Evolution of bonding in Al_nN clusters: A transition from nonmetallic to metallic character

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The evolution of the equilibrium geometry, binding energy, and electronic structure of Al_nN clusters has been studied using first-principles calculations based on density-functional theory. The bonding in small ($n \leq 6$) Al_nN clusters, in analogy with the electronic structure of bulk aluminum nitride, is found to be intermediate between ionic and covalent. However, the electronic structure takes on a metallic character in $Al_{12}N$ and the cluster's chemistry is seen to mimic the chemistry of an alkali atom. The calculations also reveal the existence of an anomalously stable Al_3N cluster, in sharp contrast with the bulk stoichiometric composition. [S0163-1829(98)00804-2]

While solid compounds involving two or more elements occur only for certain stoichiometries, compound clusters can be synthesized by mixing atoms in a wide range of compositions. It is even possible to synthesize clusters of different elements that normally are immiscible in the solid phase.[1] These possibilities arise because the chemistry of clusters is very different from that of crystals. The ability to construct a cluster with specific composition and size provides the hope that a new class of materials where clusters form the building blocks can be synthesized.[2] Since the properties of clusters are unique, it is expected that cluster-assembled materials can have uncommon properties. An understanding of the evolution of the electronic structure of compound clusters is, therefore, necessary.

Consider, the case of Al and N. The only known solid phase is AlN which is an important wide band-gap semiconductor and one of the best known thermal conductors.[3] Under ambient conditions, it has a wurtzite-type structure that changes to rocksalt-type phase under pressure.[4,5] The nature of bonding in bulk AlN is partly ionic and partly covalent. It is then interesting to ask how the electronic structure would change if one could mix Al and N in different proportions. We begin with an AlN dimer. The number of valence electrons in this case is eight. If the stability of the AlN dimer could be understood from a jellium model,[6] as has been found to be the case for simple metal clusters, one would expect AlN to be a magic number since eight electrons are needed for the closing of the first two electronic shells. In a similar vein, Al_5N containing 20 valence electrons should also be magic as the first four shells can be completely closed. However, if the nature of bonding between the atoms is not metallic in small Al_nN clusters, the magic numbers cannot be inferred from the jellium model. Clearly, when the number n of Al atoms in a cluster is very large, Al_nN would have metallic character. Just how large does this n have to be before metallization sets in?

In this paper we address these issues by studying systematically the geometries, binding energies, and electronic structure of Al_nN clusters containing 1–6 and 12 Al atoms. Our theoretical studies are based on the linear combination of atomic-orbitals–molecular-orbitals approach and are carried out self-consistency within the density-functional scheme. We first show that the electronic structure of small

Al_nN clusters ($n \leq 6$) are dominated by bonding characteristics that are intermediate between ionic and covalent character. More importantly, we find Al_3N to be an unusually stable cluster. The ionization potential decreases monotonically as the metallic component of the cluster is increased. The electronic structure of $Al_{12}N$, which is icosahedral with a central N atom, is found to be metallic. It has 41 valence electrons, one more than 40 required to fill the electronic shells in a jellium picture. The chemistry of $Al_{12}N$ should, therefore, be like that of an alkali atom. This is, indeed, the case. We show that $Al_{12}N$ has a low ionization potential comparable to alkali atoms and $(Al_{12}N)Cl$ is an ionic ''molecule.''

We now describe our theoretical approach. The atomic orbitals were represented by a set of Gaussian orbitals. We considered all electrons and 6-311 G** basis set for Al and N.[7] The total energies were calculated using the density-functional theory and two levels of approximation for the exchange-correlation energy functional. The simpler one is based on the local spin-density approximation (LSDA) that made use of Vosko, Wilk, and Nusair form for the exchange-correlation functional.[8] Improvements in this formulation were made by adopting the generalized gradient approximation (GGA) due to Becke.[9] The GAUSSIAN 94 software was used. The calculated bond lengths and binding energies of AlN, Al_2, and N_2, as well as the ionization potential of Al and N atoms using LSDA and GGA, are given in Table I and compared with the corresponding experimental values.[10] As expected, the LSDA energies lead to overbinding while the bond lengths are insensitive to particular choices in the exchange-correlation functional. Since the binding energies obtained using GGA provide better agreement with experiment, we have calculated all properties of Al_nN clusters ($n \leq 6$) using the GGA level of theory and BPW91 provision of the GAUSSIAN 94 code. To optimize the geometries of Al_nN clusters, we started with several initial configurations of each cluster and relaxed all the geometrical parameters without regard to symmetry constraint. The path of steepest descent was followed in the energy minimization procedure. We obtained not only the global equilibrium structure, but also several higher-energy structures corresponding to local minima in the potential energy surface.

