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LETTER TO THE EDITOR

Ground-state geometries and the stability of some $\mathrm{Li}_n\mathrm{Al}_m$ clusters investigated using density-based *ab initio* molecular dynamics

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Abstract. Density-based *ab initio* molecular dynamics has been used to investigate the stability and ground-state geometries of heteronuclear clusters of $\mathrm{Li}_7\mathrm{Al}_n$ $(n = 1, 7)$ and $\mathrm{Li}_n\mathrm{Al}$ $(n = 1, 8)$. Our investigations of these clusters indicate that the s–p bonded electrons favour a tetrahedral coordination, which plays a significant role in stabilizing the geometries of these clusters. We also report a remarkable ground-state structure for the $\mathrm{Li}_8\mathrm{Al}_6$ cluster, namely a face-centred cube with the Al atoms at the face centres forming an octahedron and Li atoms at the corners of the cube. The stability analysis based on the energetics shows that these clusters do not conform to the magic shell numbers observed for homonuclear alkali atom clusters.

In the last decade a number of *ab initio* investigations on small clusters have been reported that were undertaken with the aim of achieving an understanding of their ground-state geometries, binding energies, relative stabilities and abundance. The majority of these studies were carried out on clusters of homonuclear atoms. The experimental investigations of alkali and noble-metal clusters indicate magic numbers in the mass abundance spectra and have been interpreted on the basis of closed-shell electron configurations within the spherical jellium model [1, 2, 3]. It is of considerable interest to investigate the geometries and the stability of heteroatom clusters like Li–Al where the atoms belong to the open-shell system. It is also known that small Al clusters deviate from the magic shell numbers and show significant sp hybridization. The *ab initio* molecular dynamics investigations on heterogeneous clusters are more difficult, because the configuration space that has to be spanned to get reliable ground-state geometries is large. A recently developed density-based molecular dynamics method [4] appears promising as regards handling such calculations.

In the earlier study of $\mathrm{Li}_n\mathrm{Al}$ $(n = 1, 8)$ clusters [5], it was reported that at least for small clusters with $n < 5$ the bonding is covalent-like, and the magic numbers do not conform to those from the spherical jellium model. This study was confined to a single Al atom in different Li clusters. In the present work we focus our attention on the ground-state geometries and stability of $\mathrm{Li}_n\mathrm{Al}_m$ clusters. To investigate the evolutionary pattern of heteronuclear clusters as a function of one of the constituents, we have studied a number of clusters of $\mathrm{Li}_7\mathrm{Al}_n$ $(n = 1, 7)$, $\mathrm{Li}_n\mathrm{Al}$ $(n = 1, 8)$ and $\mathrm{Li}_8\mathrm{Al}_6$. We have obtained the ground-state geometries, total energies, second differences in energy and dissociation energy to get an idea of the stability.

The technique used is the orbital free molecular dynamics (OFM) with the electronic charge density as the basic variable. The method is shown to yield correct ground-state

