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Silicon-doped icosahedral, cuboctahedral, and decahedral clusters of aluminum

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Most stable structures and physical properties are studied for silicon-doped Al_{13} , Al_{19} , and Al_{23} clusters using the *ab initio* molecular-dynamics method within the framework of a plane-wave pseudopotential approach and the local density as well as the generalized gradient approximations. The lowest energy structures of the undoped clusters are found to be Jahn-Teller distorted icosahedron, double icosahedron, and decahedron, respectively. Substitutional doping with a Si impurity makes these clusters electronically closed shell and leads to a large gain in the binding energy, which decreases with an increase in the cluster size in a nonmonotonic way. The heat of solution of a Si atom in clusters is found to be exothermic as compared to endothermic behavior in bulk aluminum. Further, a Si impurity is found to stabilize the $Al_{18}Si$ cluster in cuboctahedral structure. However, a capped icosahedron as well as a double icosahedron are found to be nearly degenerate with about 1.77 eV higher binding energy. For $Al_{22}Si$, the decahedral isomer has the lowest energy with a highest-occupied lowest-unoccupied molecular-orbital gap of 0.82 eV. It is also found to be very stable when heated at 700 K. Similar results are likely to hold in the case of doping with germanium. We discuss the significance of these results for the understanding of the stability of silicon-doped quasicrystals.

I. INTRODUCTION

Currently, there is much interest in studies on clusters due to their technological applications as well as the possibilities of developing novel cluster-based materials using the size dependence of their properties. In this direction, there are efforts to develop new magic clusters. Doping of clusters is an interesting possibility that has not yet been much explored. It cannot only enhance¹ the stability of certain magic clusters but also it may change their properties very significantly due to the finite size. An important aspect of doping in clusters is the possibility² of mixing some of those elements that do not mix in bulk. In a cluster the strain due to size mismatch can be significantly less as compared to bulk due to the finite size as well as different atomic structures such as those based on an icosahedral packing, which are quite common for several metal and rare gas clusters. In an icosahedron, the center to vertex distance is about 5% shorter than the nearest-neighbor bond length between two vertices. Therefore, a slightly smaller size atom at the center of an icosahedron is favorable for improving the bonding between the vertex atoms as compared to strain by such an impurity in a bulk crystal with nonicosahedral nearest neighbor environment. Moreover, the electronic structure of a cluster could be significantly different from its bulk or surfaces and therefore, it may give rise to a different interaction of an impurity. A striking example is the heat of solution of a Si atom in aluminum, which is endothermic.³ However, substitutional doping of Al_{13} cluster with a Si atom is highly exothermic.^{1,3,4} The large binding energy was shown¹ to be due to chemical bonding rather than relaxation of the vertex

atoms of the icosahedral $Al_{12}Si$ cluster. Furthermore, doping could add a new dimension in the search of magic clusters with regard to their shape. There could be a symmetry breaking of the lowest energy isomer of an undoped cluster and it may become possible to stabilize one of the other isomers, which may not be stable or only metastable otherwise. Here, we explore the effects of doping on aluminum clusters with a silicon atom.

Clusters of aluminum have been extensively studied both from experiments⁵⁻⁷ as well as theory,^{1,4,8-10} particularly in the small size range. In bulk, aluminum is a nearly free electron like metal and therefore, the gross features of a jellium model¹¹ of metal clusters, such as the electronic shell closing for 20, 40, 58, 70, . . . valence electrons, could be expected to hold for its clusters. However, due to the odd number of valence electrons in the atom, most of its clusters do not have electronic closed shell structures. Replacement of an aluminum atom with a tetravalent impurity could make several aluminum clusters magic with a closed electronic shell. These include 11, 13, 19, 23, 35, 37, 55, . . . atom clusters. Here we study substitutional doping of Si in 13, 19, and 23 atom clusters as these are the closest to the prominent shells with 40, 58, and 70 electrons. We show that it is possible to obtain electronically closed shell clusters in three important structures, namely icosahedral (*i*) $Al_{12}Si$, cuboctahedral (*c*) $Al_{18}Si$, and decahedral (*d*) $Al_{22}Si$.

