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S. N. Khanna
Virginia Commonwealth University

C. Ashman
Virginia Commonwealth University

B. K. Rao
Virginia Commonwealth University

P. Jena
Virginia Commonwealth University

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Geometry, electronic structure, and energetics of copper-doped aluminum clusters

S. N. Khanna,[a] C. Ashman, B. K. Rao, and P. Jena
Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284-2000

Using density functional theory and generalized gradient approximation for exchange-correlation potential, we have calculated the equilibrium geometries and energetics of neutral and negatively charged Al_nCu ($n=11,12,13,14$) clusters. Unlike the alkali atom-doped aluminum clusters in the same size range, the copper atom resides inside the aluminum cluster cage. Furthermore, the $3d$ and $4s$ energy levels of Cu hybridize with the valence electrons of Al causing a redistribution of the molecular orbital energy levels of the Al_n clusters. However, this redistribution does not affect the magic numbers of Al_nCu clusters that could be derived by assuming that Cu donates one electron to the valence levels of Al_n clusters. This behavior, brought about by the smaller size and large ionization potential of the copper atom, contributes to the anomalous properties of Al_nCu^- anions: Unlike Al_nX^- (X=alkali atom), the mass ion intensities of Al_nCu^- are similar to those of Al_n^-. The calculated adiabatic electron affinities are also in very good agreement with experiment. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1367381]

I. INTRODUCTION

Since the pioneering work of Knight *et al.*[1] exhibiting a direct relationship between the pronounced peaks in the mass ion intensities (commonly referred to as magic numbers) of Na clusters and electronic shell closure, considerable theoretical and experimental work has been carried out to search for new magic numbers in compounds as well as charged metal clusters.[2] The electronic shell closure derived from the Jellium model dictates that metal clusters with 2, 8, 20, 40,... electrons are particularly stable as they correspond to complete filling of $1s$, $1s$ $1p$, $1s$ $1p$ $1d$ $2s$, $1s$ $1p$ $1d$ $2s$ $1f$ $2p$,... groups of orbitals, respectively. As Al, Cu, and alkali metal atoms exhibit free-electron-like behavior in their respective bulk phases, one would expect the atomic and electronic structure as well as relative stabilities of copper-doped aluminum clusters to exhibit the same behavior as those of alkali atom-doped aluminum clusters[3,4] since both clusters contain the same number of valence electrons. For example, if clusters are born neutral, $Al_{13}Cu$ clusters should exhibit enhanced stability (and, hence, a peak in the mass spectra) over their neighbors as it would contain 40 valence electrons. On the other hand, if clusters are born negatively charged the intensity of the mass spectra of Al_nCu^- clusters should exhibit a dip at $n=13$ as these clusters contain one electron more than that needed for shell closing. This behavior has, indeed, been observed for $Al_{13}X^-$ (X=alkali atom) clusters.[5]

In a recent study of the mass ion intensity distribution of Al_nCu^- clusters, Bowen and co-workers,[6] however, observed a different behavior. The pronounced peaks corresponding to Al_nCu^- were the same as those of Al_n^-. This implies that the magic numbers in Al_n^- clusters are not affected by copper doping. Consider, in particular, clusters of Al_{13}^-, $Al_{13}K$, and $Al_{13}Cu$. All three clusters have 40 valence electrons and Al_{13}^- has been known[7] to be highly abundant in the mass spectra. Since $Al_{13}Cu^-$ and $Al_{13}K^-$ have 41 electrons, their mass ion intensity peaks should not have pronounced structures. Thus, the experimental observation that the peak intensity of $Al_{13}Cu^-$ is higher than those of $Al_{12}Cu^-$ and $Al_{14}Cu^-$ seems anomalous. Similar effects were earlier observed in the magic numbers associated with Na_n and Na_nMg clusters[8] where Na_8Mg was found to be more stable than Na_7Mg and Na_9Mg. It was shown[9] that the doping of Mg into Na_n clusters led to a rearrangement of the molecular energy levels that, in turn, explained the observed abundance in the mass spectra.