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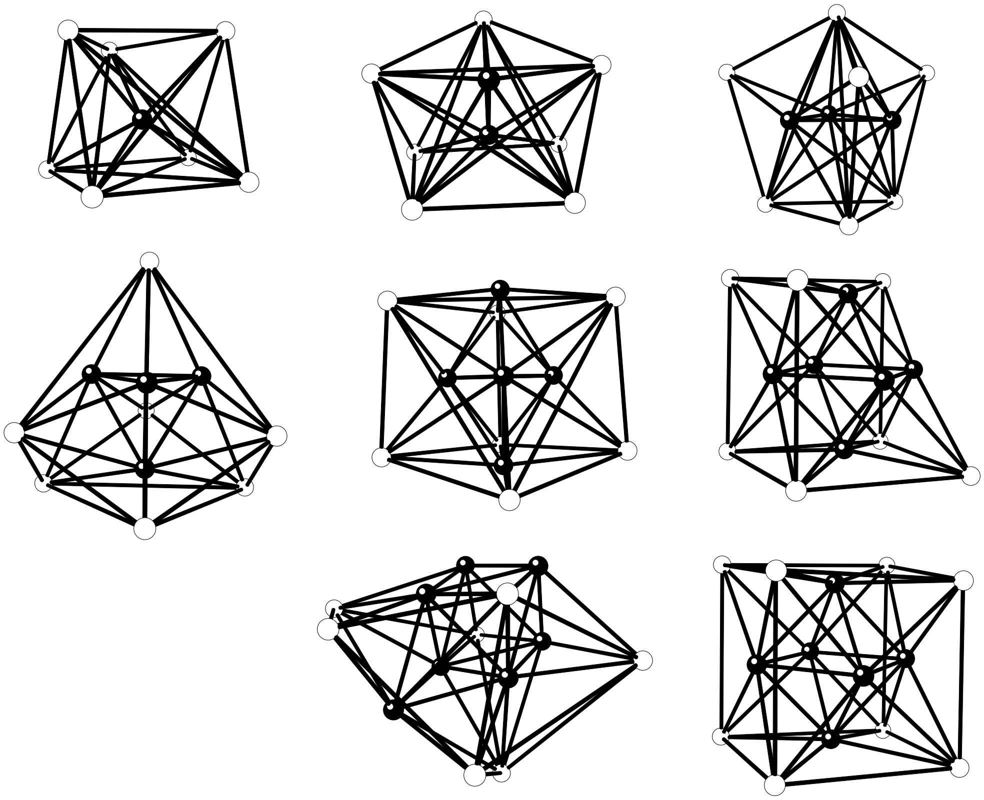


Figure 1. The ground-state geometries of $\mathrm{Li_7Al}_n$ $(n = 1, 7)$ clusters. The lighter spheres represent Li atoms and the darker spheres represent Al atoms. The FCC geometry at the bottom right-hand corner is that of the $\mathrm{Li_8Al_6}$ cluster.

geometries for a number of small clusters [4, 6]. The kinetic energy functional $T[\rho]$ used in the present work is

$$T[\rho] = F(N_e)T_{TF}[\rho]T_W[\rho] \tag{1}$$

where ρ is the charge density, N_e is the total number of valence electrons, T_{TF} is the Thomas–Fermi term, T_W is the gradient correction given by Weizsacker and the factor $F(N_e)$ is

$$F(N_e) = \left(1 - \frac{2}{N_e}\right)\left(1 - \frac{A_1}{N_e^{1/3}} + \frac{A_2}{N_e^{2/3}}\right) \tag{2}$$

with the optimized parameter values $A_1 = 1.314$ and $A_2 = 0.0021$ [7]. The geometry minimization has been performed using the Car–Parrinello simulated annealing strategy [8], while the conjugate-gradient technique was used for the electron energy minimization. The exchange–correlation potential of Ceperley and Alder, as interpolated by Perdew and Zunger [9], and Bachelet, Hamann and Schlüter pseudopotentials [10] have been used throughout the calculations. For $\mathrm{Li_7Al}_n$ $(n = 1, 7)$ clusters a periodically repeated unit cell of length 35 au with a $64 \times 64 \times 64$ mesh and time-step $\Delta t \sim 20$ au was used, whereas for $\mathrm{Li}_n\mathrm{Al}$ $(n = 1, 8)$ clusters a unit cell of length 30 au with a $54 \times 54 \times 54$ mesh was used. We have chosen to use the plane-wave expansion on the entire fast Fourier transform

