# *Ab initio* molecular-dynamics studies of doped magic clusters and their interaction with atoms

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We present results of the atomic and electronic structure of icosahedral $Al_{12}X$ ($X$=Si, Ge, and Sn) clusters using the *ab initio* molecular-dynamics method within the local density functional theory. Substitutional doping of a $Al_{13}$ cluster by a tetravalent atom leads to a substantial gain in energy in all the cases studied. Tin is found to have a lower energy at a vertex site in contrast to the central site for Si and Ge, leading to surface segregation of Sn in these clusters. Also in the case of a $Al_{13}Si$ cluster, Si occupies the central site of a capped icosahedral structure. These results when interpreted in terms of the interaction of closed shell clusters with atoms leads to a relatively strong interaction of $Al_{12}Si$ with Al as compared to the weak interaction of rare gas atoms with other elements. [S0163-1829(98)04104-6]

## I. INTRODUCTION

During the past few years much interest has grown in the understanding of the physical and chemical properties of metal clusters and their evolution to bulk behavior. One of the most important findings has been the observation of magic clusters of metals with 8, 20, 40, . . . , valence electrons. The stability of such clusters has been understood from a spherical jellium model[1,2] according to which a cluster is magic if the number of valence electrons is sufficient to completely fill an electronic shell, e.g., $1s, 1p, 1d, 2s, \ldots$. For some clusters, the geometric factor has been found to play an important role in the stability as highly symmetric clusters may be particularly stable. From both of these points of view the $Al_{13}$ cluster is interesting as it has 39 valence electrons which is just one short of the electronic shell completion and has been shown to have a nearly regular icosahedral geometry.[3,4] Ultraviolet photoemission spectroscopy (UPS) studies[5] show large electron affinity for $Al_{13}$ and indeed $Al_{13}^-$ has been found to be highly abundant in the mass spectra of Al cluster ions.[6] An interesting way to complete the electronic shell is by substitutional doping as the chemical bonding can lead[7] to further stability of a cluster. It is to be noted that Nakajima *et al.*[8] have found $Al_{12}B^-$ to be strongly abundant similar to $Al_{13}^-$.

In the case of $Al_{13}$, the electronic shell can be completed if an Al atom is replaced by a tetravalent atom such as Si, Ge, or Sn. Khanna and Jena[9] and Gong and Kumar[7] used this idea to study icosahedral $Al_{12}C$ and $Al_{12}Si$ clusters with the dopant at the center and indeed found these to be significantly lower in energy than $Al_{13}$. The center to vertex distance in an icosahedron is about 5% shorter than the vertex to vertex distance. Substitution of a smaller atom at the center is expected to contract vertex-vertex Al bonds which are strained in the $Al_{13}$ cluster. However, from these studies, it is not clear if the doping is preferred at the center or a vertex site of the icosahedral structure. The tetravalent impurity such as Si in these doped clusters appears to act as a metal

atom, though in bulk, Si is a covalently bonded semiconductor. Binary metal clusters are known to have the problem of segregation where the impurity atom can segregate at the surface. Here we study the nature of bonding in these doped clusters and show that Sn tends to segregate at the surface whereas Si and Ge prefer the central site.

Further to these studies, closed shell clusters have been attracting much attention due to the possibility of developing cluster assembled materials.[10,11] $Al_{12}X$ clusters, referred to as *superatoms*, are particularly interesting as these have high symmetry. Whether such *superatoms* would keep their identity upon interaction with other atoms/clusters is still not clear. An understanding of such interactions would help the development of novel cluster materials. We consider here the interaction of an Al atom with $Al_{12}Si$ and find that the interaction is weaker as compared to the corresponding value in aluminum clusters but is much stronger than the known behavior of rare gases. In Sec. II, we give the computational details while the results are presented in Sec. III.

