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Reactivity and electronic structure of aluminum clusters: The aluminum–nitrogen system

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The stability of anionic aluminum–nitrogen clusters has been examined and Al_2N^-, $Al_3N_2^-$, $Al_5N_2^-$, $Al_6N_3^-$, $Al_8N_3^-$, and $Al_9N_2^-$ are found to be particularly stable. Theoretical density functional calculations on neutral and anionic Al_nN ($n=1-8$) clusters were performed and the stability and reaction energetics with oxygen examined. Clusters requiring less than 5.7 eV to remove an electron and an Al atom are shown to be resistant to the reaction with oxygen. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1333017]

I. INTRODUCTION

A vast number of investigations have attempted to specifically address the stability of various metal-containing clusters.[1–6] These studies have implemented both experimental and theoretical approaches, with efforts focused mainly on understanding the factors that influence the reactivities and properties of cluster systems. Recently, another unified objective has surfaced. Instead of emphasizing the search for highly stable species, attention is shifting toward the prospects of forming new materials, through the concept of cluster assembly.[3–5] Ideally, these species would preserve their stable constituent properties and ultimately retain their integrity when coupled to one another and/or the appropriate counter-ion, thereby making them suitable as building blocks in the process of synthesizing new nanoscale materials.

With these goals in mind, the search to develop tailor-designed materials, through the assembly of clusters, is currently underway.[6] As one can imagine, prospective candidates are limited, not only by the obvious paucity of theoretical calculations, but by the lack of experimental evidence for those clusters which readily retain desirable properties. It is therefore understandable why aluminum, being a free electron system, has been so thoroughly studied,[7] since it is readily amendable to theory and previous experimental results have shown the unique stability that intrinsically exists.

This pronounced stability also provides substantial insight into the role of the frontier orbitals in reactivity. Leuchtner and co-workers,[8] for example, showed the unique stability of Al_{13}^-, Al_{23}^-, and Al_{37}^- in the presence of oxygen, while Leskiw and Castleman[9] revealed similar findings for AlC^- and Al_7C^-. These observed stable cluster species essentially contain a sufficient number of valence electrons that correspond to the predicted electronic shell closings of the Jellium model[10,11] and, as a result, confirm its applicability. In the present article, an experimental and theoretical investigation of stable aluminum–nitrogen cluster species is presented, with particular emphasis placed on the applicability of a composite Jellium[9] system and the prospects of forming cluster assembled materials.

II. EXPERIMENT

The apparatus used in this study is a fast flow reactor[12,13] in which an aluminum rod is vaporized in the presence of a helium carrier gas and a small percentage of nitrogen. The ablated species, upon mixing with these gases, exit a conical nozzle and enter a flow tube. As the thermalized cluster ions proceed toward the detector, additional species (oxygen) may be added, through a reactant gas inlet (RGI), to establish the stability of the cluster distribution. The cluster ions are mass selected with a quadrupole mass analyzer and subsequently detected with a channeltron electron multiplier.

III. RESULTS

Figure 1 shows the distribution of pure Al_n^- ($n=2-28$) clusters while Fig. 2 illustrates an obtained Al_n^- ($n=2-21$), $Al_nN_m^-$ ($n=2-20$, $m=1-3$) cluster distribution. Although the $m=1$ variety (Al_nN^-) appear as the most abundant species in the spectra (Fig. 2), $Al_nN_m^-$ ($m=2$ and 3) species are indeed present, but are only readily discernible at low ion intensities, or after oxygen addition. Figure 3 not only demonstrates the progressive decrease in the initial distribution after the addition of 50 sccm (standard cubic centimeters per minute) of oxygen, it hints at the stable entities that emerge as the harsh reactive oxygen environment intensifies. In Fig. 4, 200 sccm of oxygen have been added through the RGI, and the stable species are dominant. The enhanced intensity of particular clusters can be accounted for in terms of the etching of higher order species that feed smaller ones of greater stability.