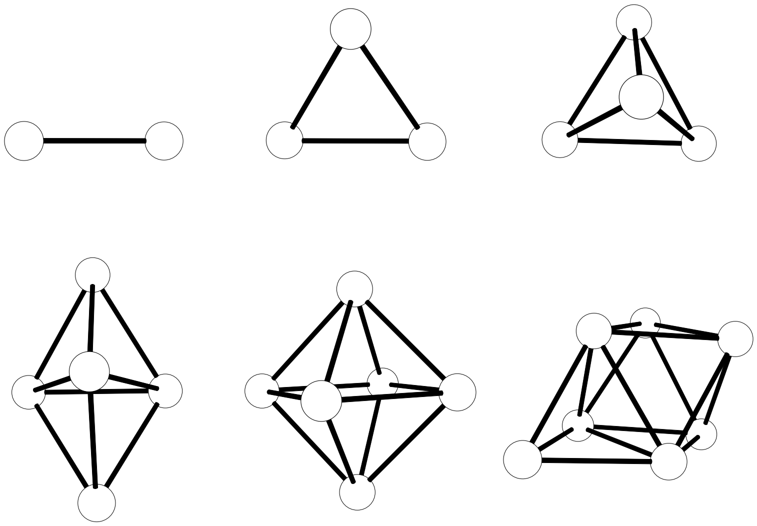
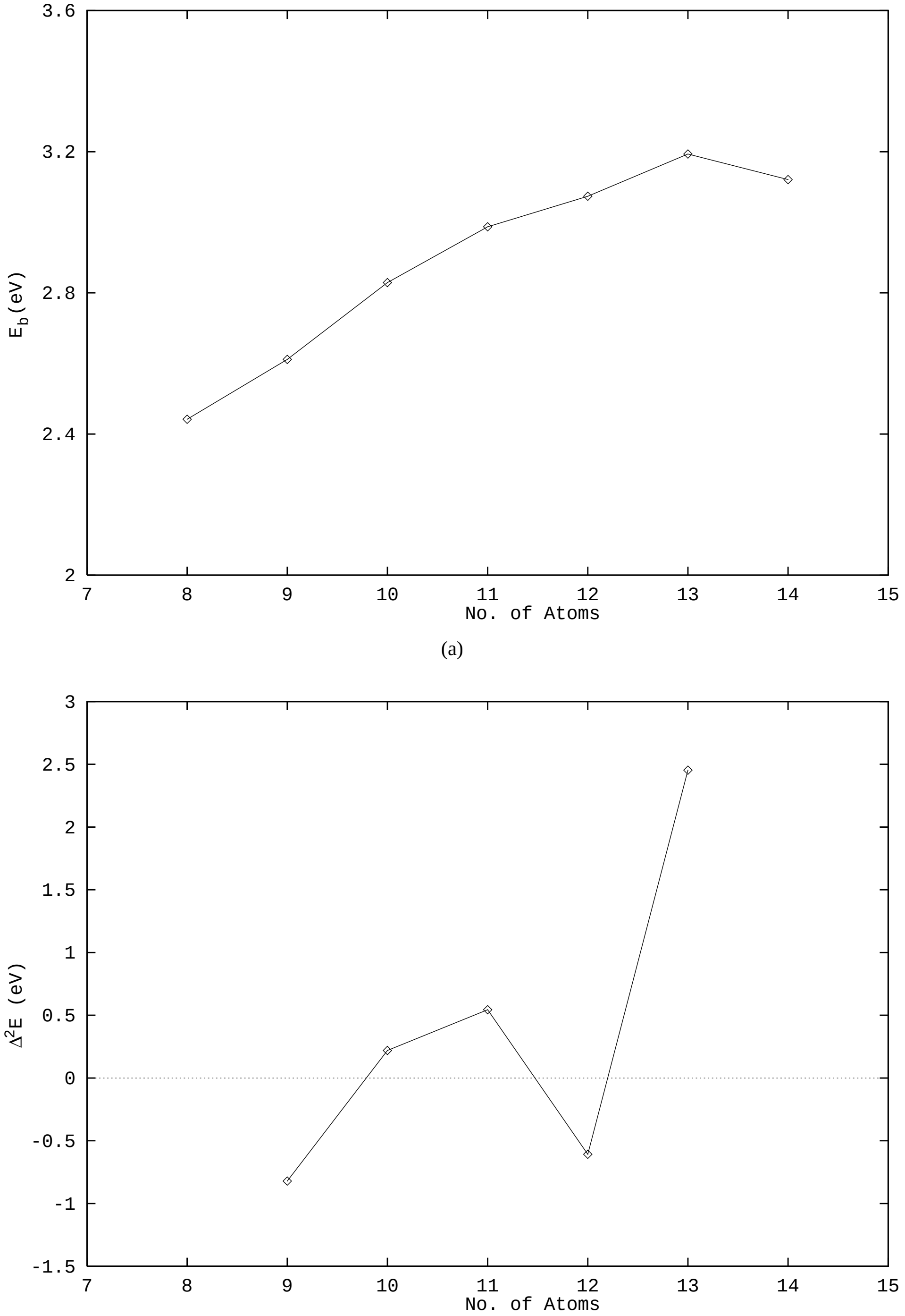