## II. COMPUTATIONAL DETAILS

We have used the *ab initio* molecular-dynamics method[12,13] with the norm-conserving pseudopotentials[14] in the separable form[15] for the electron-ion interaction and a plane wave basis set with 11.5 Ry cutoff. The cluster is placed in a fcc supercell with periodic boundary conditions. The lattice constant is chosen to be 38.5 a.u. so that the interaction between the cluster and its periodic images is negligible. Only the $\Gamma$ point is used to represent the Brillouin zone of the molecular-dynamics supercell. Exchange correlation energy is calculated within the local density approximation (LDA) using the Ceperley and Alder[16] data as parametrized by Perdew and Zunger.[17]

## III. RESULTS

### A. Al−$X$ dimers

Table I shows the binding energies and bond lengths for $Al_2$, Al-Si, Al-Ge, and Al-Sn dimers. The binding energy for

TABLE I. Binding energy (BE) and bond lengths for Al-$X$ dimers.

| Cluster | BE (eV) | Bond length (a.u.) |
|---|---|---|
| Al$_2$ | 1.55 | 4.75 |
| Al-Si | 2.32 | 4.28 |
| Al-Ge | 2.31 | 4.28 |
| Al-Sn | 2.10 | 4.58 |

Al-Si and Al-Ge dimers is nearly the same and the bond is much stronger than in Al$_2$. The bond length is 10% shorter than its value in Al$_2$. For the Al-Sn dimer there is an elongation of the bond as compared to Al-Si and there is a decrease in the binding energy. However, the binding energy is still much larger and the bond is shorter as compared to Al$_2$.

### B. Al$_{12}$X clusters

Al$_{12}$X clusters with $X =$ Si, Ge, and Sn have been studied by taking a regular icosahedron structure with the impurity either at the center or a vertex site. The ions are displaced randomly and the energy is minimized with respect to the electronic and the ionic degrees of freedom. A cuboctahedral Al$_{12}$Si cluster with the Si atom at the center is also studied and is found to relax to the icosahedral structure, indicating the latter to be particularly stable. The binding energies of clusters are calculated with respect to the free atoms including the spin polarization corrections and are given in Table II. It is noted that in all the three cases, doping leads to a substantial gain in the binding energy. Our results on Al$_{12}$Si and Al$_{12}$Ge are in agreement with the earlier work of Gong and Kumar[7] obtained from a linearized combination of atomic orbital method. As in the case of dimers, we find that both Si and Ge behave very similarly and prefer the central site of the icosahedron. However, Sn prefers a vertex site leading to the segregation of the Sn atom at the surface in this cluster. Both Si and Ge are slightly smaller in size and have higher melting temperatures than Al. On the other hand, Sn is oversized and has a lower melting temperature than Al. According to theoretical models of surface segregation in binary systems[19] the larger atom or constituent with lower melting temperature tend to segregate at the surface. Our result on Sn segregation is, therefore, in agreement with these theories.

The calculated structures of the clusters are shown in Fig. 1(a) and the corresponding bond lengths are given in Table III. Our calculations show that in Al$_{13}$ one of the golden rectangles of the regular icosahedron gets slightly distorted with the angles 88.77° and 91.23° and the bond lengths vary between 5.05 and 5.65 Å. When a Si or Ge atom is doped at the center, there is a slight contraction of the center to vertex bond length as compared to Al$_{13}$ which is expected from the smaller size of Si and Ge atoms and also from the behavior in dimers. This leads to a better bonding between the vertex Al atoms also. In the case of the doping at the vertex site, the relaxed cluster has a fivefold symmetry. An interesting finding is that one of the Al-Al bonds [10–12 in Fig. 1(a)] on the opposite side of the dopant gets significantly contracted. We trust that it is due to the charge density variations induced by the impurity atom in the cluster. Also the bond length be-

TABLE II. Binding energy (BE) and segregation energy ($Q$) for Al$_{12}$X clusters. A negative value of $Q$ means that segregation of $X$ is favorable at the surface. C and S in the second column refer to center and surface sites for atom $X$ in the icosahedron. C1 corresponds to Si at the center with Al at the bridge site and S1 (S2) correspond to Si at the bridge (threefold) site on the Al$_{13}$ cluster.

| Cluster | Position of $X$ | BE (eV) | $Q$ (eV) |
|---|---|---|---|
| Al$_{13}$ | | 37.54 | |
| | | 35.97[a] | |
| | | 36.66[b] | |
| | | 36.40[c] | |
| | | 38.61[d] | |
| Al$_{12}$Si | C | 40.46 | |
| | | 39.20[a] | |
| Al$_{12}$Si | S | 39.83 | 0.63 |
| Al$_{12}$Ge | C | 40.27 | |
| | | 39.12[a] | |
| Al$_{12}$Ge | S | 39.84 | 0.43 |
| Al$_{12}$Sn | C | 39.28 | |
| Al$_{12}$Sn | S | 39.70 | −0.42 |
| Al$_{13}$Si | C1 | 42.67 | |
| Al$_{13}$Si | S1 | 42.11 | 0.56 |
| | S2 | 42.08 | 0.53 |
| Al$_{14}$ | | 40.96 | |