To understand the anomalous behavior of the mass ion intensity in Al_nCu^- vis-à-vis alkali metal atom-doped aluminum clusters, we have calculated the equilibrium geometry and total energy of neutral and anionic Al_nCu ($n=11,12,13,14$) clusters using first principles theory. We show that unlike the alkali atoms, copper prefers to occupy internal sites in the aluminum clusters. This is because the size of the copper atom is smaller than that of aluminum. Second, the large ionization potential of Cu (7.72 eV) makes it energetically unfavorable to transfer its outermost s electron to the Al_n cage and thus does not form an ionic bond between Al_{13}^- and Cu^+ as is the situation with alkali metal atom-doped Al_{13} cluster. We find instead that analogous to Na_nMg clusters, the doping of copper modifies the molecular orbital energy levels. Consequently the mass ion intensity distribution of Al_nCu^- shows the same magic numbers as Al_n^-. We have also calculated vertical and adiabatic detachment energies of Al_nCu^- clusters as well as the vertical ionization potentials of Al_nCu clusters. The low electron affinity and large highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap of $Al_{13}Cu$, in comparison to its neighboring clusters, indicate

[a]Electronic mail: khanna@hsc.vcu.edu

that $Al_{13}Cu$ corresponds to a closed electronic shell system in spite of the rearrangements of the molecular energy levels resulting from Cu doping. The calculated electron affinities of these clusters agree very well with experiment providing indirect evidence of the accuracy of the computed geometries. In the following we provide a brief outline of our computational procedure. A discussion of our results and a summary are given in Secs. III and IV, respectively.

II. COMPUTATIONAL PROCEDURE

The theoretical calculations were carried out within the density functional formalism using a linear combination of atomic orbitals molecular orbital approach.[10] Here, the molecular orbitals are formed from a linear combination of atomic orbitals centered at the atomic sites. The atomic orbitals were represented by Gaussian functions and the exchange correlation contributions were included using a gradient corrected density functional recently proposed by Perdew *et al.*[11] The actual calculations were done at the all electron level using the NRLMOL code developed by Pederson and Jackson.[12] In this implementation, the multicenter integrals required to solve the Kohn–Sham equations are calculated by integrating numerically over a mesh of points. The basis set consisted of $6s$, $5p$, and $3d$ Gaussian functions for Al and $7s$, $5p$, and $4d$ Gaussian functions for Cu. The atomic basis sets were supplemented by an additional d function in each case. The basis sets used here are well tested and the reader is referred to earlier papers[13] for details. Since the number of atoms in most of the clusters studied here do not correspond to a closed geometrical shell, determination of the ground state geometry can be a tedious task. To explore the vast configurational space, several initial configurations were tried and the geometry was optimized without symmetry constraint using a conjugated gradient approach. The final structures thus include possible Jahn–Teller distortions.

III. RESULTS AND DISCUSSION

Even though K and Cu are monovalent atoms belonging to the same row of the periodic table, their size and ionization potentials are different. While the radii of K^+ and Cu^+ are 1.54 and 0.96 Å, respectively, the ionization potentials of K and Cu atoms are 4.34 and 7.72 eV, respectively. These differences in size and ionization potentials affect the properties of Al_nK and Al_nCu clusters both in neutral and charged configurations. For example, the binding energy and bond length of the AlCu dimer are, respectively, 2.42 eV and 2.38 Å, while those of the AlK dimer are 0.62 eV and 3.68 Å, respectively. These differences persist to larger clusters as well. In Al_nK ($n = 12,13,14$) clusters, K always resides outside the Al_n cluster cage.[4] However, the situation is entirely different for Al_nCu clusters.