IV. DISCUSSION

The basis behind the search for stable cluster species has been rooted in the fundamental differences in the properties of matter for the bulk state and systems of limited size.
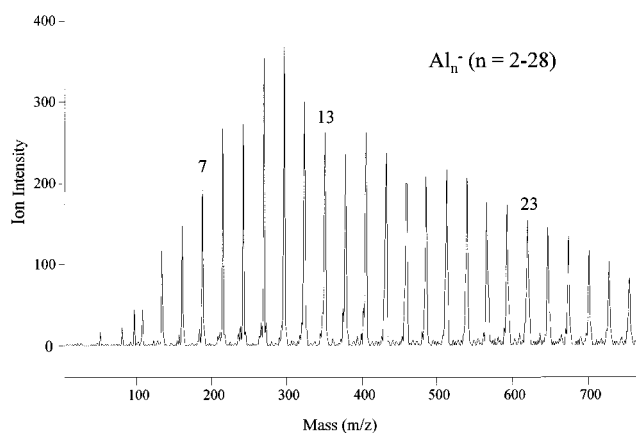
FIG. 1. Pure aluminum anion cluster distribution obtained using a laser vaporization source without reactant gas.

These discrepancies have thus lead to the prospects of forming new materials with unique properties such that all are retained at bulk proportions. Of course, problems stem in identifying suitable candidates, but the use of the Jellium concept, for example, seems to be a valuable starting point for assessing those species that warrant additional consideration.

The observed stability of Al_2N^- in the presence of oxygen is shown in Fig. 4 and can be explained through its behavior as an eight-electron ''Jellium-like'' species.[9] In this model, clusters containing 2, 8, 18, 20, ... valence electrons correspond to the filled electronic shells and are particularly stable. Al is a trivalent metal, and the electronic configuration of an Al atom is $3s^2 3p^1$ with the spacing between the $3s$ and $3p$ states being 4.79 eV. As the Al atoms are brought together, the bond formation leads to an overlap between the bands formed out of s and p states and the metallic character sets in. In the case of pure Al_n clusters, such a transition is proposed to occur around Al_9. Below this size, however, the s and p states remain separated and Al behaves as a monovalent atom. Since N has five valence electrons, Al_2N^- can be
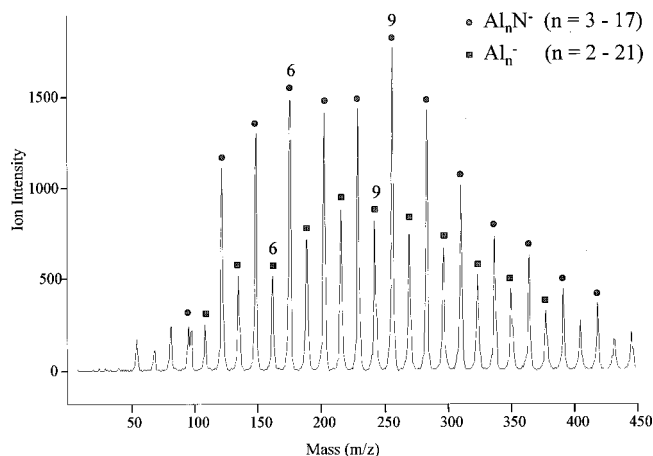

FIG. 2. Distribution of aluminum and aluminum–nitrogen anion clusters obtained by introducing nitrogen gas into the laser vaporization source. Note: $Al_nN_m^-$ distribution is typically of greater intensity than the proximate Al^- distribution.

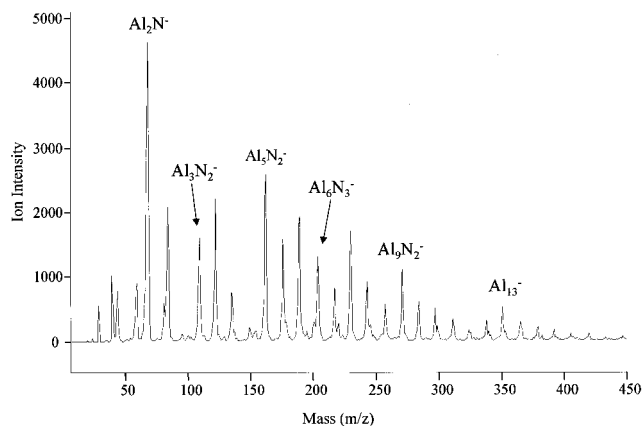
FIG. 3. Distribution of $Al_nN_m^-$ with the addition of 50 sccm oxygen.

considered an eight-electron system. The stability of $Al_3N_2^-$, $Al_6N_3^-$, and $Al_8N_3^-$ could also be explained in accordance with the Jellium model with the stability of $Al_5N_2^-$ and $Al_9N_2^-$ demonstrating conformity to the composite Jellium concept.