Figure 2. The geometries of the cluster of Al atoms within the ground-state configurations of Li_7Al_n $(n = 1, 7)$ clusters.

mesh without any truncation, yielding the energy cut-off of 95 rydbergs. The ground-state configurations are obtained by dynamical simulated annealing where the cluster is heated to 600–650 K and then cooled very slowly. In all of the cases the stability of the final ground-state configurations has been tested by reheating the clusters and allowing them to span the configuration space for a few thousand iterations and then cooling them to get the low-energy configurations. For other details the reader is referred to [4].

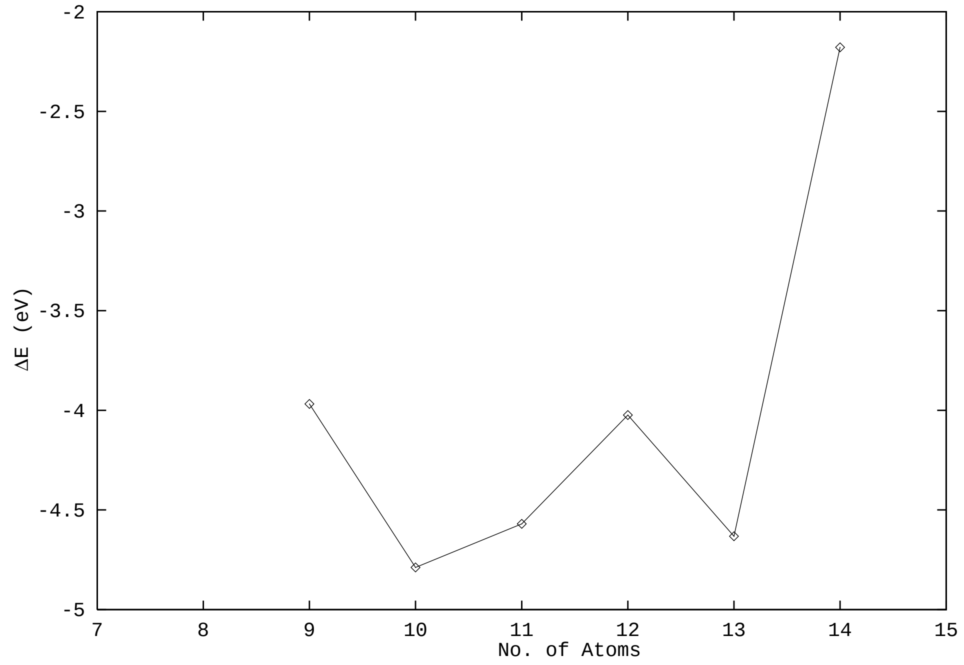
We begin the discussion of our results by noting the systematics of the ground-state geometries observed for Li_7Al_n $(n = 1, 7)$ which are shown in figure 1. The lighter spheres represent Li and the darker spheres represent Al. Let us note that we have started with an eight-atom ten-electron system of Li_7Al and added one aluminium (three electrons) subsequently. This cluster has C_{1h} symmetry and the Al atom is trapped inside the seven Li atoms. Li_7Al_2 has a C_s symmetry with the Al atoms forming a dimer within the Li atoms. It should be noted that the dimer is not at the centre of the cluster. Li_7Al_3 is a highly symmetric cluster with C_{3v} symmetry and the aluminium atoms form an equilateral triangle inside the Li atoms. The cluster of Li_7Al_4 has a C_{3v} symmetry with the inner Al atoms forming a tetrahedron and the Li atoms capping the faces of this tetrahedron. The Al atoms in the Li_7Al_5 clusters form a trigonal antiprism with the Li atoms capping the faces and the cluster has C_s symmetry. The cluster of Li_7Al_6 has a strikingly interesting geometry—an incomplete FCC cell. The Al atoms are at the faces of the cell and form an octahedron whereas the Li atoms are situated at the corners. It is very tempting to conclude that the most stable structure would be obtained by capping all the faces of the Al octahedra, i.e. a Li_8Al_6 cluster. Indeed our simulated annealing calculation shows this cluster to be the most stable and as having the geometry of the face-centred cube. Such a cubic structure has not been found to be the ground state but has been reported as one of the low-lying structures