We now start with our results on small Al_nN clusters. In Figs. 1 and 2, we give the ground-state geometries and the

TABLE I. Binding energies and bond lengths of Al_2, N_2, and AlN dimers and ionization potentials of Al and N atoms calculated using local spin-density approximation and generalized gradient approximation.

	Binding energies (eV)			Bond lengths (Å)			Ionization potential of atoms		
	LSDA	GGA	Expt. (Ref. 10)	LSDA	GGA	Expt. (Ref. 10)	LSDA	GGA	Expt. (Ref. 10)
Al_2	1.96	1.53	1.56	2.46	2.49	2.56	6.46	6.08	5.99
N_2	11.73	10.12	9.76	1.09	1.11	1.10	15.44	14.72	14.53
Al-N	3.54	2.78	3.08	1.78	1.80				

geometries of clusters that are found to be nearly degenerate with the ground-state structures. The preferred spin multiplicity of the ground state, the binding energy, and the ionization potential of the clusters are given in Table II. The ground state of AlN [Fig. 1(a)] is a spin triplet with a bond length of 1.80 Å and a binding energy per atom of 1.39 eV. Note that the binding energy/atom of AlN is larger than that in Al_2. Thus, in small Al_nN clusters, the equilibrium geometry should correspond to a structure that would maximize the number of Al-N bonds. For Al_2N we tried both triangular and linear structures. The ground state [Fig. 1(b)] was a linear Al-N-Al chain with a Al-N bond length of 1.74 Å and a binding energy of 2.62 eV per atom. Two striking features in Al_2N should be pointed out. First, the total binding energy of Al_2N is about 5 eV larger than that of AlN dimer, in spite of the fact that AlN contains eight valence electrons, which, according to the jellium model, is enough to close the first two electronic shells. Thus, Al_2N is much more stable than

AlN. This sharp departure is an indication that the bonding in small AlN clusters is far from metallic. Second, the AlN bond distance in Al_2N is *shorter* than that in AlN—again indicative of increasing covalent character of the cluster. We also note that the preferred spin multiplicity of Al_2N is a doublet, which is the lowest it can have for a cluster containing an odd number of electrons. We will see in subsequent cases that the preferred spin multiplicities are always the lowest, i.e., singlet for even-numbered electron systems and doublet for odd-numbered electron systems.

For Al_3N we tried three initial configurations: one three-dimensional and two planar structures. A planar structure with a central N bound to three Al atoms was found to be the ground state [Fig. 1(c)]. The AlN bond length increases to 1.86 Å as does the binding energy. It is important to note that the binding energy/atom of Al_3N is the largest among all Al_nN ($n \leq 6$) clusters studied. This factor combined with the observation of Al_3N as a planar structure with a threefold coordination of N provides a glimpse of the chemistry of the N atom. We recall that N is trivalent and NH_3 is a very stable molecule although the geometry of NH_3 is three dimensional. The reason Al_3N is planar has to do with the fact that the bonding between Al and N is dominated by p electrons whereas in NH_3, the bonding is with the s electrons of H.

FIG. 1. The ground-state and next high-energy geometries and bond lengths of Al_nN ($n \leq 4$) clusters. The numbers in parentheses are the Mulliken charges at the various sites. The bond lengths are given in Å.
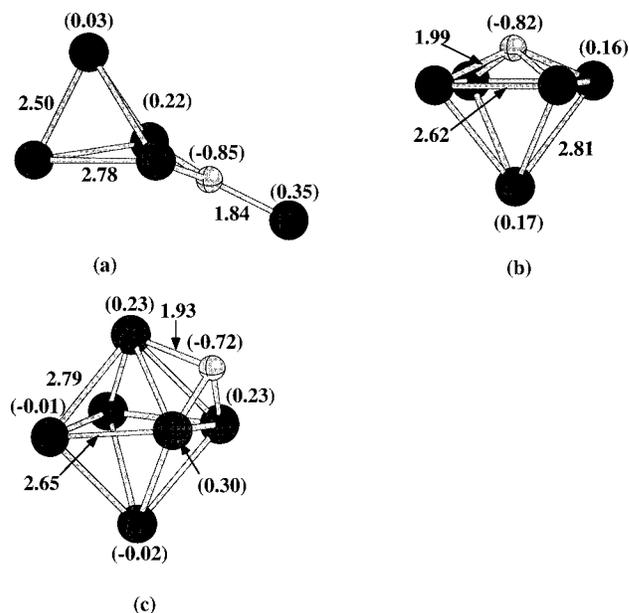
FIG. 2. The ground-state and next high-energy geometries and bond lengths of Al_nN ($4 < n \leq 6$) clusters. The numbers in the parentheses are the Mulliken charges at the various sites. The bond lengths are given in Å.