[a]Discrete variational method (DVM)-LDA, Gong and Kumar, Ref. 7.
[b]Gaussian-local spin density, Khanna and Jena, Ref. 11.
[c]DVM-X$\alpha$, Cheng et al., Ref. 18.
[d]Car-Parrinello-LDA, Yi et al., Ref. 4.

tween the impurity and the atom at the center is significantly smaller (4.74 Å) than its value 5.04 Å when the impurity is at the center. It can be understood within the effective medium theory[20] according to which an impurity atom tries to find its density corresponding to maximum bonding. Due to the missing atoms on the vertex, there is a decrease in the embedding charge density which is compensated by a reduction in the Al-$X$ bond length. It is interesting to note that with Sn doping at the center, the largest Al-Al bond is
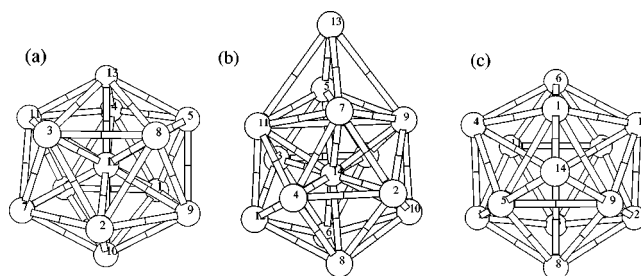


FIG. 1. (a) Icosahedral structure for Al$_{13}$ and Al$_{12}$X clusters. The impurity atom $X$ is placed at site 12 (center) or 13 (vertex). (b) Interaction of an Al or Si atom at the bridge site (atom 13) of Al$_{12}$Si or Al$_{13}$ cluster, respectively. (c) Structure for the Al$_{14}$ cluster. It has threefold symmetry. The central atom (not seen in the figure) of the Al$_{13}$ icosahedron is beneath atom 14.

TABLE III. Bond lengths for different clusters. The notation for the position of $X$ is the same as given in Table II. In column 2, the list of bonds are given which have numbering of atoms as given in the figures for the clusters.

| Position of $X$ | Bonds | $Al_{12}Si$ | $Al_{12}Ge$ | $Al_{12}Sn$ |
|---|---|---|---|---|
| C | center-vertex | 5.04 | 5.04 | 5.13 |
|  | vertex-vertex | 5.30 | 5.30 | 5.39 |
| S | 12-13 | 4.71 | 4.74 | 5.01 |
|  | 10-12 | 4.96 | 4.95 | 4.95 |
|  | 3-12,4-12,5-12,8-12,11-12 | 5.08 | 5.06 | 5.07 |
|  | 1-12,2-12,6-12,7-12,9-12 | 5.08 | 5.08 | 5.11 |
|  | 3-13,4-13,5-13,8-13,11-13 | 5.15 | 5.18 | 5.40 |
|  | 1-4,1-5,2-3,2-8,3-7,4-6 5-9,6-11,7-11,8-9 | 5.29 | 5.29 | 5.27 |
|  | 1-10,2-10,6-10,7-10,9-10 | 5.33 | 5.31 | 5.27 |
|  | 3-8,3-11,4-5,4-11,5-8 | 5.33 | 5.33 | 5.40 |
|  | 1-6,1-9,2-7,2-9,6-7 | 5.38 | 5.37 | 5.36 |

shorter than its value in $Al_{13}$. However, an increase in the center to vertex distance upon doping leads to the segregation of Sn in this cluster.

The electronic charge density surfaces for the $Al_{12}Si$ cluster are shown in Fig. 2 along with those obtained for $Al_{13}$ at three different values of the density. It is clear that Si impurity in the cluster behaves quite similar to Al atom at the center and the bonding between Al and Si is metallic in nature.

### C. $Al_{13}Si$ cluster and superatom-atom interaction

We have studied $Al_{13}Si$ and $Al_{14}$ clusters in order to obtain the segregation behavior with size. The additional atom is placed on a bridge or a threefold site of the icosahedral $Al_{13}$ or $Al_{12}Si$ cluster. These results are then used to study the interaction of a closed shell cluster such as $Al_{12}Si$ with other atoms.