(a)

(b)

Figure 3. (a) The binding energy per atom E_b (in eV) for the Li_7Al_n clusters as a function of the total number of atoms. (b) The second difference in energy (in eV) as a function of the total number of atoms in the Li_7Al_n clusters. The maxima pertain to more stable clusters and the minima to the least stable ones. (c) The dissociation energy (in eV) as a function of the total number of atoms in Li_7Al_n clusters. Minima show the more stable clusters and maxima show the less stable ones.



(c)

Figure 3. (Continued)

of Li_{14} [11]. The last cluster studied in this series, Li_7Al_7, has no particular symmetry, but the seven Al atoms have a C_{1h} symmetry and the Li atoms cap this inner Al cluster.

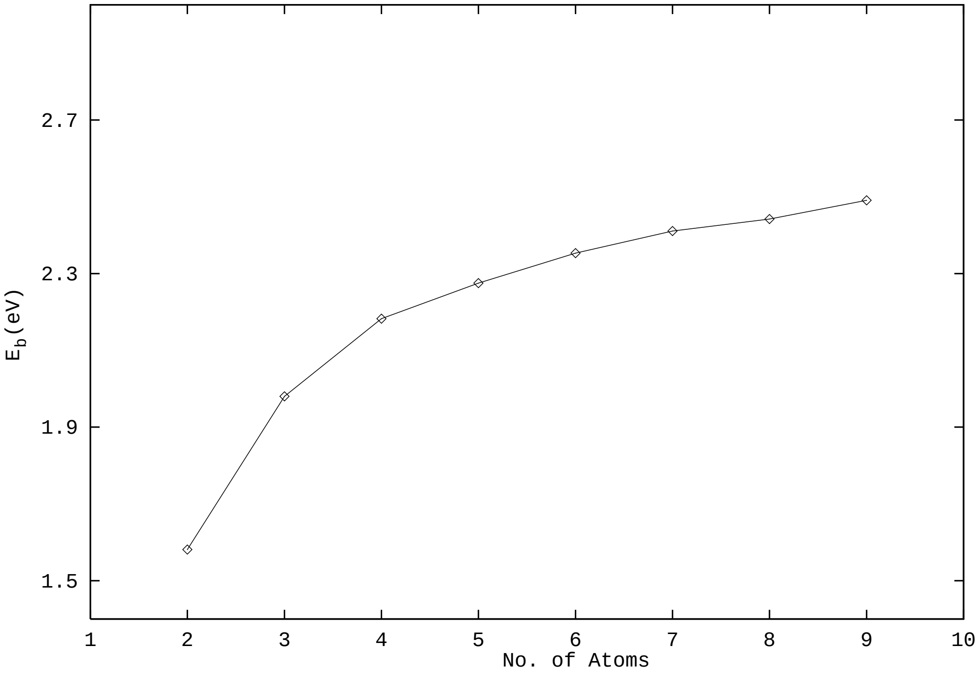
It is interesting to note that in all of these clusters the Al atoms form an inner cluster, not necessarily central, and the Li atoms cap to form tetrahedral coordination wherever possible. This is especially evident from Li_7Al_4, Li_7Al_5 and Li_7Al_6 clusters. The geometries of the Al_n $(n = 1, 7)$ clusters found in the Li_7Al_n $(n = 1, 7)$ clusters are shown in figure 2. These geometries show highly symmetric structures (with the exception of the Al_7 cluster) and do not correspond to the free Al clusters. In the homonuclear Al clusters [12] the ground-state geometry of Al_4 is a planar rhombus, in contrast to the present 3D form (a tetrahedron); Al_5 has C_s symmetry while the present symmetry is that of a more symmetric triangular biprism, and Al_6 takes the form of a D_{3d} trigonal antiprism formed by slight distortion of an octahedron. Thus it is evident that the geometries of the Li_7Al_n $(n = 1, 7)$ clusters are primarily determined by the formation of the Al clusters which are then capped by Li in such a way as to form dominant tetrahedral bonding between Li and Al atoms. We believe that the stability of these clusters is dictated by the s–p bonding between the Li and Al atoms.