Studies⁵ on abundance and reactivity of negatively charged aluminum clusters show Al_{13}^- and Al_{23}^- to be magic and inert with respect to interaction with oxygen. In the neutral state, both these clusters are one electron short of the electronic shell closing in the jellium model and therefore,

the large abundance of these negatively charged clusters can be understood. The electron affinity of Al_{13} is indeed quite high (3.75 eV) and is similar to the value for chlorine (3.61 eV). Theoretical studies⁸⁻¹⁰ on aluminum clusters have shown Al_{13} to be a slightly distorted icosahedron. Recently *i*, *d*, and *c* isomers of aluminum clusters have been studied⁹ using the local spin density approximation (LSDA) up to a size of 23 atoms. It has been shown that for Al_{19} and Al_{23} clusters, a double icosahedron and a decahedron, respectively, have the lowest energy. Substitutional doping of Al_{13} by Si has been studied^{1,4,12} earlier to obtain an electronically closed shell *i*- Al_{12}Si cluster. The important findings of these studies were a large highest occupied - lowest unoccupied molecular orbital (HOMO-LUMO) gap of nearly 2.0 eV, a substantial gain of about 3.0 eV in energy with doping and a preference of Si to be at the center of the icosahedron. Here, we continue these investigations for larger clusters to explore the effects of doping in Al_{19} and Al_{23} . The Al_{19} and *d*- Al_{23} fragments with doping are found in several complex aluminum alloys.¹³ Moreover, doping with silicon has been found to stabilize the quasicrystalline *i* phase¹⁴ of several such alloys. Therefore, it is of interest to know if silicon doping enhances the range of icosahedral growth of aluminum clusters. Also, most of the earlier studies on aluminum clusters are within the local density approximation (LDA) or LSDA. We have performed calculations using both the LDA as well as the generalized gradient approximation (GGA) with spin-polarization. Our results from GGA are in very good agreement with experimental values¹⁵ of the binding energy on pure clusters and we hope that our results on doped clusters would provide a good estimate of the heat of solution of silicon in these clusters.

In the next section, we present a brief description of the calculational procedure. In Sec. III, we present the results. Our conclusions are given in Sec. IV.

II. COMPUTATIONAL PROCEDURE

The calculations have been performed using the *ab initio* molecular-dynamics method with a plane-wave basis.¹⁶⁻¹⁸ The electron-ion interaction is represented by the norm-conserving pseudopotentials¹⁹ in the Kleinman-Bylander separable form²⁰ with *s* and *p* nonlocality. The cut-off energy of the plane wave is taken upto 16.2 Ry. The exchange and correlation (XC) energy is calculated within the LDA using the Ceperley-Alder data²¹ as parametrized by Perdew and Zunger.²² For Al_{13} and Al_{19} , simulated annealing calculations were performed within LDA. In addition, a few other isomers were studied using the steepest descent method. The converged structures were taken as the starting point for further calculations with spin polarization and the GGA (Ref. 23) using the Vienna *ab initio* simulation package (VASP).^{18,24} This uses exact evaluation of the electronic ground state at each molecular-dynamics step using efficient matrix diagonalization schemes as compared to the above LDA calculations where the electron minimization was done for an initial configuration of the ions and then the electronic wave functions and ions were allowed to evolve to reach the minimum energy configuration, the kinetic energy of the electrons being kept small by occasional electron minimization. Also in the VASP code, ultrasoft Vanderbilt

pseudopotentials²⁵ have been used. The cut-off energy for plane waves in these calculations was 11.07 Ry. The geometries were again fully optimized using the conjugate gradient technique. The Brillouin zone was represented by the gamma point.