In Fig. 1 we present the equilibrium geometries of Al_nCu ($n = 11,12,13,14$) clusters in anionic and neutral configurations. Note that in all these clusters Cu resides inside the Al_n cage irrespective of their size and charge states. Both neutral and anionic $Al_{11}Cu$ clusters form a structure that is a precursor to an icosahedric structure. The $Al_{12}Cu$ cluster both in neutral and anionic forms is a slightly distorted icosahedron.
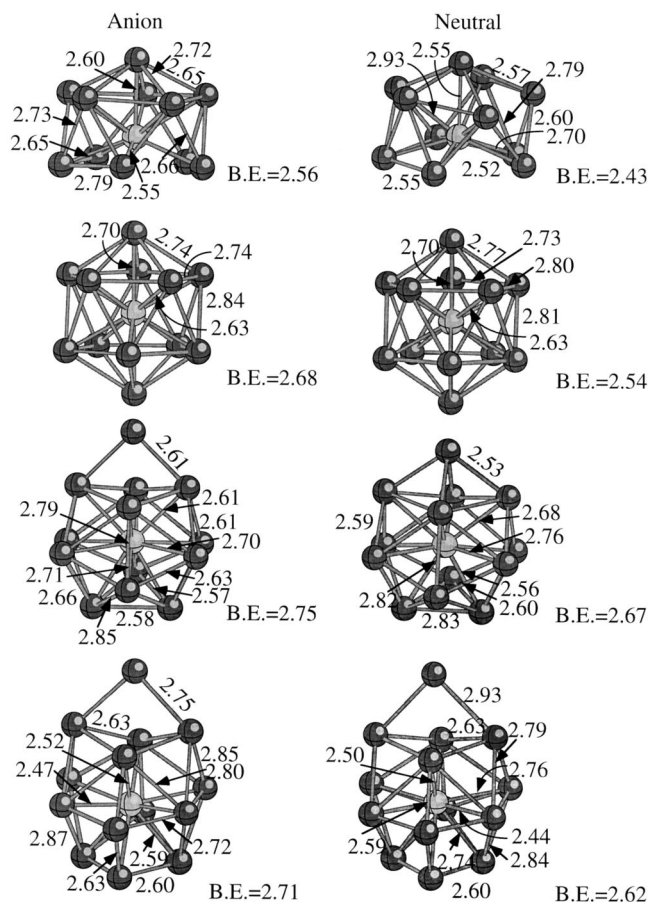

FIG. 1. Equilibrium geometries of neutral and anionic Al_nCu Clusters. The lighter spheres are the Cu atoms while the darker spheres are the Al sites. The bond lengths are in Å and the binding energies are in eV.

In a perfect icosahedron there are 30 identical surface bonds that are 5% elongated over the 12 identical radial bonds. Note that in $Al_{12}Cu$ clusters the surface bond lengths are not exactly equal to each other, as is the case with radial bonds. Moreover, Cu occupies the central position and remains there as more Al atoms are added. The $Al_{13}Cu$ cluster is noticeably distorted from an icosahedric form both in neutral and anionic forms. In contrast, the structure of $Al_{13}K$ is that of a nearly perfect Al_{13} icosahedric cluster[14] with the K atom residing outside the cage at a threefold coordinated site. Similarly, the structure of $Al_{14}Cu$ is very different from that of $Al_{14}K$. In $Al_{14}K$ one of the Al atoms and the K atom attach to the Al_{13} icosahedric cage at opposite ends. The icosahedric motif is broken in the $Al_{14}Cu$ cage with the Cu atom residing in the interior.

In Table I we list the total energies of optimized Al_nCu^- and Al_nCu clusters. Also listed in Table I are total energies of neutral Al_nCu cluster having Al_nCu^- geometry and cationic Al_nCu^+ cluster having the neutral ground state geometry. While the difference in the total energies between the ground states of the neutral and anionic clusters provides the adiabatic electron affinity, that between the anion and the neutral with the anion geometry provides the vertical electron affinity. The vertical ionization potential is obtained by calculating the energy difference between the neutral and cationic cluster having the geometry of the neutral. These

TABLE I. Total energies (a.u.) of Al_nCu clusters in neutral and charged configurations for various geometrical forms.