To assess the stability of the Li_7Al_n $(n = 1, 7)$ clusters, we shall discuss these structures in the context of their energetics. Towards this end we show the binding energies per atom

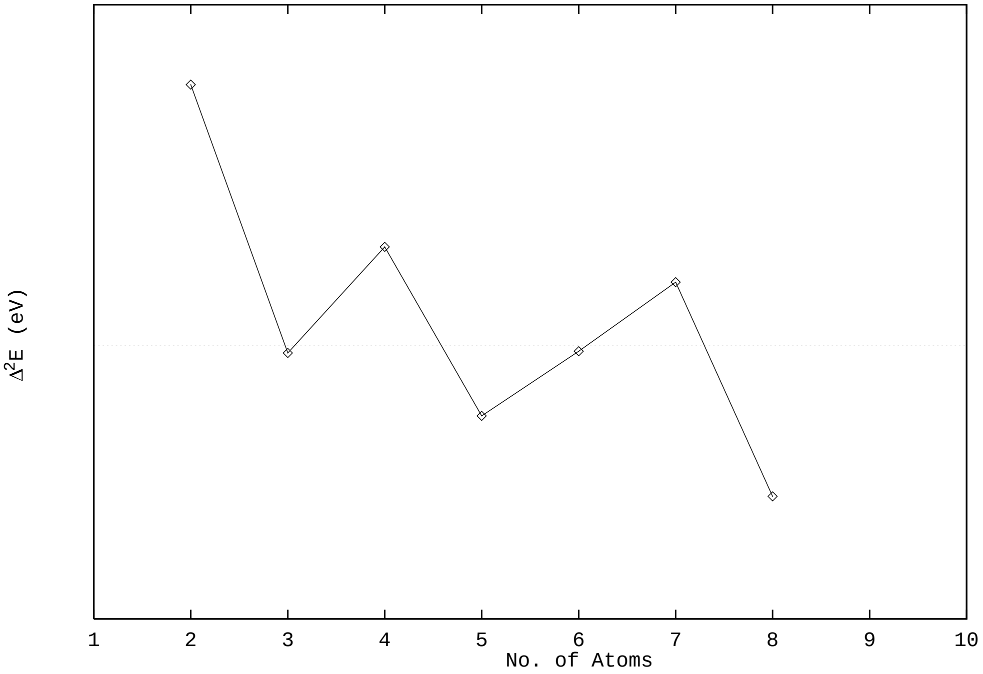
$$E_b[\mathrm{Li}_n\mathrm{Al}_m] = (-E[\mathrm{Li}_n\mathrm{Al}_m] + nE[\mathrm{Li}] + mE[\mathrm{Al}])/(n+m)$$

in figure 3(a), the second difference in energy defined as

$$\Delta^2 E[\mathrm{Li}_n\mathrm{Al}_m] = -2E[\mathrm{Li}_n\mathrm{Al}_m] + E[\mathrm{Li}_{n+1}\mathrm{Al}_m] + E[\mathrm{Li}_{n-1}\mathrm{Al}_m]$$