III. RESULTS

A. Pure aluminum clusters

In the size range of clusters, that we have studied, there are three growth modes that have been recently suggested⁹ to compete. These are icosahedral, decahedral and cuboctahedral isomers. As it is well known, the LDA and LSDA binding energies are significantly overestimated as compared to the experimental values.¹⁵ Therefore, we have calculated the energies of the pure aluminum clusters in GGA in order to compare our results with the earlier work.⁸⁻¹⁰ For Al_{13} and Al_{19} , besides the simulated annealing calculations, we have studied *d* isomer for Al_{13} as well as *d* and *c* isomers for Al_{19} . For Al_{13} , simulated annealing LDA calculations predict a Jahn-Teller distorted icosahedron structure and this agrees with the earlier work.⁸⁻¹⁰ The *d*- Al_{13} isomer is also distorted and is locally stable in LDA. However, in GGA with spin polarization, conjugate gradient minimization led the *d* isomer finally converge to the *i* isomer. Therefore, in GGA, the *d* isomer is not even locally stable. A similar result has been independently obtained recently by Akola *et al.*²⁶ with LSDA. They reported transformation of the decahedral structure into icosahedral one at about room temperature. For Al_{19} , the *d* and *c* isomers relax very significantly and a tendency has been found for developing double icosahedral structure. For Al_{13} and Al_{19} , both the LDA as well as the GGA predict *i* isomers to be of lowest energy. This agrees with the LSDA calculation in Ref. 9 and also with a GGA calculation²⁷ for Al_{13} . However, our result is different from a very recent paper²⁸ that we found after the completion of our paper and that reports the *d* isomer to be of lowest energy for Al_{13} . In the case of Al_{23} , Akola *et al.*⁹ have reported the *i* isomer to be significantly more favorable than the *c* isomer whereas the *d* isomer was found to have 0.011 eV higher binding energy as compared to the *i* isomer in LSDA. We, therefore, considered the *i* and the *d* isomers for this cluster. In LDA, the *i* isomer has 0.224 eV higher binding energy than the *d* isomer. However, in GGA with spin polarization, the *d* isomer is the lowest in energy and the binding energy is 0.128 eV higher than the *i* isomer very similar to the result obtained in LSDA. In Fig. 1, we have shown the structures of the lowest energy and the nearly degenerate isomers obtained from the spin-polarized GGA calculations.

The open shell structure of the undoped clusters leads to Jahn-Teller distortions and therefore, the nearest-neighbor bond lengths vary significantly. Also the different center to vertex and vertex to vertex bond lengths in an icosahedron add to this significant variation. We define a mean nearest-neighbor bond length as

$$d_m = \frac{1}{N_b} \sum_i^{N_b} d_i, \quad (1)$$

where, d_i is the nearest-neighbor bond length of the *i*th bond and N_b is the number of bonds below a certain cut-off bond

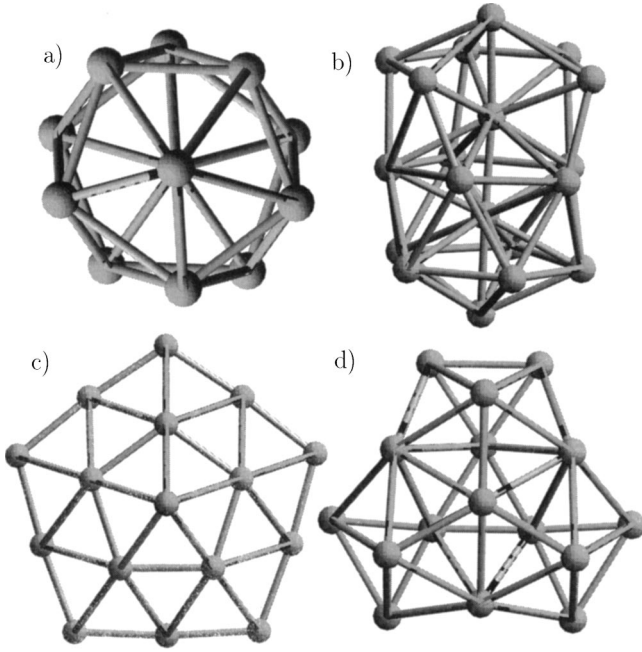


FIG. 1. Projections of lowest energy structures for (a) i -Al₁₃, (c) d -Al₂₃, and (d) i -Al₂₃ isomers. (b) shows the Al₁₉ double icosahedral structure which has large distortions.

length, which is taken to be 3.27 Å. The mean values as well as the range of bond lengths in different clusters as obtained in GGA are given in Table I. For Al₁₃, the nearest-neighbor bond lengths vary between 2.75 and 2.96 Å with a mean value of 2.77 Å. In the case of Al₁₉, the distortions are large as one can see from the broken bonds in one of the icosahedra in Fig. 1. The bond lengths vary from 2.50 to 3.27 Å and the mean value is 2.79 Å. This is larger than the value in the case of Al₁₃. Al₂₃ is the most compact out of the three clusters we have studied. Its bond lengths vary between 2.63 and 2.91 Å and the mean value is 2.76 Å.

