# Atomic and electronic shells of $Al_{77}$

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We have carried out a first-principles calculation on the atomic and electronic shell structures for the experimentally characterized $Al_{77}$. The onionlike $Al_{77}$ structure can be described by a stable $Al_{13}$ inner core covered by a two-layer atomic shell. The stability of $Al_{77}$ is confirmed by structural optimization and electronic structure calculations. The interaction between $Al_{77}$ and its ligands is found to be ionic like. Our results on the electronic structure provide important information on electronic shell structures in large Al clusters.

The atomic and electronic structures of metal clusters have been the subject of intensive theoretical and experimental studies. For metallic clusters with predominantly $sp$ valence electrons, the shell structure of the jellium model provides a useful guideline for describing the electronic structures.[1–6] The electronic shell structure has been verified for medium-sized Al clusters both experimentally and theoretically.[7,8] A theoretical calculation for the $Al_{13}$ cluster revealed that its stability can be substantially enhanced by closing the electronic shell through doping or charging.[9] As a result, the impurity-doped $Al_{13}$ cluster has been viewed as a building block for cluster assembled solids.[9–11] However, it remains unclear if the electronic shell structure is still valid for large clusters. It is expected that triply charged ionic cores of Al clusters will lead to strong perturbations to the shell structures. In this regard, recent experiments[12] on the photoelectron spectroscopy of Al clusters have shown that the electronic shell structure diminishes for $n \simeq 75$. Therefore, an accurate first-principles study for large metallic clusters is clearly desirable.

Recently, Ecker and co-workers[13] successfully synthesized a compound containing a large metallic $Al_{77}$ cluster unit. The $Al_{77}$ cluster is probably the largest metallic cluster whose structure has been measured by x-ray diffraction so far. The $Al_{77}$ cluster constitutes a fascinating prototype for studying the crossover between metallic clusters and the bulk metal of main-group elements. The experimentally characterized $Al_{77}$ cluster is onionlike, having three layers of atoms covering the central atom. The three layers consist of 12, 44, and 20 atoms, respectively. The central atom is coordinated by 12 neighbors, similar to the bulk, arranged in a distorted icosahedral ($I_h$) environment. The coordination number for the atoms in the outer shells decreases from the center outward, undergoing a transition from a metallic center to a molecular surface. The atoms in the second shell have a coordination number of 10, while the atoms in the outermost layer are arranged in a distorted $I_h$ symmetry, with only four neighbors from the inner shell. The nearest-neighbor distance is about 2.7 Å for the central atom and 2.6 Å for the outer atoms. The latter value indicates a small compression, similar to values for the Al surface. However, little is known about the electronic structure of such a large metallic cluster. A outstanding question concerning the stability of $Al_{77}$ is whether the $Al_{77}$ cluster itself is the stable core unit, or the chemical interaction between $Al_{77}$ and its ligands is crucial.

Inspired by the experimental work,[12,13] we report in this paper a successful density-functional study of the electronic and structural properties of $Al_{77}$. Our attention is directed to its atomic and electronic shell structures. Through a detailed analysis of the electronic structure, we find that there exist strong inter-atomic-shell interactions and significant charge transfer between $Al_{77}$ and its ligands. Moreover, the electronic shell structure for $Al_{77}$ can no longer be identified beyond the $1h$ shell, in agreement with recent experimental observations.

Our calculations are based on the *ab initio* molecular dynamics method.[14] The electronic density is expressed in Kohn-Sham orbitals that are expanded in plane waves with an energy cutoff of 130 eV. Only the valence charge density is treated explicitly and the interaction with the ionic cores is described by ultrasoft pseudopotentials. The local-density approximation to density-functional theory is used for the exchange correlation potential.[15] The total energy is minimized up to a precision of $10^{-4}$ eV by the conjugate gradient method. The forces acting on the ions are converged to within 0.05 eV/Å for the structural relaxation. A large cubic supercell with a length of 21 Å in each dimension is used to reduce the interaction between the cluster and its images. The $\Gamma$-point approximation is employed.

A test performed for the bulk fcc phase of Al gives 3.95 Å for the lattice constant and 4.1 eV for the cohesive energy, in good agreement with the corresponding experimental values.[16] Our calculation on a 13-atom structure with perfect $I_h$ symmetry yields an equilibrium distance of 2.5 Å between the center atom and the vortex atoms, a binding energy of 3.3 eV/atom. These results are in good agreement with previous theoretical calculations.[9]