Cluster	Anion (optimized)	Neutral (with anion geometry)	Neutral (optimized)	Cation (with neutral geometry)	Cation (optimized)
$Al_{11}Cu$	−4306.036 67	−4305.932 40	−4305.941 26	−4305.712 03	−4305.719 25
$Al_{12}Cu$	−4548.421 76	−4548.313 44	−4548.314 82	−4548.072 21	−4548.079 39
$Al_{13}Cu$	−4790.790 77	−4790.697 16	−4790.711 10	−4790.472 51	−4790.477 51
$Al_{14}Cu$	−5033.105 07	−5033.004 16	−5033.013 64	−5032.799 89	−5032.808 90

energy differences, as well as the HOMO–LUMO gap of the neutral clusters are given in Table II.

Also listed in Table II are the energy gains, ΔE, in adding an Al atom to an Al_nCu cluster. This is defined as

$$\Delta E_n = -[E(Al_nCu) - E(Al_{n-1}Cu)] - E(Al),$$

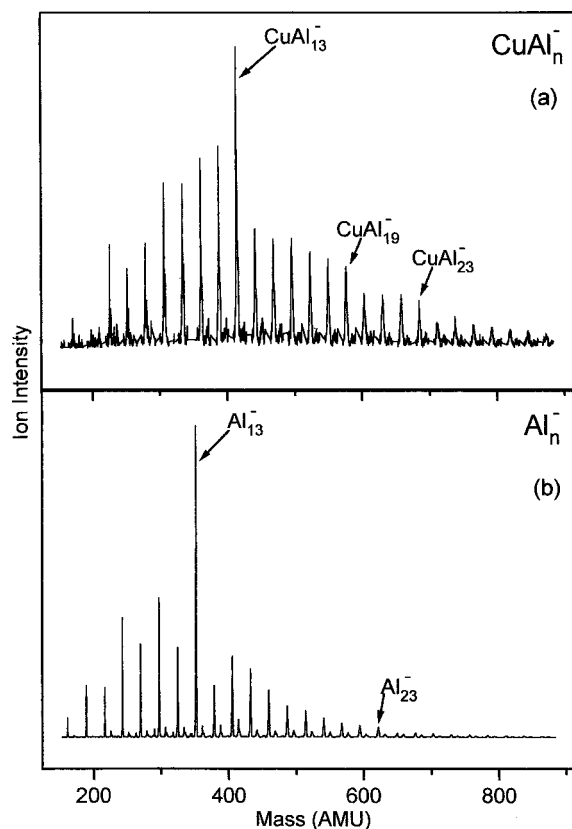$$\Delta E_n^- = -[E(Al_nCu^-) - E(Al_{n-1}Cu^-)] - E(Al),$$

where E is the total energy of the respective systems. Note that one of the factors that contributes to the relative peak heights in the mass spectra of clusters is the magnitude of this energy gain. For neutral Al_nCu clusters the energy gain, ΔE_n in going from the $Al_{11}Cu$ cluster to $Al_{12}Cu$ is 3.80 eV while that in going from $Al_{12}Cu$ to $Al_{13}Cu$ is 4.42 eV. The energy gain in going from $Al_{13}Cu$ to $Al_{14}Cu$ is substantially lower, namely 1.87 eV. This suggests that neutral $Al_{13}Cu$ should be more abundant than $Al_{12}Cu$ and far more abundant than $Al_{14}Cu$. This is consistent with the electronic shell closing if one assumes that $Al_{13}Cu$ corresponds to a 40 valence electron system. Thus, if Al_nCu clusters are born neutral, the enhanced stability of $Al_{13}Cu$ would indicate that in the anion mass spectra more of the $Al_{13}Cu^-$ clusters are observed since there are more of them to which the extra electron has attached. In Fig. 2 we reproduce the experimental mass spectra[6] of Al_nCu^- for clarity. Note that the drop in the intensity from $Al_{13}Cu^-$ to $Al_{14}Cu^-$ is much more than the rise from $Al_{12}Cu^-$ to $Al_{13}Cu^-$. This is again consistent with the ΔE_n values in Table II. We also note from Table II that ΔE_n^- for the Al_nCu^- clusters monotonically decreases from $n = 12$ to 14. This clearly is inconsistent with the distribution of mass ion intensities and provides further evidence that the mass ion intensities of Al_nCu^- clusters may be tied to the abundance of the neutral clusters.