Our results of the binding energies and the HOMO-LUMO gaps are also given in Table I. It is found that the binding energies calculated within the GGA are lower than those obtained by using the LDA. In the case of Al₁₃, our LDA binding energy is higher than the value reported in Ref. 10 due to the inclusion of the p non-locality in the calculations. However, our GGA result is in close agreement with the experimental value of 2.481 eV/atom obtained by Ray *et al.*¹⁵ This is also in good agreement with the value of 2.616 eV/atom reported recently by Calleja *et al.*²⁷ using a linear combination of atomic orbitals and the GGA of Perdew-Burke-Ernzerhof.²⁹ However, the binding energy reported in Ref. 28 using GGA in GAUSSIAN 94 code appear to be too low (2.12 eV) as compared to the experimental value. Also their result that the d -Al₁₃ isomer has 0.43 eV higher binding energy is different from our GGA calculations, which predict it not even locally stable. In fact, during the minimization runs, the d isomer first appeared to have converged with a 0.24 eV lower binding energy than the i isomer. However, when the minimization was continued further, the d isomer transformed to the i isomer.

The spin-polarization is found to lower the energy of these clusters only marginally. All the studied clusters favor low-spin configurations and the lowest energy state is a dou-

blet. In the case of decahedral Al₁₉ isomer, a configuration with 5 μ_b magnetic moments was found in the minimization runs with about 1.132 eV lower binding energy. This transforms to the i isomer by a rotation of the central pentagon. An important effect of taking into account the spin polarization is the lowering of the HOMO-LUMO gap as it can be seen in Table I where we have given the GGA values with and without spin polarization. In the spin-polarized calculation, one finds that the HOMO-LUMO gap for Al₁₃ is only 0.36 eV and this should make it quite reactive as indeed one finds¹⁰ from the large binding energy of an aluminum atom on Al₁₃. For Al₁₉ and Al₂₃ clusters, the gap is very similar with values 0.35 and 0.38 eV, respectively in the GGA. The Kohn-Sham energy spectra for all the clusters are shown in Fig. 2 using a Gaussian broadening of variance 0.025 (eV)² so that we could compare our results with the photoemission data of Li *et al.*⁷ For Al₁₃, we have taken the spectrum of the d isomer obtained during the optimization runs. We find that around -4 eV, our calculated spectrum of the i isomer is in very good agreement with the photoemission result. In the experimental data on Al₁₃⁻, there is a shoulder towards higher binding energy as we also see in Fig. 2(c) for i -Al₁₂Si whereas in the d isomer, the shoulder is towards the lower binding energy. Considering Si to add an electron in Al₁₃ and make it highly symmetric as we would expect it for Al₁₃⁻, we can conclude that in experiments also, the observed isomer is icosahedral. In going from Al₁₃ to Al₁₉ and Al₂₃, one finds that the gaps found in the case of Al₁₃ at 20 and 40 electrons get very significantly reduced and the states are quite evenly distributed. For Al₂₃, the i isomer has a broad peak near the HOMO, which is closer to the photoemission data. It is possible, that with an increase in the size of clusters, the number of isomers present in the experiment may be more than one due to a decrease in the energy difference. For the d isomer, however, the energy gaps are more prominent than in the i isomer.

B. Si-doped clusters

Substitutional doping of Al₁₃ with Si was earlier shown^{1,4,12} to be favorable at the center of the aluminum icosahedron. We have computed the energy of this cluster in GGA and also for the d isomer. It is found that in GGA also, the i isomer has the lowest energy with the value 2.813 eV/atom and the HOMO-LUMO gap is 1.99 eV. Our calculations show that the d isomer is not stable. Similar to the case of pure Al₁₃, a decahedral structure, when relaxed, seems to first converge to the d isomer with binding energy and HOMO-LUMO gap of 2.776 eV/atom and 1.58 eV, respectively. However, when the minimization is continued further, it converges to the i isomer. The center to vertex and vertex to vertex bond lengths in this cluster are 2.64 and 2.77 Å as compared to the values 2.67 and 2.81 Å found¹² in LDA.

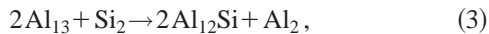
Considering the reaction



the enhancement in the stability of Al₁₃ with Si doping is found to be by 2.738 eV. This value is significantly lower than 3.177 eV obtained from LDA calculation. Also considering the reaction

TABLE I. Structure, range of the nearest-neighbor bond lengths, d_i , its mean value, d_m in Å, binding energies calculated from LDA, GGA (spin-unpolarized), and GGA-sp (spin-polarized) in eV and the HOMO-LUMO gap in eV for the undoped and the doped aluminum clusters. The bond lengths are given only from the spin-polarized GGA calculations for the undoped and the GGA calculations for the doped clusters. Experimental value of the binding energy for Al_{13} is from Ref. 15. For Al_{13} and $Al_{12}Si$, the decahedral isomer finally converges to the icosahedral isomer and the values are given from the metastable configurations during the optimization runs. For Al_{19} and $Al_{18}Si$, both the double icosahedral and decahedral isomers distort significantly and have similar structures.