*Atomic shells.* The electronic structure calculations show that $Al_{77}$ and its inner core $Al_{13}$ are stable. We show in Fig. 1 the calculated electronic density of states (DOS) for the clusters of $Al_{13}$, $Al_{57}$, and $Al_{77}$, along with that for $I_h$-$Al_{13}$. We find that $Al_{13}$ has all the features of the electronic structure of $I_h$-$Al_{13}$. Since the highest occupied orbital of $Al_{13}$ is not completely occupied, the structure of $I_h$-$Al_{13}$ is unstable against Jahn-Teller distortion. The structural distortions are reflected in the electronic structure, in which the peaks in the density of states are split. The existence of a gap just above

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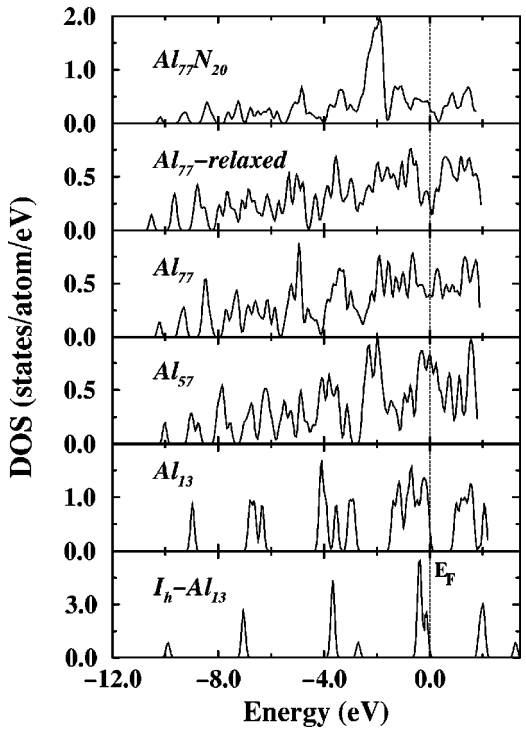


FIG. 1. The electronic density of states for Al clusters. Structural optimization of $Al_{77}$ does not change the basic features of the DOS, except for the DOS at the Fermi level being smaller. The Fermi level is shifted to zero.

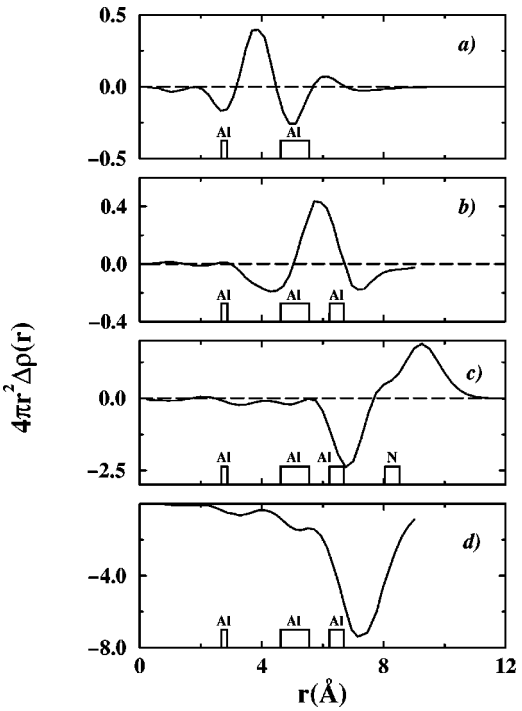


FIG. 2. The radial electron density difference $4\pi r^2\Delta\rho(r)$ for $Al_{77}$ and relevant layered clusters, specifically, (a) $Al_{57}$, (b) $Al_{77}$, (c) $Al_{77}N_{20}$; and (d) the radial electron density difference between neutral $Al_{77}$ and $Al_{77}^{16+}$. The radial distribution of atoms for each cluster, calculated from the center atoms, is shown on the bottom of each panel. The large charge density buildup between atomic layers suggests strong interactions. Charge transfer between $Al_{77}$ and 20 N atoms is evident.

the Fermi level indicates that the structure of the inner core is very stable with electron donation. For $Al_{57}$, we find that more peaks appear below the Fermi level. The Fermi level being on a high peak implies that this cluster is unstable against structural relaxation. However, with another layer of 20 atoms added, $Al_{77}$ becomes stable indicated by the Fermi level being in a dip. It is instructive to compare the electronic structure of $Al_{57}$ and $Al_{77}$. Both are quite similar in the low energy part; a difference appears only around the Fermi energy.

Onionlike $Al_{77}$ is stable against geometry optimizations. Shown in Table I is the binding energy gain from relaxation. We find that the relaxation changes only slightly the structure of $Al_{13}$ with an energy gain of 0.06 eV/atom. The structure of $Al_{77}$ is stable, in the sense that the relaxation slightly changes the structure of the outermost shell with a small energy gain of 0.04 eV/atom, but the structure of the inner shell ($Al_{57}$) undergoes little distortion. This is consistent with the low density of states at the Fermi level. The electronic structure of the $Al_{77}$ cluster remains almost the same after relaxation (see Fig. 1). On the contrary, $Al_{57}$ is quite unstable against relaxation. Not only does the structure of the outermost shell change, but also the structure of the inner shell, with a large energy gain of $\sim$0.18 eV/atom due to geometry optimization. Based on the above analysis, $Al_{77}$ can be considered as a two-layer atomic shell covering a very stable inner core of $Al_{13}$.