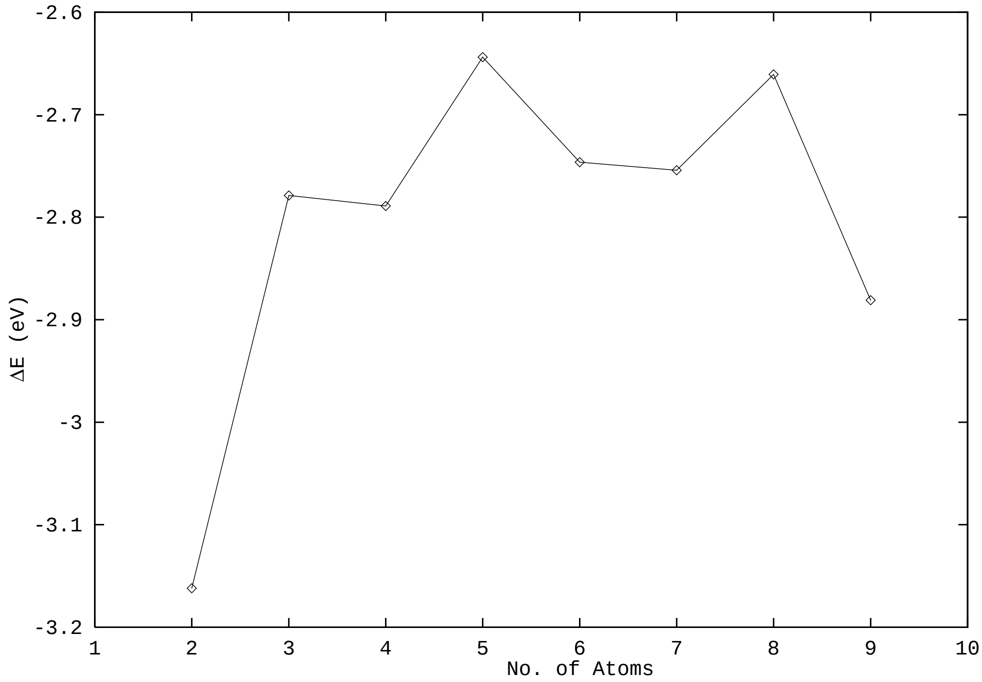


(a)



(b)

Figure 4. (a) The binding energy per atom E_b (in eV) for the Li$_n$Al clusters as a function of the total number of atoms. (b) The second difference in energy (in eV) as a function of the total number of atoms in the Li$_n$Al clusters. (c) The dissociation energy (in eV) as a function of the total number of atoms in Li$_n$Al clusters.



(c)

Figure 4. (Continued)

in figure 3(b) and the dissociation energy defined by

$$\Delta E[\mathrm{Li}_n\mathrm{Al}_m] = E[\mathrm{Li}_n\mathrm{Al}_m] - (E[\mathrm{Li}_n\mathrm{Al}_{m-1}] + E[\mathrm{Al}])$$

in figure 3(c). It is seen that there is a monotonic increase in the binding energy with the increase in the number of Al atoms, and it peaks when the total number of atoms is equal to 13, which is in the $\mathrm{Li_7Al_6}$ system. It may be noted that this has the incomplete FCC structure discussed above. Completing this geometry by adding one Li atom gives a higher binding energy of -3.21 eV as compared to -3.19 eV for the $\mathrm{Li_7Al_6}$ cluster, indicating that $\mathrm{Li_8Al_6}$ is a more stable cluster. Furthermore, the second differences in energies indicate that amongst the $\mathrm{Li_7Al}_n$ clusters, $\mathrm{Li_7Al_6}$ is the most stable along with $\mathrm{Li_7Al_4}$. The dissociation energies show that $\mathrm{Li_7Al_3}$ and $\mathrm{Li_7Al_6}$ are the most stable and $\mathrm{Li_7Al}$, $\mathrm{Li_7Al_5}$ and $\mathrm{Li_7Al_7}$ are least stable as regards the dissociation of a single Al atom from the cluster.