Cluster	Isomer	d_i, d_m	XC	B.E.	Gap
Al_{13}	icosahedron	2.75-2.96 2.77	LDA	3.167	
			GGA	2.595	1.57
			GGA-sp	2.602	0.36
	decahedron		LDA	3.137	
			GGA	2.578	1.46
			GGA-sp	2.584	0.30
	Expt.		2.481		
Al_{19}	double	2.50-3.27	LDA	3.249	
	icosahedron	2.79	GGA	2.666	0.52
			GGA-sp	2.670	0.31
	decahedron		LDA	3.249	
			GGA-sp	2.610	0.19
Al_{23}	decahedron	2.63-2.91 2.76	LDA	3.356	
			GGA	2.746	0.61
			GGA-sp	2.750	0.38
	icosahedron	2.49-2.96 2.82	LDA	3.366	
$Al_{12}Si$	icosahedron	2.64,2.77 2.73	LDA	3.412	
			GGA	2.813	1.99
	decahedron		LDA	3.365	
			GGA	2.776	1.58
$Al_{18}Si$	double icosahedron	2.47-3.19 2.78	LDA	3.360	
			GGA	2.770	0.64
	decahedron		LDA	3.367	
			GGA	2.770	0.64
	simulated annealing	2.56-3.06 2.78	LDA	3.368	
			GGA	2.766	0.58
$Al_{22}Si$	cuboctahedron	2.67,2.74 2.71	LDA	3.285	
			GGA	2.675	0.23
	decahedron	2.58-2.81 2.75	LDA	3.445	
			GGA	2.834	0.82
icosahedron	2.48-3.00 2.81	LDA	3.440		
		GGA	2.813	0.23	
Bulk	fcc	2.86	expt.	3.39	



the gain in energy is 1.709 eV per cluster which is very large³⁰ as compared to bulk where a silicon impurity in aluminum is energetically not favorable³ and the heat of solution is +0.5 eV (endohedral). Among all the clusters, we have studied, $Al_{12}Si$ has the largest gain in the binding energy as well as the highest HOMO-LUMO gap (1.99 eV). Therefore, among Si-doped aluminum clusters, we would expect this to be strongly abundant. The HOMO-LUMO gap is in agreement with the previous LDA results,¹ but the gain in energy is smaller in GGA.

The above result of the stability of the *i*- $Al_{12}Si$ is very interesting as doping of some of the aluminum based alloys with silicon has been found to stabilize the quasicrystalline *i* phase of such alloys. It is also interesting that for *d*- $Al_{12}Si$,

the gain is about 0.48 eV less as compared to the *i*- $Al_{12}Si$ isomer. A natural question then is, whether silicon doping would stabilize larger aluminum clusters in icosahedral structure. Considering the double icosahedron of Al_{19} cluster, substitution of a Si atom can be at one of the centers of the two icosahedra. The resulting structure does not have high symmetry. On the other hand, substitutional doping of Si at the center of a cuboctahedron keeps the high symmetry of this cluster. Often, magic clusters have been found to have structures of high symmetry. It is plausible that doping could make the *c* isomer stable. We carried out steepest descent calculations for the cuboctahedral as well as the double icosahedral structures. Further, a simulated annealing calculation was performed to find the lowest energy structure within LDA. The resulting structures were further optimized using the GGA and the results are shown in Fig. 3. It is