Cluster	Binding energy/atom (eV)	Ionization potential (eV)	Spin multiplicity
AlN	1.39	9.0	3
Al_2N	2.62	7.84	2
Al_3N	2.86	7.74	1
Al_4N(a)	2.62	7.30	2
Al_4N(b)	2.58	6.11	2
Al_5N(a)	2.52	6.25	1
Al_5N(b)	2.48	6.69	1
Al_6N	2.41	6.48	2

For Al_4N, we tried five different initial configurations: two planar and three three-dimensional geometries. The ground state was found to be a planar structure with a central N surrounded by four Al atoms forming a square [Fig. 1(d)]. However, the binding energy atom of this cluster is only 0.24 eV less than that of Al_3N. This is caused by two factors: First, nitrogen has fourfold coordination while it would prefer to be threefold coordinated due to its chemistry. Second, because of larger coordination, the Al-N bond stretches from 1.86 to 1.97 Å. An extensive search was carried out to look for energetically nearly degenerate isomers of Al_4N. Indeed, there exists another planar structure [see Fig. 1(e)] that lies only 0.2 eV above the ground state. Note that in this structure N is threefold coordinated to Al and the Al-N bond length resumes its 1.86 Å value seen in Al_3N.

For Al_5N, we tried four initial structures: a triangular bipyramid of Al_5 with a central N, the square-centered Al_4N decorated by an Al atom, a D_{2d} Al_4 with a central N decorated by an Al atom, and a capped triangular bipyramid with N as the capping atom. Two nearly degenerate structures (Fig. 2) were found that are derivatives of the Al_4N geometries. The ground state of Al_5N is composed of a planar Al_3N structure that is attached to two Al atoms so that the four nearest Al atoms form a tetrahedron [Fig. 2(a)]. Note that the Al-N distance in Al_5N is 1.84 Å and is very close to the 1.86 Å distance noted earlier. The fact that Al_5N builds on the original Al_3N structure further establishes the unusual stability of Al_3N. It is interesting to note that this bonding pattern is present in the bulk wurtzite structure where N is threefold coordinated to Al atoms in a manner similar to that in NH_3. Furthermore, the AlN bond distance in the wurtzite structure is 1.89 Å, which is very close to the bond length seen in clusters. The structure of Al_5N that lies only 0.24 eV above the ground state [Fig. 2(b)] has a fourfold coordinated N atom with an Al-N bond distance of 1.99 Å (similar to that in the ground-state structure of Al_4N).

Finally, for Al_6N we tried three initial structures: an octahedron of Al_6 with a central or outside N atom and a pentagonal bipyramid with Al_5 forming the base. The N atom capping the triangular face of the octahedron was found to be the ground state [Fig. 2(c)] with a binding energy of 2.41 eV per atom (see Fig. 2). The vertical ionization potentials of Al_nN given in Table II decrease smoothly as the Al content is increased.

From the above results one notes that the gain in energy as an Al atom is added to the preceding $Al_{n-1}N$ is 5.08, 3.58, 1.66, 1.78, and 1.97 eV for Al_2N, Al_3N, Al_4N, Al_5N, and Al_6N, respectively. Al_2N and Al_3N can thus be interpreted as magic clusters. As mentioned before, the magic numbers in metal clusters can be understood within a simple jellium picture. In this picture, the one electron levels in a spherical potential well are filled for 2,8,18,20,40, . . . electrons and cluster with these electron counts are particularly stable. If one were to apply such a model to all Al_nN clusters, one would expect AlN with 8 and Al_5N with 20 valence electrons to be particularly stable. They would also be spin singlet because of the filled electronic shell. On the contrary, the present calculation shows that AlN has the lowest binding energy per atom and is a spin triplet. Al_5N, on the other hand, is a spin singlet and does not have a particularly large binding-energy per atom. This shows that at very small sizes, the simple jellium picture does not apply, and the bonding is not metallic. Note that the bonding in solid AlN is a mixture of covalent and ionic components.