TABLE I. The binding energies of Al clusters (eV/atom) with and without relaxation. The binding energies for the unrelaxed Al cluster (except for $I_h$-$Al_{13}$) are obtained at the experimental atomic distances.

| | $I_h$-$Al_{13}$ | $Al_{13}$ | $Al_{57}$ | $Al_{77}$ |
|---|---|---|---|---|
| Unrelaxed | 3.09 | 3.11 | 3.38 | 3.54 |
| Relaxed | 3.17 | 3.17 | 3.56 | 3.58 |
| $\Delta E$ | 0.08 | 0.06 | 0.18 | 0.04 |

*Charge transfer*. The fundamental features of the electronic structure of $Al_{77}$ remain intact with added ligands and charge. The experimentally synthesized compound consists of the $Al_{77}$ cluster unit and ligands. The ligand is composed of 20 nitrogen atoms, 30 silicon atoms, and 120 methyl groups. To study the effect of the ligands on the electronic structure of $Al_{77}$, we include a layer of 20 N atoms at the experimentally determined positions. The calculated electronic structure of $Al_{77}N_{20}$ is shown in the top panel of Fig. 1. It is readily observable that the predominant contribution from 20 N atoms to the DOS is a feature around $-2$ eV. Apart from this, the main feature in the DOS of $Al_{77}$ remains. As a matter of fact, our calculation on the charged cluster confirmed the rigid band behavior of the $Al_{77}$ electronic structure.

The strong interaction between the atomic layers is indicated by the large redistribution of the charge density in developing the atomic shells of $Al_{77}$. Figure 2 shows the radial charge density difference, i.e., the charge density changes, in adding an atom layer to the inner shell. For instance, on adding the 44-atom shell to the inner core $Al_{13}$, the charge density difference amounts to $\Delta\rho(Al_{57})=\rho(Al_{57})-\rho(Al_{13})$

$-\rho(Al_{44})$, where the subsystem densities $\rho(Al_{13})$ and $\rho(Al_{44})$ are separately evaluated. All the charge densities are calculated at the experimentally determined atomic positions. As seen in Fig. 2, on adding one layer of 44 atoms to $Al_{13}$ in forming $Al_{57}$, the charge builds up between the two layers and a deficit of charge appears around the shell region. A slight increase of charge just outside the outer shell suggests the high reactivity of $Al_{57}$. Similarly, a large buildup of charge density is observable between $Al_{57}$ and the outmost 20-atom shell. On the contrary, the charge density gets more compressed in the outermost layer after being added, indicating the stability of $Al_{77}$.

There exists a clear charge transfer between $Al_{77}$ and the ligands. Shown in Fig. 2(c) is the radial charge density redistribution with 20 N atoms capped on $Al_{77}$. Although there exists a small charge density deficit in the core region of $Al_{77}$, the significant deficit is around the outermost layer of $Al_{77}$. The charge transfer to the N atom layer can be readily observed. After integration of the negative $\Delta\rho(r)$, one finds that $\sim 3$ electrons are transferred to the N atom layer, much fewer than the previousely estimated 18 electrons. Although the use of 20 N atoms is an approximation for the complete passivation layers in the experimentally synthesized compound, we believe that the major interactions between $Al_{77}$ and its ligands have been included.[17] Therefore, our calculation results demonstrate that, owing to the high stability of $Al_{77}$, the charge transfer of as many as 18 electrons between $Al_{77}$ and its ligands is very unlikely. Figure 2 also shows the radial charge density deficit between $Al_{77}$ and $Al_{77}^{16+}$. Again, the largest deficit is around the outermost shell. The similarity between Fig. 2(d) and the negative part of Fig. 2(c) indicates that the interaction between $Al_{77}$ and its ligands is ioniclike.

*Electronic shells.* The electronic structure of Al clusters can be well described by the spherical jellium model up to a certain cluster size where the separate *s* and *p* levels overlap. The most recent photoelectron spectroscopy experiment on size-selected Al clusters showed[12] that the critical size is around $N=9$, above which the jellium model starts to be valid. First-principles results confirmed that the jellium model holds for $Al_{13}$.[4,9] However, the experiment also found that the shell effect diminishes above $Al_{75}$.