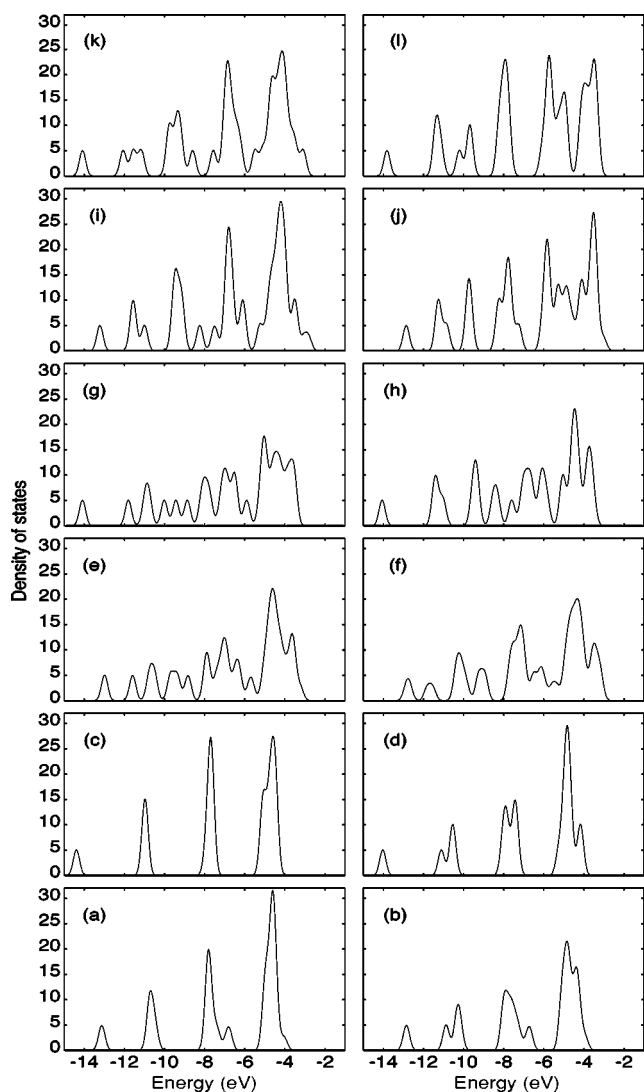


FIG. 2. The density of occupied states obtained by broadening the Kohn-Sham energy eigenvalues with a Gaussian of half width 0.158 eV. For the undoped clusters the LUMO was also included as the photoemission experiments in Ref. 7 were on negatively charged clusters. (a) i -Al₁₃, (b) d -Al₁₃, (c) i -Al₁₂Si, (d) d -Al₁₂Si, (e) i -Al₁₉, (f) d -Al₁₉, (g) i -Al₁₈Si, (h) capped icosahedral Al₁₈Si, (i) i -Al₂₃, (j) d -Al₂₃, (k) i -Al₂₂Si, and (l) d -Al₂₂Si.

found that substitution of a Si atom indeed stabilizes the c isomer in contrast to the Al₁₉ cluster for which it is not even locally stable. However, it does not have the lowest energy. The HOMO-LUMO gap is also small (0.23 eV). We find that the distorted double icosahedron structure with a Si atom on one of the centers has significantly lower energy. A decahedral structure was also optimized and it converged to a similar distorted structure as obtained from the relaxation of the double icosahedral structure. Simulated annealing calculations within LDA give another structure (Fig. 3) in which the Al₁₂Si icosahedron is capped symmetrically on two sides by three atoms. In LDA, it has the lowest energy. However, when optimization was carried out within GGA, then its binding energy was found to be 0.083 eV lower than the value for the double icosahedron structure. The HOMO-LUMO gap in GGA for the capped and the double icosahedron