To determine the nature of bonding in clusters, we carried out a Mulliken population analysis of the resulting charge at each site. These are given in Figs. 1 and 2. Note that there is a significant charge transfer from Al to N site in all clusters. This indicates that the bonding in Al_nN clusters has, at least, some ionic character. In fact, the electrostatic attraction between N and Al in AlN, dimer, assuming that the Mulliken charges are localized at the sites, would be 1.23 eV compared to its binding energy of 2.78 eV. This shows that there is also a significant covalent contribution. The relative strength of covalent, ionic, and metallic nature changes with size. This is reflected in the Mulliken charge at the N site as n increases. In Al_3N and Al_4N, the nitrogen atom carries almost one extra electron. This charge slightly diminishes with increasing cluster size indicating that the clusters take on an increasingly metallic character.

To examine the cluster size where Al_nN could be metallic, we carried out electronic structure calculations on an icosahedric $Al_{12}N$ cluster. Because of its large size, these studies were carried out using a program that makes use of Gaussian atomic bases and norm-conserving nonlocal pseudopotentials.[11] Since these potentials are based on relativistic atoms using a local-density functional, no gradient corrections were added to maintain consistency. The basis sets for pseudo-wave-functions were obtained via a nonlinear fit of the pseudo-atomic-orbital calculated on a radial mesh. The pseudo-basis-sets for Al and N had $5s$ and $4p$ Gaussians for each atom. For an AlN dimer, this approach gives a bond length of 1.80 Å and a binding energy of 2.94 eV, which compares well with the corresponding LSDA results (see Table I) based on the all-electron calculations. From our earlier studies,[12] the ground state of Al_{13} was found to be icosahedral with a radial bond length of 2.68 Å and a binding energy of 36.7 eV. The studies on $Al_{12}B$ or $Al_{12}C$ have shown that when an Al atom in Al_{13} is replaced by a smaller atom, the smaller atom occupies the central site. In the present case, we therefore optimized the geometry of an icosahedral $Al_{12}N$ cluster with the N atom occupying the central site. The cluster had a radial bond length of 2.55 Å and a binding energy of 38.6 eV. Note that it is more stable than an Al_{13} cluster that lacks one electron to complete the

electronic shells. There are two factors that contribute to the enhanced stability of $Al_{12}N$. First, in an icosahedral Al_{13} cluster, the surface bonds are 5% longer than the radial bonds. Replacement of the central Al by N reduces the radial bond length, thus relaxing the surface strain and enhances the stability. Further, the AlN bond is stronger than the Al_2 bond, which also adds to the stability of the $Al_{12}N$ cluster. To see if the cluster would behave like an alkali atom, we first calculated the vertical ionization potential of the cluster. It was found to be 5.82 eV. Note that the ionization potential of a Li atom is 5.39 eV and that of an Al_{13} cluster is 7.2 eV. Replacing an Al atom by a nitrogen atom lowers the ionization potential of Al_{13} and $Al_{12}N$ can thus be regarded as a superalkali atom.

The chemical similarity between $Al_{12}N$ and an alkali atom can be further elucidated by studying the formation of molecules when combined with halogen atoms, i.e., studying a $(Al_{12}N)Cl$ ''molecule.'' The geometry optimization involved varying the distance of the Cl atom from the center of the icosahedron as well as the radius of the icosahedron. The preferred site of the Cl atom corresponds to the threefold surface site of the $Al_{12}N$ icosahedron. There is minimal change in the radial distance of the $Al_{12}N$ icosahedron while the Cl atom was 4.56 Å from the center of the icosahedron. The Cl atom was bound to the cluster by 2.69 eV. A Mulliken population analysis of the resulting charges showed that the Cl atom gains about $0.3\,e^-$ confirming that the $Al_{12}N$ loses electrons as would an alkali atom. This is interesting since neither N nor Al are alkali atoms.

To summarize, we have shown that the nature of bonding between N and Al atoms progresses from ionic and covalent character to metallic character in $Al_{12}N$ cluster. Like bulk AlN which is a semiconductor, the bonding in small Al_nN is dominated by the ionic and covalent character. These bonding features, together with the chemistry of the N atom, make Al_2N and Al_3N unusually stable clusters. However, further addition of Al atoms results in the development of metallic bonding and the stability of $Al_{12}N$ is governed by metallic character. In particular, $Al_{12}N$ cluster behaves like an alkali atom and forms an ionic ''molecule'' when combined with Cl. It is our hope that this study will stimulate experimental interest in these clusters.

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