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Enhanced Stability of Magic Clusters: A Case Study of Icosahedral $Al_{12}X$, X =B, Al, Ga, C, Si, Ge, Ti, As

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We present results of the electronic structure and stability of some 40 valence electron icosahedral $Al_{12}X$ (X =B, Al, Ga, C, Si, Ge, Ti, and As) clusters within the local spin density functional theory. It is shown that the stability of the Al_{13} cluster can be substantially enhanced by proper doping. For neutral clusters, substitution of C at the center of the icosahedron leads to the largest gain in energy. However, $Al_{12}B^-$ is the most strongly bound in this family. These results are in agreement with the recent experiments which also find $Al_{12}B^-$ to be highly abundant.

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A few years ago Knight *et al.* [1] observed Na and K clusters with $8, 20, 40, \ldots$ atoms to be particularly abundant. The stability of these so-called magic clusters has been understood from a spherical jellium model [1, 2] according to which clusters whose number of valence electrons is sufficient to completely fill an electronic shell, e.g., $1s$,$1p$,$1d$, ..., are magic. A classic example for which this model should be applicable is aluminum. However, none of its clusters satisfy the criterion of shell completion, though Al_7, Al_{13}, and Al_{23} do fall close to it. One way to complete the shell is by doping. In fact Jena and co-workers [3] recently used this idea to study the stability of icosahedral $Al_{12}C$ cluster with C at the center and indeed found it to be ≈ 1 eV lower in energy than Al_{13} . However, contrary to other known results such as C embedded in a homogeneous electron gas [4] and C at the center of an octahedral Ni cluster [5], surprisingly they obtained the Al-C bond length to be slightly longer than the corresponding Al-Al bond length in Al_{13}. As the center to vertex distance R is about 5% shorter [6] than the vertex to vertex distance in an icosahedron, one should have expected a contraction in R with the substitution of C, a smaller atom, at the center of the icosahedron. Besides the search for very stable clusters, icosahedral Al clusters are also of interest for understanding the stability of Al based quasicrystals. Here we present results of a systematic study of some icosahedral $Al_{12}X$ clusters with X =B, Al, Ga, C, Si, Ge, As, and Ti. Our results not only show a contraction of the bond length with C doping, but also a substantial gain of nearly 4 eV in the binding energy which should make this cluster very promising for making new cluster assembled materials.

We have used a symmetrized linear combination of atomic orbitals for the wave functions,

$$\Psi_i^{\Gamma} = \sum_{\mu n l \gamma} C^i_{\mu n l \gamma} \phi^{\Gamma\gamma}_{\mu n l},$$

where $\phi^{\Gamma\gamma}_{\mu n l}$ is the basis function symmetrized according to the irreducible representation of the point group embodied by the cluster. The basis set was chosen to be the numerical solution of the self-consistent-field Schrödinger equation for the atom and except for Ti (in which case the d orbital was also included) in all cases only the s and the p orbitals were taken to represent the valence electron wave functions. μ is the atom index and n and l are the principal and angular quantum numbers for the atomic orbitals. With these wave functions the Kohn-Sham equations have been solved self-consistently using the discrete variational method [7(a)] by the quasirandom integration scheme [7(b)] within the local spin density approximation. We have used the Barth-Hedin [8] form for the exchange-correlation energy and frozen core approximation in our calculations. Since several theoretical studies [9] suggest an icosahedral structure for Al_{13}, we have used in this study a regular icosahedron structure for all the clusters with the impurity at the center. The optimized structure has been obtained by calculating the binding energy as a function of R for each cluster. In order to compare our results with other calculations we calculated the binding energy, ionization potential (IP), and the electron affinity (EA) for Al_{13}. The EA (IP) is taken as the difference of the binding energies of Al_{13} and Al_{13}^- (Al_{13}^+ and Al_{13}) clusters at equilibrium. These results are presented in Table I. It is clear that the agreement is quite good, although different basis functions and exchange-correlation approximations are used in different calculations.

In Fig. 1 we present the binding energies as a function of R for all the clusters we have studied except $Al_{12}Ti$ and in Table II results are presented for the lowest binding energies, the equilibrium center to vertex distance R_0, and the energy gap E_g between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Our calculations indicate that one can gain in binding energy substantially over that of Al_{13} by adding an electron or by doping. Among all the neutral clusters, we find $Al_{12}C$ to be the most compact and with the highest binding energy. This is about 1.4 eV larger than for $Al_{12}Si$ and $Al_{12}Ge$ which are nearly degenerate and 4.5 eV larger than for Al_{13}. This can be understood as follows: (1) There is a large gain in energy of about 3

TABLE I. Comparison of the equilibrium binding energy (BE), nearest neighbor distance (R_0), ionization potential (IP), and electron affinity (EA) for icosahedral Al_{13} cluster with other calculations (Ref. [9]).