In addition to this we have also studied the ground-state geometries and energetics of $\mathrm{Li}_n\mathrm{Al}$ ($n = 1, 8$) clusters. Our results for the ground-state geometries and their symmetries are in agreement with those of Cheng *et al* [5]. Interestingly the ground-state geometries of free Li clusters [11] having the same total number of atoms are different from the ground-state geometries of these clusters. For example, the presence of an Al atom makes the $\mathrm{Li_3Al}$ cluster three dimensional (a tetrahedron) with $\mathrm{C_{3v}}$ symmetry as against $\mathrm{Li_4}$ which is planar with $\mathrm{D_{2h}}$ symmetry. $\mathrm{Li_5}$ is also planar with $\mathrm{C_{2v}}$ symmetry but $\mathrm{Li_4Al}$ has $\mathrm{C_{4v}}$ symmetry, $\mathrm{Li_6}$ is the first 3D structure in the free Li clusters and has $\mathrm{C_{5v}}$ symmetry while $\mathrm{Li_5Al}$ has $\mathrm{C_{4v}}$ symmetry, $\mathrm{Li_7}$ has $\mathrm{D_{5h}}$ symmetry unlike $\mathrm{Li_6Al}$ which has $\mathrm{O_h}$ symmetry with Al embedded inside the Li atoms forming a most symmetric and most stable structure, and $\mathrm{Li_8}$ has $\mathrm{T_d}$ symmetry compared to $\mathrm{Li_7Al}$ which has $\mathrm{C_{1h}}$ symmetry and $\mathrm{Li_9}$ has $\mathrm{C_{2v}}$ symmetry, whereas

Li_8Al is highly symmetric and has D_{4d} symmetry. Thus it can be seen that adding one Al atom to the Li clusters changes the symmetries and that there is an early appearance of 3D geometries. This also confirms the role of s–p bonding noted earlier and the preference towards tetrahedral coordination.

To study the stability of these clusters we present the results for the binding energy per atom, in figure 4(a), the second difference in energy, in figure 4(b), and the dissociation energy, in figure 4(c). It can be seen that the binding energy increases with increasing number of Li atoms. Initially the increase is large and later it is uniform, which is expected since the effect of one atom impurity as the cluster size increases will be less pronounced. The second difference in energy and the dissociation energy indicate that besides the dimer, Li_3Al and Li_6Al with four and seven as the total numbers of atoms are the most stable. Their ground-state geometries are highly symmetric. The least stable clusters are those of Li_2Al, Li_4Al and Li_7Al.

An examination of the most stable clusters in terms of the total number of electrons indicates that none of these clusters show the magic shell numbers (2, 8, 20, 34, 40, ...) seen in the abundance spectra of alkali metals. It may be mentioned that this fact has been brought out in the calculations reported by Cheng *et al*. Quite clearly, the role of ion cores and proper treatment of electron bonding effects need to be incorporated to understand the stability of such clusters.

In this communication we have reported our results on the geometries and stability of Li_nAl_m clusters using the density-based *ab initio* molecular dynamics. Our systematic and extensive investigation of Li_7Al_n $(n = 1, 7)$ and Li_nAl $(n = 1, 8)$ clusters indicate that their ground-state geometries differ from that of homonuclear Li and Al clusters. We find that the stabilities of these clusters appear to be dominated by tetrahedral coordination between Li and Al atoms. We also report a very interesting FCC structure for an Li_8Al_6 cluster with the Al atoms forming an octahedron. We find no evidence for the conventional magic numbers in these systems. It is hoped that studies such as these will provide the impetus for more experimental studies of heteronuclear clusters.

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