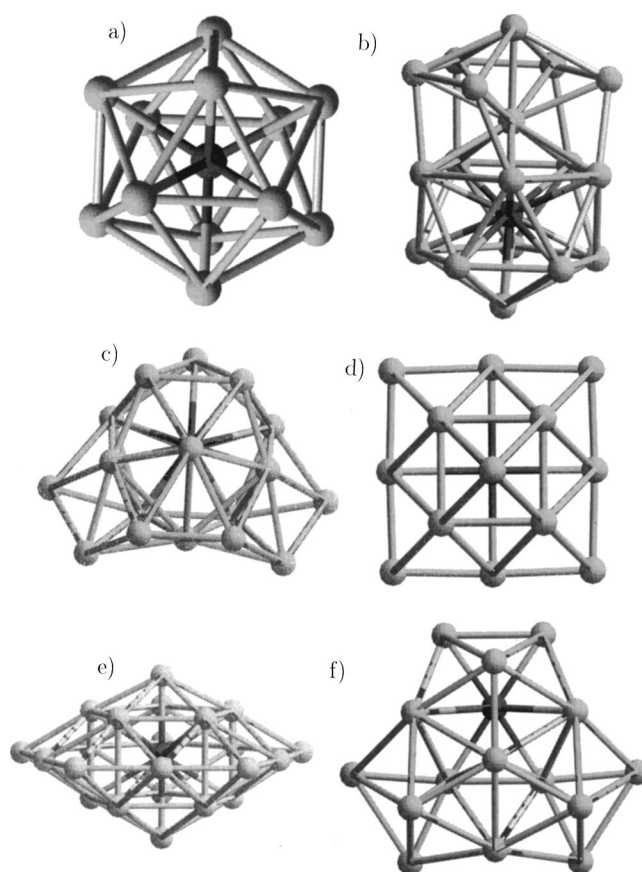


FIG. 3. The lowest energy isomers of Si-doped clusters. (a) i -Al₁₂Si with Si at the center, (b) Al₁₈Si with Si at the center of the lower icosahedron, (c) Al₁₈Si icosahedron with Si at the center and two caps of three Al atoms, (d) c -Al₁₈Si with Si at the center of the cuboctahedron, (e) d -Al₂₂Si with Si at the center, and (f) three interpenetrating icosahedra with Si at the center of one of them.

structures are 0.58 and 0.64 eV, respectively, which also suggests a higher stability for the double icosahedron structure in GGA. However, as the energy difference is very small, under experimental conditions of finite temperature, one may observe both of these isomers. These results show that the growth process in clusters could be quite complex where the adatoms arrange themselves in a particular order on a cluster, such as Al₁₂Si here, or reconstruct it, which is very similar to what happens on surfaces.

The nearest-neighbor bond lengths in the double icosahedral isomer vary from 2.47 to 3.19 Å and the mean value is 2.78 Å. Considering reactions (2) and (3) above, the gain in energy by doping Al₁₉ with a Si atom is 1.90 and 0.871 eV, respectively. Though it is significantly less as compared to the value for Al₁₂Si, these energies are still large and exothermic.

Doping of Al₂₃ cluster is interesting not only to understand the growth behavior of aluminum clusters, but also a doped 23-atom decahedral fragment is found in many complex aluminum alloys. Also there is a 23-atom icosahedral cluster which has been found to be magic for Lennard-Jones clusters.³¹ Since silicon impurity enhances the stability of icosahedral clusters, an interesting question would be, if the icosahedral isomer becomes more favorable with Si doping.

We have optimized both the structures and found that the Si-doped decahedral cluster remains energetically more favorable by 0.482 eV than the *i* isomer in GGA. This is a relatively large energy. This result is also reverse from the finding in the case of Al_{12}Si where decahedral isomer had a lower binding energy and was in fact not stable. This behavior has origin in the electronic structure of the two isomers as for the undoped Al_{23} cluster also, the *d* isomer is more favorable. The doping of a Si atom at the center of the decahedron leads to 1.923 eV higher binding energy. This is again a large gain but it is significantly smaller than the value of 2.738 eV for Al_{12}Si . Interestingly, this value is slightly higher than the one obtained in the case of Al_{18}Si . Considering the reaction (3) above, the gain is 0.895 eV which is again higher than the value for Al_{18}Si . We believe that this is due to the electronic shell closing effect. If we consider that a silicon atom adds an electron to the undoped clusters, then the large difference in the energy gain in the case of Al_{18}Si and Al_{22}Si as compared to Al_{12}Si can be roughly seen from the large difference in the value of the LUMO in Al_{13} (−4.03 eV) and in Al_{19} (−3.22 eV) and Al_{23} (−3.02 eV) clusters. This is also supported from the fact that the Kohn-Sham eigenvalue spectra of the undoped and the doped clusters are quite similar except that the HOMO-LUMO gap for the doped clusters is larger (Fig. 2). Our results also show that the binding energy of a dopant approaches the bulk value in an oscillatory way rather slowly as the size of the cluster increases and may continue to be quite different as long as the cluster structure is different from its bulk.