	Present calculations	Khanna *et al.*	Cheng *et al.*	Yi *et al.*
BE (eV)	35.97	38.6	36.4	38.6
R_0 (a.u.)	5.32	5.10	5.25	
IP (eV)	7.10	6.8	6.0	7.15
EA (eV)	4.36		2.9	3.81

TABLE II. The calculated properties of $Al_{12}X$ clusters.

Cluster	BE (eV)	R_0 (a.u.)	E_g (eV)	B (eV/a.u.^{3})
Al_{13}	35.97	5.32	0.0	0.108
Al_{13}^-	40.33	5.20	1.72	0.176
$Al_{12}Ga^-$	40.99	5.16	1.79	0.101
$Al_{12}B^-$	43.92	5.00	2.10	0.173
$Al_{12}C$	40.56	5.05	2.21	0.124
$Al_{12}Si$	39.20	5.22	1.99	0.189
$Al_{12}Ge$	39.12	5.22	2.01	0.187
$Al_{12}Ti$	36.41	5.68	0.0	
$Al_{12}As^+$	31.46	5.39	1.90	0.093
$Al_{12}As$	38.21	5.32	0.0	0.098
Bulk Al	3.39	5.41		0.067

eV when the Al atom at the center is replaced by Ge, Si, C,... without allowing any relaxation of the cluster and (2) optimization of the bond lengths leads to a further gain in energy by about 0.5 eV. The large contribution due to chemical bonding as obtained here is consistent with the fact that compounds of Al with Si and C have large heats of formation. These results, though they differ from those of Khanna and Jena [3], are consistent with the general trends obtained from embedding Al, Si, and C in a homogeneous electron gas [4]. According to these calculations, the embedding energies of Al, Si, and C are in ascending order. As the optimal binding energy for Ge, Si, and C is obtained for successively larger densities than for Al, a contraction of the cluster not only facilitates this but also improves bonding between the twelve Al atoms as in Al_{13} these are strained. This leads to a large gain in the binding energy of these clusters. These results are also consistent with the behavior of C in Ni. Among several impurities in the *interstitial site* (this should be contrasted with the substitutional site in our case) of an octahedral Ni cluster, studied by Painter and Averill [5], the gain in energy for C is the largest while the expansion of the Ni cluster is the minimum and only marginal. As carbon is much smaller than Si or Ge, compression of the $Al_{12}C$ cluster costs much less as compared to $Al_{12}Si$ or $Al_{12}Ge$, whereas an expansion leads to a rapid decrease in the binding energy for $Al_{12}C$. Thus if R for $Al_{12}C$ is taken to be slightly larger than for Al_{13}, then the gain in energy for $Al_{12}C$ is about 2 eV which is closer to the value obtained by Khanna and Jena. Whether the central site is the most favored site for C is unclear. However, *ab initio* molecular dynamics simulations [10] up to 2000 K show that the carbon atom remains at the central site.

For the negatively charged clusters, Al_{13}^-, $Al_{12}B^-$, and $Al_{12}Ga^-$ with 40 valence electrons, we find a contraction in the bond length and a gain in energy by a few eV as compared to the neutral clusters. Whereas for positively charged clusters such as $Al_{12}As^+$, there is an increase in the bond length and the binding energy decreases. In order to understand and to find the distribution of excess charge, we have shown in Fig. 2 the difference of the electron charge densities between the charged

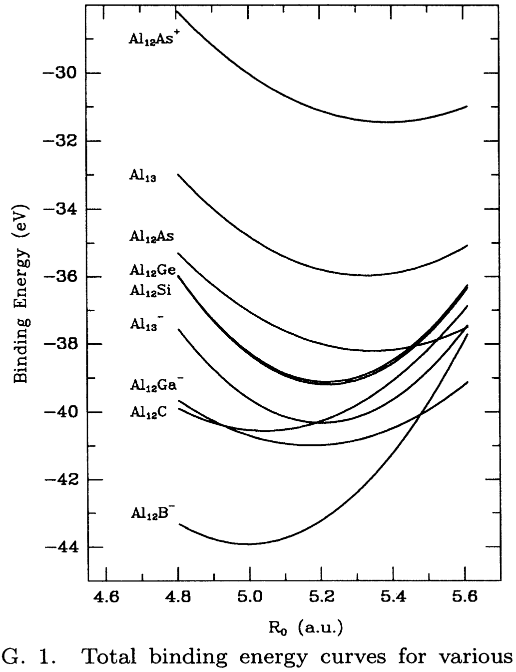

FIG. 1. Total binding energy curves for various $Al_{12}X$ clusters as a function of distance from the center to the vertex of an icosahedron.