V. THEORETICAL CONSIDERATIONS

Admittedly, the Jellium concept is an oversimplified approach for deducing the properties and accounting for observations of cluster reactivities. It does, however, provide some general guidance towards searching for species that may be useful candidates when considering the nearly infinite variety that are available. *Ab initio* calculations are therefore needed to understand the experimental findings and to identify potential candidates when forming cluster materials. We have therefore carried out electronic structure calculations on anionic and neutral Al_nN clusters containing up to eight Al atoms.

The theoretical studies were carried out using a linear combination of atomic orbitals molecular orbital approach.[14] The molecular orbitals were formed out of atomic orbitals located at the atomic sites. The atomic orbitals in turn were expressed as a linear combination of Gaussian functions while the exchange correlation effects were incorporated using a density functional approach.[15] A gradient-corrected
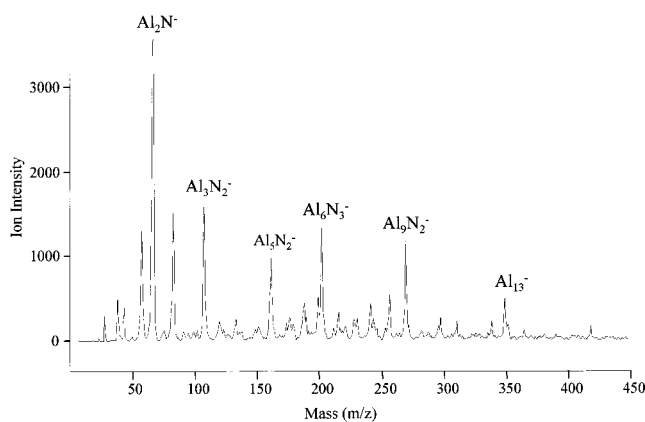

FIG. 4. Distribution of $Al_nN_m^-$ with the addition of 200 sccm oxygen.

TABLE I. Multiplicity, bond lengths, and atomization energies (AE) for AlN and AlN$^-$ dimers.

Molecule	Source	Multiplicity	Bond length (Å)	AE (eV)
AlN	Present	3	1.79	3.04
	Previous (Refs. 19 and 20)	3	1.79, 1.80	2.45, 2.78
	Expt. (Ref. 21)		1.79	3.08
AlN$^-$	Present	2	1.72	4.59
	Previous (Ref. 20)	2	1.71	3.96

density functional recently proposed by Perdew *et al.*[16] was used. All the calculations were done at the all-electron level and the multicenter integrals required to solve the Kohn–Sham equations were calculated by integrating numerically over a mesh of points. The actual calculations were done using the NRLMOL[17] code developed by Pederson and Jackson. The basis set consisted of $6s$, $5p$, and $3d$ Gaussian functions for Al and $5s$, $4p$, and $3d$ Gaussian functions for N. These were supplemented by one d function in each case. These basis functions are well tested[18] and the reader is referred to earlier papers[17] for details. In all cases, several initial configurations were used and the geometry was optimized without symmetry constraint by moving the atoms in the direction of forces. The final geometries therefore include possible Jahn–Teller distortions.

One can estimate the accuracy of the calculations by comparing the results of calculations on atoms and dimers for which experiments or the previous calculations exist. For Al and N atoms we obtain ionization potentials of 6.07 and 14.73 eV, respectively, with the corresponding experimental

values being 5.99 and 14.53 eV. In Table I we have compared the ground state spin multiplicity, bond length, and the atomization energy (AE) of AlN and AlN$^-$ with previous[19–21] theoretical and experimental studies. Note that our calculated spin multiplicities agree with previous calculations based on the coupled cluster approach. The present AE are, however, slightly higher but, in the absence of experimental data, it is difficult to judge which result is more accurate.