The nearest-neighbor bond lengths in *d*- Al_{22}Si vary between 2.58 and 2.81 Å and the mean value is 2.75 Å. The Kohn-Sham eigenvalue spectrum is shown in Fig. 2. The HOMO-LUMO gap for the *d* isomer is 0.82 eV, which is significant and much larger than the value (0.38 eV) for Al_{23} as well as the values of 0.32 for the *i*- Al_{22}Si isomer. This result shows that the structure or shape of a cluster also plays an important role in the formation of a larger HOMO-LUMO gap, which is important for the stability and abundance of a particular cluster. This is in agreement with the finding of a stronger stability of clusters with a certain number of electrons in a deformed jellium model.³² The HOMO-LUMO gap for Al_{22}Si is larger than the value for Al_{18}Si and reflects the stronger stability of 70 electron clusters as compared to 58 valence electron clusters. This is in agreement with experiments that also show no specific feature regarding magic behavior of Al_{19}^- . To further study the stability of this structure, we heated the cluster upto 700 K and the mean square displacement is shown in Fig. 4. This is found to be oscillatory. It shows that the basic structure remains intact and the ions vibrate around their equilibrium positions. This result suggests that the *d* isomer is very stable. On the other hand, when we heated the Al_{18}Si cluster at 700 K, the mean square displacement was larger (Fig. 4) and there was a structural transformation which suggests that this structure is not so stable, as one would also expect from a small HOMO-LUMO gap.

IV. SUMMARY AND DISCUSSION

In summary, we have studied the atomic and electronic structure of pure Al_{13} , Al_{19} , and Al_{23} clusters within LDA

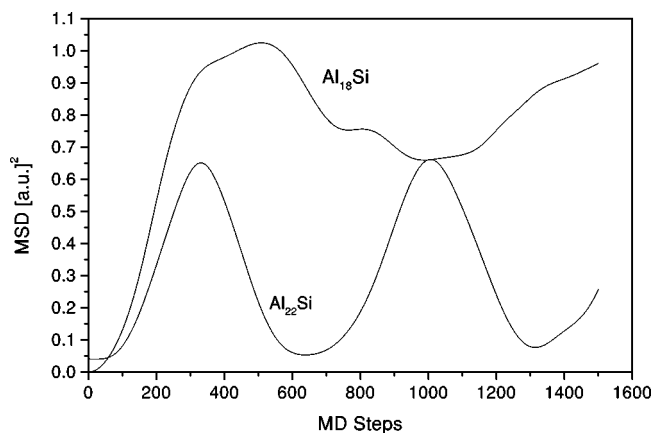


FIG. 4. The mean square displacement for Al_{22}Si and Al_{18}Si clusters at 700 K as a function of the number of molecular-dynamics steps.

as well as GGA and the effects of doping these clusters with a silicon impurity. The lowest energy structures of these clusters in GGA are Jahn-Teller distorted icosahedron, double icosahedron and a decahedron in conformity with a LSDA calculation.⁹ Among the doped clusters, the *i*- Al_{12}Si isomer with a regular icosahedral structure has the highest stability with a large HOMO-LUMO gap of 1.99 eV, which should make it strongly abundant. The doping is found to stabilize the Al_{18}Si cluster in a symmetric cuboctahedral structure but it is a local minimum. Two other nearly degenerate isomers based on two different ways of capping of an icosahedron have about 1.77 eV lower energy. For Al_{22}Si , the decahedral isomer is very stable with a relatively large HOMO-LUMO gap of 0.82 eV. The heat of solution of a silicon impurity is found to decrease in an oscillatory way with an increase in the cluster size and in all the cases that we have studied, it is exothermic as compared to the endothermic behavior in bulk aluminum. The electronic structure of the clusters seems to play a very important role in stabilizing Al_{12}Si in the icosahedral structure and Al_{22}Si in the decahedral structure with significant energy gains. In the case of Al_{13} the large gain is due to its large electron affinity as it was also shown¹ for the case of Al_{13}^- . In Al_{19} and Al_{23} the LUMO shifts by about 1 eV towards lower binding energy and leads to a smaller gain in the binding energies of Al_{18}Si and Al_{22}Si . For larger clusters, however, the structure may continue to play a very important role for the impurity binding energy. In icosahedral structures, a silicon impurity in aluminum in fact reduces the strain between aluminum-aluminum bonds in contrast to creating strain between aluminum-aluminum bonds in the bulk. Therefore, the heat of solution could be exothermic even for large clusters as the transformation to bulk structures (and in particular for doped clusters) may occur for clusters with several hundred to several thousand atoms. This can also explain the stabilization of icosahedral quasicrystals of certain complex alloys, which have icosahedral or decahedral local environments in abundance. Further, the behavior of doping with a germanium atom was found¹ to be similar to silicon in Al_{12}Ge and therefore, we would expect very similar results to hold for larger clusters in the case of doping with a germanium atom.

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