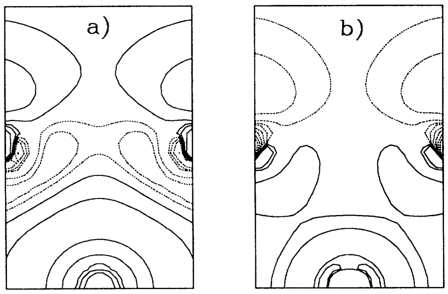

FIG. 2. The contour plots of the difference charge density. (a) Al_{13}^--Al_{13} and (b) $Al_{12}As^+$-$Al_{12}As$. The full (broken) curves indicate excess of negative (positive) charge.

and neutral clusters for Al_{13} and $Al_{12}As$. It is clearly seen that the negative charge is distributed around the atom at the center and outside the vertex atoms whereas the positive charge is distributed completely outside the vertex atoms. The excess positive charge thus leads to a repulsion between the vertex Al atoms and consequently to an increase in the bond length, whereas the negative charge provides extra binding. Thus we find $Al_{12}B^-$ to be the most stable cluster in the whole family. This agrees with their large abundance in the mass spectrometer [11].

The most interesting point is that Al_{13}^-, $Al_{12}B^-$, $Al_{12}Ga^-$, $Al_{12}Si$, $Al_{12}Ge$, $Al_{12}C$, and $Al_{12}As^+$, all with 40 valence electrons, are isoelectronic and have $E_g \approx 2.0$ eV (Fig. 3). This large gap between HOMO and LUMO would make these clusters behave like an inert gas atom and therefore relatively unreactive. It is to be noted that in a study of Mg clusters Kumar and Car [12] found the magic clusters of Mg to have a large HOMO-LUMO gap and lower Mg on Mg_n chemisorption energy as compared to neighboring clusters. In fact Leuchtner, Harms, and Castleman [13] have studied the behavior of anion aluminum clusters when exposed to oxygen. They found only Al_{13}^- and Al_{23}^- left after the reaction with O_2, whereas other anion clusters reacted with oxygen. Our results are also in agreement with the recent experiments by Nakajima *et al.* [11], who found Al_{13}^- and $Al_{12}B^-$ clusters to be magic.

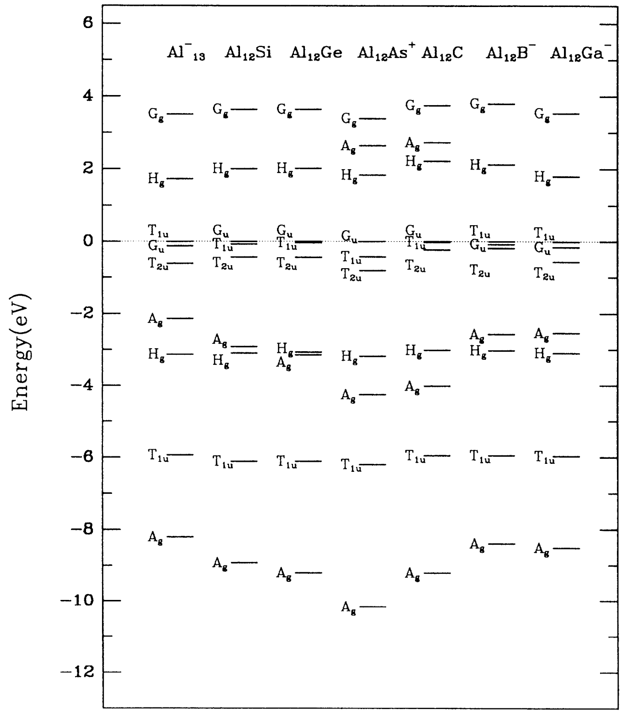

FIG. 3. One electron energy levels for the magic $Al_{12}X$ clusters.