Figure 5 shows the ground state geometries, bond length, and the spin multiplicities of the anionic and neutral Al$_n$N clusters. The ground state structure for Al$_2$N is bent while the neutral and anionic Al$_3$N clusters have a D$_{3h}$ and C$_{2v}$ structure, respectively; the addition of the electron to the neutral cluster evidently has a large effect on geometry. For Al$_4$N, the anion and the neutral both have a D$_{4h}$ ground state. The geometry of Al$_5$N could be envisioned as an Al$_3$N cluster with an Al$_2$ dimer attached to one side while Al$_6$N$^-$ can be considered as a distorted octahedron with a central N atom. Al$_6$N, however, is a distorted D$_{2d}$ structure, and in Al$_7$N and Al$_8$N, the N atom becomes centrally located. Note that since we plan to discuss the reactivity of these clusters with oxygen molecules and one of the possible channels involves the formation of NO$_2$, such a channel could be excluded in these clusters. Also note that, except for AlN, the ground states all correspond to the lowest spin multiplicities.

Table II contains the AE of the neutral and anionic clusters. For the anionic clusters, the AE corresponds to the dissociation into Al$^-$, N, and the remaining neutral Al atoms. To gain insight on the relative stability of various clusters, we have also listed the energy gain as an Al atom is added to the preceding size (ΔE_n and ΔE_0). Note that Al$_2$N$^-$ has the
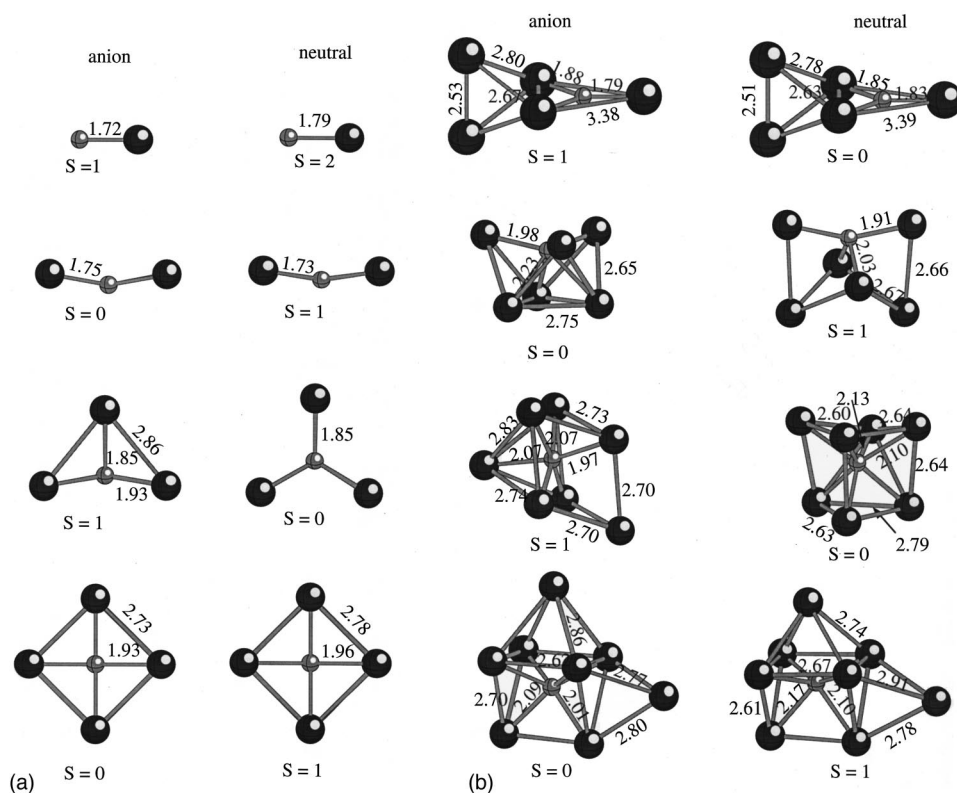

FIG. 5. The ground state geometries and spin multiplicities of neutral and anionic Al$_n$N$^-$ ($n=1-8$) clusters. The small circles are N atoms while the big circles (not to scale) are Al atoms. Bond lengths are in Å.