Interaction of a Si atom with an $Al_{13}$ cluster has been recently studied by Kumar[3] who found that the bridge site
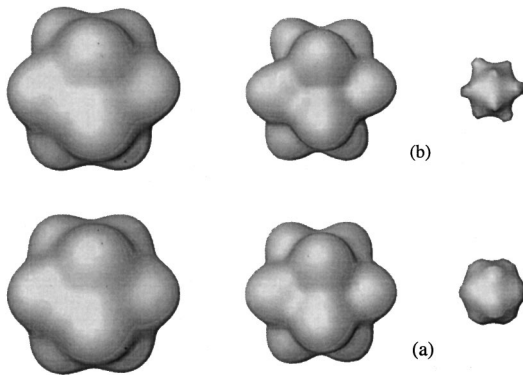


FIG. 2. Electronic charge density surfaces for (a) $Al_{12}Si$ with Si at the center of the icosahedron with densities 0.0105, 0.0225, and 0.0350 $e/\Omega$ (left to right) and (b) $Al_{13}$ with densities 0.0101, 0.0231, and 0.0348 $e/\Omega$, $\Omega$ being the volume of the primitive cell.

TABLE IV. Binding energy of Al on $Al_{12}Si$ and Si on $Al_{13}$ clusters.

| Cluster | Position of $X$ | BE (eV) |
|---|---|---|
| $Al_{12}Si$-Al | C1 | 2.20 |
| $Al_{13}$-Si | S1 | 4.58 |
| $Al_{13}$-Al | S2 | 3.42 |

[Fig. 1(b)] is only 0.03 eV lower in energy than the threefold site [Fig. 1(c)], suggesting that a Si atom on the surface of this cluster could be quite diffusive. We treat the $Al_{13}Si$ cluster as if an Al atom is interacting with a $Al_{12}Si$ cluster. In this case we have considered both a bridge as well as a threefold site for Al. However, Al at the threefold site converges to the bridge site after relaxing the cluster.

$Al_{12}Si$ has a closed shell electronic configuration and therefore, one may expect it to interact weakly with other atoms. Our calculated binding energies are given in Table IV. We find that the structure with a Si atom at the center is lower in energy by 0.55 eV than the one where a Si atom is interacting with an $Al_{13}$ cluster at the bridge site [Fig. 1(b)]. Therefore, for $Al_{13}Si$ also, we find that Si prefers a higher coordination site as in $Al_{12}Si$. The gain in energy by substitutional doping of Si in $Al_{14}$ is 1.71 eV as compared to 2.92 eV for $Al_{13}$ which is quite large and it shows how significantly seemingly similar systems could differ due to quantum effects. Considering the $Al_{13}Si$ cluster from the point of view of *superatom-atom interaction*, the binding energy of Al on $Al_{12}Si$ is 2.2 eV. This energy is much smaller than the interaction energy (3.42 eV) of an Al atom on $Al_{13}$. Also the binding energy of a Si atom on $Al_{13}$ is 4.58 eV. Therefore, the $Al_{13}$ cluster is very reactive but $Al_{12}Si$ interacts relatively weakly with other atoms. However, from the binding energy as well as bond lengths of 5.11 a.u. [bonds 5–13 and 7–13 in Fig. 1(b)] we conclude that this interaction is chemical in nature rather than van der Waals type known for rare gases, though in both the cases there is a $p$ shell closing. A similar result was obtained[21] from the study of an fcc solid formed from $Al_{12}Si$ clusters.

### IV. CONCLUSION

Substitutional doping of the icosahedral $Al_{13}$ cluster with a tetravalent atom such as Si, Ge, and Sn is shown to improve the binding of the cluster. This result is in agreement with the earlier work on C and Si doping. The impurity atom in this cluster behaves as a metal atom though Si and Ge are covalently bonded in bulk. Si and Ge are found to prefer the central site of the icosahedron whereas Sn prefers a vertex site. This segregation of Sn is consistent with the models of surface segregation in binary alloys. The segregation behavior is found to continue for $Al_{13}Si$ cluster in which case also a Si atom occupies a high coordination site. Considering the $Al_{13}Si$ cluster as an Al atom interacting with a $Al_{12}Si$ superatom, we find that the binding of an Al atom to the superatom is much weaker as compared to an $Al_{13}$ cluster. However, this bonding is chemical in nature as compared to the van der Waals bonding known for inert gas atoms.

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