	2.738	1.53	C_{5v}(S)	3.09	2.944
	C_s(S)	3.03	2.722	1.67	C_s(S)	3.02	2.903
	C_s(S)	3.02	2.704	1.39	C_{2v}(S)	3.22	2.894
	C_{2v}(S)	3.17	2.688	1.19	C_s(S)	3.01	2.880
	I_h(C)	2.79	2.522	1.83	I_h(C)	2.81	2.697

dicating the latter particularly stable, which is consistent with the earlier work.[4,9] The HOMO-LUMO gaps of the four isomers are smaller than that of I_h structure, and generally, the nearest bonding lengths of Si-Al in the isomers are longer than that in the I_h-$Al_{12}Si$, as shown in Table I. In our calculations, C_{5v}-$Al_{12}Ge$ is only about 0.06 eV more stable than I_h-Ge@Al_{12} cluster. However, with *ab initio* molecular-dynamics calculation, Kumar *et al.*[9] found that the binding energy of I_h-Ge@Al_{12} is about 0.43 eV more stable than that of C_{5v}-$Al_{12}Ge$ with the Ge atom migrating to the cluster surface. So, at present calculation levels, the C_{5v}-$Al_{12}Ge$ and I_h-$Al_{12}Ge$ may be degenerated in energy. Moreover, the HOMO-LUMO gap of 1.62 eV for C_{5v}-$Al_{12}Ge$ is obviously smaller than the gap of 1.99 eV in I_h-Ge@Al_{12}.

For larger atoms, Sn and Pb, the calculated results show that the binding energy of C_{5v}-$Al_{12}Sn(Pb)$ is about 1.64(2.81) eV higher than the icosahedral counterpart, with HOMO-LUMO gap of ~1.5 eV as listed in Table I. One can notice that in most of the isomers of $Al_{12}Sn(Pb)$ clusters, substitutional atoms of Sn and Pb prefer a position at the cluster surface, as shown in Fig. 1, indicating that I_h-$Al_{12}Sn(Pb)$ clusters are energetically less stable. One may also notice that the average nearest bonding lengths of X-Al in C_{5v}-$Al_{12}X$ (X=Ge, Sn, Pb) clusters are generally longer than that in their corresponding isomers, however, the Al-Al bonding lengths are shorter, making the overall binding energies larger. The above results suggest that larger substitutional atoms [(Ge)Sn and Pb, in the present work] with lower melting temperature tend to migrate on the surface of the binary cluster, in close agreement with the theoretical models of surface segregation in binary systems.[29]

For the anionic clusters, doping one electron to the $Al_{12}X$ (X=Ge, Sn, Pb) clusters enhances the tendency of the substitutional atoms migrating to the cluster surface. In order to find out the most stable structures of $Al_{12}X^-$, we have used the same procedure as that in searching the ground state structures of neutral $Al_{12}X$. The structures with larger binding energies are also shown in Fig. 1, and the average binding energies are listed in Table I. We find that I_h-Si@Al_{12}^- is more stable than C_{5v}-$Al_{12}Si^-$, however, the energy difference between these two structure is reduced to 0.28 eV from 0.60 eV corresponding to the neutral cluster. The stability of all the C_{5v}-$Al_{12}X^-$ clusters with X=Ge, Sn, Pb is enhanced upon the charging, as the energy difference between the C_{5v} structure and I_h symmetry for the anionic clusters have increased to 0.46, 2.03, and 3.21 eV from 0.06, 1.64, and 2.81 eV of the neutral clusters, respectively. The results for most of the isomers are similar to that of the ground state structure, as shown in Fig. 1.

We confirm that the $Al_{12}X^-$ (X=Ge, Sn, Pb) have C_{5v} symmetry, i.e., substitutional atoms located on the cluster surface other than at the cluster center as discussed by Li and Wang.[12] According to the experimental observation, it was deduced that the $Al_{12}X^-$ (X=Ge, Sn, Pb) clusters prefer I_h symmetry, based on the fact that the PES of $Al_{12}X^-$ is very similar to that of Al_{13}^-. We have calculated the DOS by expanding the eigenvalues with Lorentz form. Both the calculated DOS and the measured PES are shown in Fig. 2. For better comparison, we have also shown the PES and DOS of Al_{13}^- in panels (A) and (a). All the DOS for $Al_{12}X^-$ clusters have been shifted to align the first peaks, which are due to the extra electron in the anionic clusters. It can be seen from Fig. 2 that the overall PES of $Al_{12}X^-$ (X=Ge, Sn, Pb) clusters are very similar to that of the Al_{13}^-cluster. However, the agreement between the DOS of C_{5v}-$Al_{12}X^-$ (X=Ge, Sn, Pb) and the corresponding PES is obviously better than the DOS of the I_h-X@Al_{12}^- clusters. We notice that, the DOS of I_h-X@Al_{12}^- presented in Figs. 2(B)–2(D) show a multipeak characteristic in the range of 3.0–4.5 eV, which is due to the weak hybridization between p and s orbitals of Al atoms upon the addition of the substitutional atom X locating at the center of Al_{12} cage. While in C_{5v}-$Al_{12}X^-$ clusters, the strong hybridizations between the p and s orbitals of Al atoms upon the substitutional atom X located on the cluster surface makes the DOS showing single-peak characteristic in the range of 3.0–4.5 eV, as shown in Figs. 2(b)–2(d).