TABLE II. Atomization energy (AE) for the neutral and anionic Al_nN ($n = 1-8$) clusters. ΔE_n and ΔE_0 are the differences in energy between clusters with n and $n-1$ Al atoms for the anionic and neutral clusters, respectively. The AEA is the adiabatic electron affinity, defined here as the energy difference between the relaxed anion and the relaxed neutral cluster of the same size. ΔE_D is the difference in the atomization energies of the ground state anionic cluster of size n and the neutral cluster of size $n-1$.

| Cluster | Anion | | Neutral | | | |
	AE (eV)	ΔE_n	AE (eV)	ΔE_0	AEA (eV)	ΔE_D
AlN	4.59		3.04		1.96	
Al_2N	10.05	5.46	8.25	5.21	2.22	7.01
Al_3N	12.58	2.53	11.94	3.69	1.06	4.33
Al_4N	15.63	3.05	13.74	1.80	2.30	3.69
Al_5N	17.37	1.74	15.96	2.22	1.82	3.63
Al_6N	20.39	3.02	18.75	2.79	2.05	4.43
Al_7N	23.66	3.27	22.31	3.56	1.77	4.91
Al_8N	25.77	2.11	24.09	1.78	2.10	3.46

highest gain in energy and can be considered to be the most stable cluster. Al_2N also has a high ΔE_0 and is the most stable out of the neutral species. On the other hand, Al_5N^-, Al_8N^-, Al_4N, and Al_8N appear to be the least energetically stable. Table II also lists the adiabatic electron affinity (AEA) which corresponds to the gain in energy as an electron is added to the neutral cluster. Note that all the even Al atom clusters have higher electron affinity than the proximate odd clusters with Al_3N being the lowest.

Before we proceed further, we can compare the current findings with previous studies and experiments. Nayak *et al.*[22] have performed negative ion photoelectron spectroscopy experiments on Al_3N^- and Al_4N^- clusters and have also carried out density functional calculations. Our calculated ground states for anionic and neutral Al_3N and Al_4N are similar to their results. For Al_3N, our calculated AEA of 1.06 eV is comparable to their experimental value of 0.96 eV and their calculated value of 1.0 eV. For Al_4N, our calculated value of 2.30 eV is also comparable to their experimental value of 2.32 eV and their calculated value of 2.29 eV. Their experimental photoelectron spectra on Al_3N^- show peaks at 1.19 and 2.62 eV. The ground state of Al_3N^- is a doublet and one can consider transitions to singlet and triplet neutral states. For these transitions, their calculations give vertical detachment energies of 1.42 and 2.62 eV, respectively, compared to our values of 1.46 and 2.65 eV. For Al_4N^-, the experimental spectra show strong features at 2.32 and 3.41 eV. Nayak *et al.* only calculated the vertical transition energy from the anion to the lowest doublet state of the neutral and their calculated value of 2.31 eV is close to the first experimental peak. We calculated vertical transitions from the ground state of the anion to the ground and excited states of the neutral doublet to be 2.32 and 3.19 eV, respectively, which are also close to experiment.

We now arrive at the present experiments regarding the reactivity of Al_nN^- clusters and oxygen. The experimental spectra show a strong peak at Al_2N^-. Note that when Al_nN^- clusters are reacted with O_2, a possible reaction channel is the formation of AlO_2^-, i.e.,

$$Al_nN^- + O2 \rightarrow Al_{n-1}N + AlO_2^-.$$

The mass spectra in Figs. 2 and 3 indeed show that the intensity of AlO_2^- grows after the reaction with oxygen. In a recent paper[11] it was shown that the total energy gain in forming an AlO_2^- from an Al atom, an electron, and O_2 is 5.7 eV. Our expectation then would be that those clusters where the total energy required to remove an electron and an Al atom is less than 5.7 eV would react with O_2 to form an $Al_{n-1}N$ species. These clusters would therefore react and diminish in intensity. The last column in Table II lists the energy required to remove an Al atom and an electron from various clusters. It is gratifying to note that Al_2N^- is the only cluster that is energetically stable against such a reaction. We have also verified that Al_2N^- is stable against a reaction involving the formation of NO_2 i.e.,

$$Al_nN^- + O_2 \rightarrow Al_n^- + NO_2$$
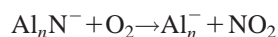
or NO_2^-. Al_2N^- is therefore a very stable cluster. An analysis of the electronic structure shows that the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is 2.51 eV and evidently has a closed electronic shell.