In all the clusters with 40 valence electrons discussed above, the spin-up and spin-down states are degenerate. But in $Al_{12}As$ and Al_{13} clusters which do not have 40 valence electrons and could not completely fill a shell, there is a small splitting between the up and down states. This is shown in Fig. 4. Comparing energy levels of Al_{13} and Al_{13}^- and $Al_{12}As$ and $Al_{12}As^+$, we find that the energy levels are quite similar, but there is a shift of the highest occupied level because of the different number of electrons. The only exceptional cluster is $Al_{12}Ti$. It has 40 valence electrons, but there is no gap between HOMO and LUMO in the icosahedral structure and therefore we do not expect this cluster to be magic. As shown in Fig. 4, the highest occupied level is degenerate and is only partially occupied. This degeneracy is likely to be lifted by Jahn-Teller distortions which we have not included. The splitting between the spin-up and spin-down states is large which leads to a large magnetic moment. There are many states near the HOMO and no large gaps can be seen in the spectrum. Thus our results indicate that when one has transition metal atoms in a cluster, the predictions of the jellium model are not likely to be applicable. The equilibrium distance R_0 is the largest for $Al_{12}Ti$ as Ti is also the largest in size among all the dopants we have studied. This is perhaps another reason for the lower binding energy in the $Al_{12}Ti$ cluster.

In order to study the compressibility of the clusters, we approximately define the volume of a cluster by $V = (4\pi/3)R_0^3$ and use the conventional formula for the bulk modulus $B = V(d^2E/dV^2)$. These results are listed in Table II for various clusters. It can be noted that $Al_{12}Si$ and $Al_{12}Ge$ have the highest bulk modulus whereas for $Al_{12}C$ it is smaller. This is not surprising because, in

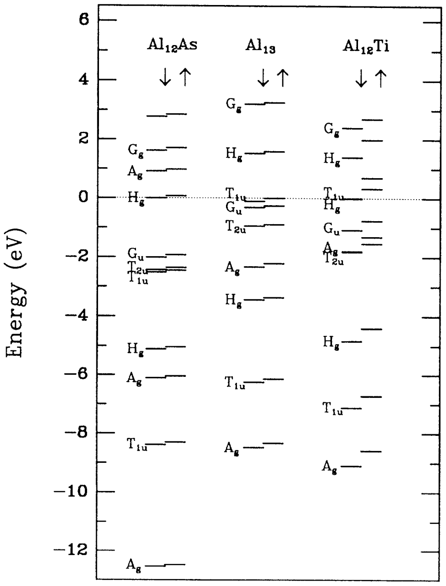

FIG. 4. Same as for Fig. 3.

the $Al_{12}C$ cluster, carbon is too small and as discussed before it costs less if compressed. However, for $Al_{12}Si$ and $Al_{12}Ge$ the atom at the center is just a little bit smaller than the aluminum atom. All the bonds, from either center to vertex or vertex to vertex, are adjusted to their energy minimum and it is harder to compress.

In conclusion, we find that the stability of the Al_{13} icosahedral cluster can be significantly enhanced by substitutional doping with, e.g., B, C, Si, and Ge. $Al_{12}C$ is the most compact and has the largest binding energy. Our results indicate that the chemical bonding plays the dominant role whereas structural relaxations as compared to the Al_{13} cluster contribute in a smaller way to the total binding energy of the clusters. All the 40 valence electron clusters except $Al_{12}Ti$ that we have studied are isoelectronic and have a large HOMO-LUMO gap of nearly 2 eV. This is largest for $Al_{12}C$. Therefore these clusters will be very stable and likely to be unreactive. This is in agreement with the experimental results on Al_{13}^- and $Al_{12}B^-$. The neutral clusters should be promising entities for making new materials. It is also worth mentioning that Bergmann, Limberger, and Martin [14] obtained evidence for electronic shell structure for cesium clusters containing oxygen. However, in this case each oxygen atom is supposed to bind two electrons from the sea of the delocalized electrons of the cesium cluster and the rest of the valence electrons can then be described as moving in a spherical potential just as in pure alkali metal clusters. Our results on doped clusters should also be relevant to studies on quasicrystals as Si has been used [15] to stabilize quasicrystals such as Al-Mn. Our calculations suggest that it should not only provide a favorable icosahedral structure for Al but also a substantial gain in the binding energy of the system. On the other hand, substitution of Ti is not so favorable and this may explain why Ti doping has not been successful for quasicrystals. Finally our trends of the binding energies of the clusters should be useful in understanding the role of impurities like B, C, Si, As, etc., at the grain boundaries in materials.

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