As pointed out by Li and Wang,[12] other isomers probably contribute to PES. To confirm this, we have calculated the DOS including both contributions from the ground state structure and some isomers with smaller binding energy. The results are presented in Fig. 3, which shows close agreement. As shown in Fig. 3(a), the small peaks in the range of about 3.2–3.7 eV are contributed by I_h-Ge@Al_{12}^- and C_s-$Al_{12}Ge^-$

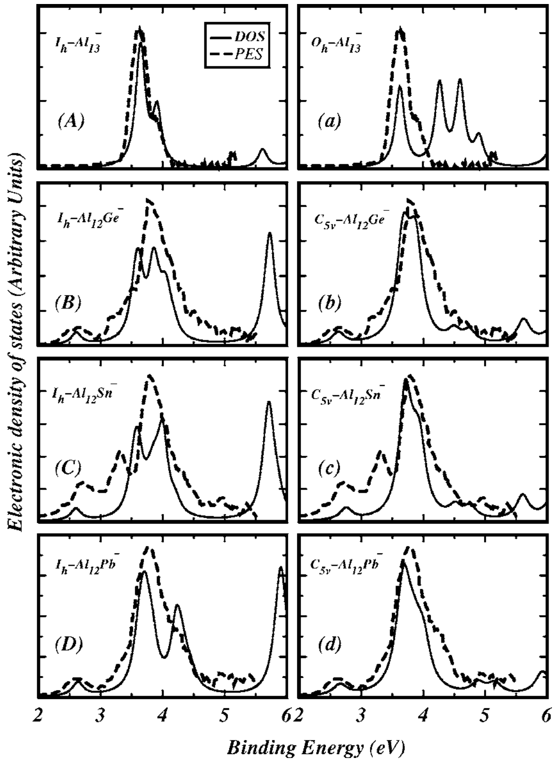

FIG. 2. Calculated electronic density of states (DOS) (solid lines) for I_h and C_{5v} symmetry $Al_{12}X^-$ clusters. A good agreement between DOS of C_{5v}-$Al_{12}X^-$ and the corresponding experimental PES (Ref. 12) can be observed in panel (b), (c), and (d) for $Al_{12}X^-$ (X=Ge, Sn, Pb), respectively.

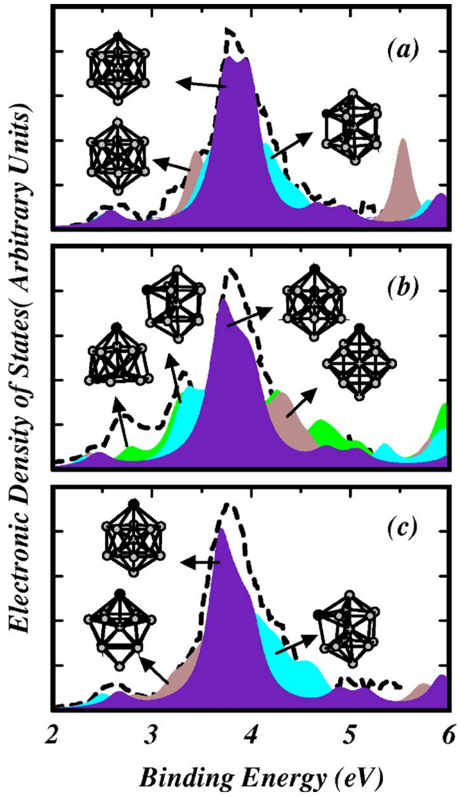

FIG. 3. (Color online) Total electronic density of states (DOS) contributed by different structures with larger binding energies for $Al_{12}X^-$ (X=Ge, Sn, Pb). The experimental PES (Ref. 12) is also shown (dashed lines) for comparison.

isomers, and the C_s-$Al_{12}Ge^-$ isomer also contributes to the peak in the range of 4.2–4.7 eV. It is clear that two distinct peaks are in the range of 2.5–3.5 eV for the PES of the $Al_{12}Sn^-$ cluster as shown in Fig. 3(b), though the main character of the DOS of C_{5v}-$Al_{12}Sn^-$ is in good agreement with the PES. Our results show that these two additional peaks are due to two isomers of C_s symmetry shown in Fig. 3(b). The peaks in the range of 4.0–5.0 eV come from the isomer of C_{2v} symmetry. From Fig.3(c), one can see that for the $Al_{12}Pb^-$ cluster the DOS fits even better with the PES, taking the contribution of C_{2v} isomer to the DOS in the range of 3.0–3.5 eV and that of the C_s isomer to the DOS in the range of 4.0–4.8 eV.

In summary, with first-principles calculations, we have studied the neutral and negatively charged $Al_{12}X$ (X=Si, Ge, Sn, Pb) clusters. We find that both the neutral and charged $Al_{12}Si$ clusters are of the I_h symmetry. However, with the size of the substitutional atom increasing, the substitutional atoms start to migrate to $Al_{12}X$ cluster surface. For the neutral $Al_{12}X$ (X=Sn, Pb) clusters, a few structures of lower symmetry have been found with larger binding energies than that of I_h symmetry. Doping one electron to $Al_{12}X$ (X=Ge, Sn, Pb) clusters strengthens the migration of the tetravalent atoms X from the center to surface of the cluster, resulting in C_{5v} symmetry rather than the I_h configuration deduced from the experimental observation.[12]

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