We would like to add that the formation of AlO_2^- is not the only reaction channel. For smaller clusters, the N atoms can react with O_2 to form NO_2 or NO_2^-. For clusters containing more than 5 Al atoms, the N sites are located on the inside of the cluster in the ground state and it would seem that such a reaction is not possible. However, we have found that these clusters do have energetically close isomers with N at the outside. For example, Fig. 6 shows the lowest isomer for Al_5N, Al_6N, and Al_7N clusters along with their energies relative to the corresponding ground states. Note that for Al_5N and Al_6N, the excited states are only 0.11 and 0.01 eV above the ground state and may exist in the beams. These isomers have exposed N sites and can react to form NO_2^-.

As mentioned above, one can try to understand the stability of Al_2N^- and other clusters using a simple Jellium concept. However, due to the spacing between the $3s$ and $3p$ states in an Al atom, Al behaves as a monovalent atom in small clusters.[23] Al_2N^- can then be regarded as an eight-electron system. We would, however, like to point out that such a simplistic approach is not absent of problems. The electronic configuration of a N atom is $2s^2 2p^3$ and the separation between the s and p states in a N atom is 4.79 eV. This $s-p$ separation is larger than in Al and if one uses the same argument as for the case of Al, a N atom would contribute three and not five valence electrons. Such an assignment would not lead to a filled shell in a Jellium model. Present *ab initio* studies also do not show any abnormally high electron affinity characteristic of filled Jellium shells. It is then surprising that despite these problems, the model does seem to make correct predictions.

VI. CONCLUSION

Experiments on aluminum–nitrogen clusters have been carried out to search for highly stable clusters that could serve as the building blocks for cluster assembled materials. The observed mass spectra obtained after reacting the clusters with oxygen show that Al_2N^-, $Al_3N_2^-$, $Al_5N_2^-$, $Al_6N_3^-$,

1.98
2.67
2.80

a.)

S = 1
ΔE = +0.11 eV

1.87
2.04
2.66
2.74

b.)

S = 2
ΔE = +0.01 eV

1.87
2.05
2.88
2.66
2.74
2.61

c.)

S = 1
ΔE = +0.43 eV
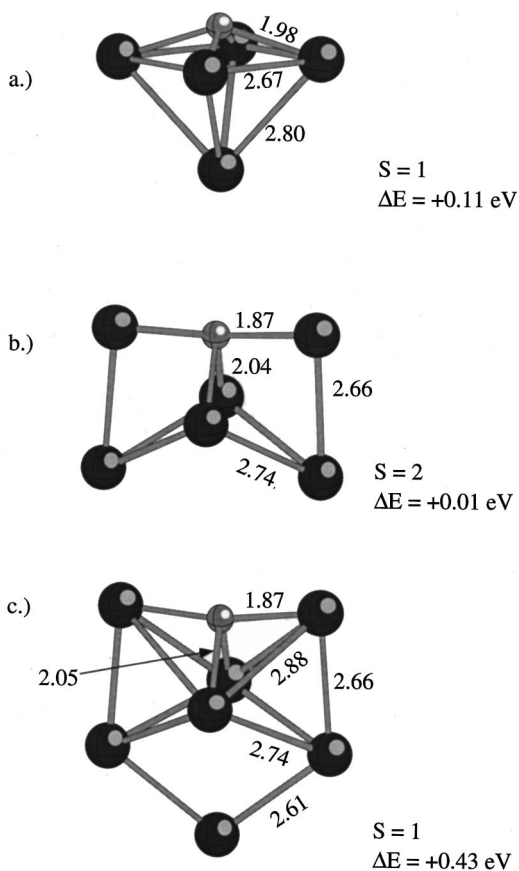
FIG. 6. The geometries and spin multiplicities of low energy anionic Al_nN^- ($n = 5-7$) clusters. The small circles are N atoms while the big circles (not to scale) are Al atoms. Bond lengths are in Å. ΔE is the energy above the corresponding ground state.

$Al_8N_3^-$, and $Al_9N_2^-$ are particularly stable. A simple Jellium model can be used to understand the stability of these clusters. The *ab initio* calculations on Al_nN clusters have been carried out to quantitatively examine the energetics of the reaction and these studies show that the prominent reaction channel is the formation of AlO_2^-. Those anionic clusters where the energy required to remove an electron and an Al atom is less that 5.70 eV are stable against such a reactions.

For clusters containing a single N atom, Al_2N^- is shown to correspond to such a cluster and may be an ideal candidate for the cluster assemblies.

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