The $Al_{77}$ cluster characterized by the experiment provides a desired system to examine the shell structure of the spherical jellium model for large Al clusters. Figure 3 shows the electronic density of states and its integrated number of electrons. It is worth noting that the density of states of $Al_{77}$ is much different from that of free-electron-like Al. Certain electronic shell structures from the jellium model can be clearly identified. For instance, $1s$, $1p$, and $1d(2s)$ states that are present in small $Al_{13}$ clusters remain visible. The large gaps just above $1g$, $1h$, and $1i$ shell states are evident. This is in remarkable agreement with the photoelectron spectroscopy observation of a closed shell at $1g$ and $1i$ for the observed Al clusters. Because of strong interaction between the $+3$ ionic core and valence electrons, beyond the $1i$ shell state, all the shell states overlap each other and the gap between the states disappears as shown in Fig. 4. These results show that the shell structure cannot be observed in Al clusters as large as $Al_{77}$, which is in accordance with the photoelectron spectroscopy experimental observations.[12]

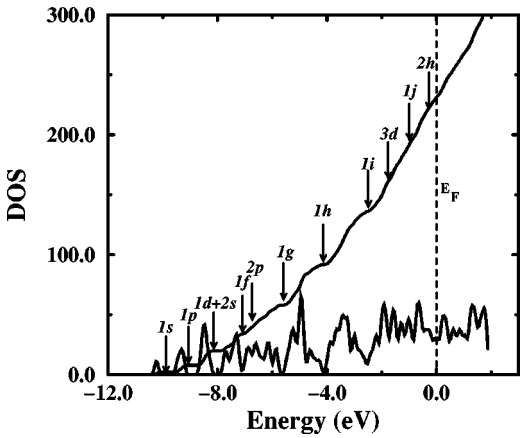


FIG. 3. The electronic density of states and integrated DOS of the $Al_{77}$ cluster. The shell structures of the spherical jellium model are labeled. The shell structures up to $1i$ are clearly observable.

The local electronic density of states from the central atom to the outer shells, as shown in Fig. 4, can help us to understand the correlation between the electronic shell and atomic shell structure in the cluster. We calculate the local electronic density of states for each atom by projecting the wave function in the Wigner-Seitz cell into atomiclike orbitals. Although the space division is somewhat arbitary, the results obtained can qualitatively locate the states for different atomic shells. We find that the local electronic density of states for all the atomic shells is quite similar to the total density of states. Although the electronic shells with lower

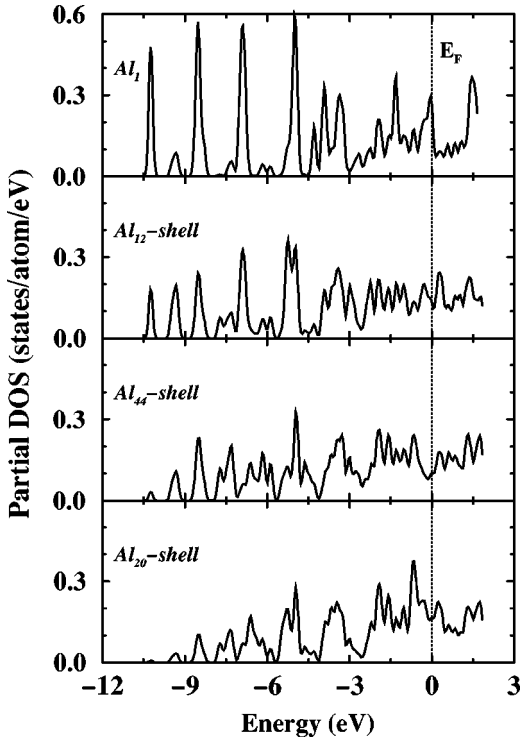


FIG. 4. The local electronic density of states on each atomic shell of the $Al_{77}$ cluster. The projection is performed at the Wigner-Seitz radius (1.4 Å), and the top panel is for the central atom.

kinetic energy are mainly distributed in the inner atomic shells and the electronic shells with higher kinetic energy have a tendency to distribute in the outer atomic shells, essentially all the electronic shells are delocalized on all atomic shells. There are no localized electronic shells, which validates the jellium model. Thus each atomic shell has a significant contribution to the density of states at the Fermi energy.

In summary, our first-principles results show that the onionlike $Al_{77}$ cluster is stable, while the $Al_{57}$ cluster with one fewer atomic shell is not. From the structural stability point of view, $Al_{77}$ can be considered as a two-atomic-layer shell of 64 atoms on a stable inner core of $Al_{13}$. There exists a strong interaction between atomic layers in the cluster. The interaction between $Al_{77}$ and its ligands is ioniclike. Our results on the electronic structure of $Al_{77}$ show that the jellium model for the electronic structure of Al cluster is valid around the $1i$ shell state for large clusters. Beyond the $1i$ shell state the gap becomes very small for numbers of atoms larger than 70, in close agreement with experimental results.

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