In order to understand the effect of Cu doping on the valence electron energy levels of Al_{13} vis-à-vis those of Al_{13}^- and $Al_{13}K$. In Fig. 3 we plot the molecular orbital energy

levels of Al_{13} and compare those with corresponding levels in Al_{13}^-, $Al_{13}K$, and $Al_{13}Cu$. Note that Al_{13}, due to its odd number of electrons, has a spin doublet ground state and consequently there are separate energy levels corresponding to spin up and down electrons. On the other hand, Al_{13}^-, $Al_{13}K$, and $Al_{13}Cu$ all have 40 valence electrons and their ground state is a spin singlet and hence each energy level contains two (spin ↑ and ↓) electrons. The HOMO–LUMO gap in Al_{13} is small, namely 0.49 eV. As an electron is attached, the LUMO level of the spin ↓ orbitals of Al_{13} gets filled and opens up a large gap (1.87 eV) between the HOMO and LUMO. In $Al_{13}K$, the occupied energy levels have very little K contribution and the shifting of the energy levels compared to those of Al_{13}^- only reflects a small residual ''covalent-'' like interaction between K and Al_{13}. The HOMO–LUMO gap in $Al_{13}K$ is very similar (namely 1.81 eV) to that of Al_{13}^-. The lack of complexity of the occupied energy levels of $Al_{13}K$ in comparison to those of Al_{13} and its

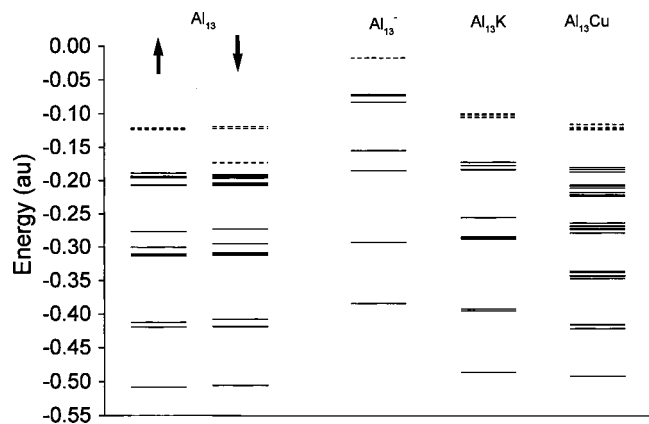FIG. 2. Experimental mass spectrum of Al_nCu^- vs Al_n^- clusters (Ref. 6).

TABLE II. Adiabatic and vertical electron affinities (AEA, VEA), vertical ionization potentials (VIP), HOMO–LUMO gaps, and energy gains (ΔE) in adding an Al atom to $Al_{n-1}Cu$ clusters.

Cluster	AEA (eV) Theor.	AEA (eV) Expt.	VEA (eV)	VIP (eV)	HOMO–LUMO gap (eV)	ΔE (eV) Neutral	ΔE (eV) Anion
$Al_{11}Cu$	2.60	2.38	2.84	6.24	0.47		
$Al_{12}Cu$	2.91	2.53	2.95	6.60	0.25	3.80	4.11
$Al_{13}Cu$	2.17	2.14	2.55	6.49	1.53	4.42	3.68
$Al_{14}Cu$	2.49	2.56	2.75	5.82	0.39	1.87	2.19

FIG. 3. One electron energy levels of Al_{13}, Al_{13}^-, Al_nK^-, and Al_nCu^- clusters.

similarity (except an energy shift) with that of Al_{13}^- indicates that in this compound cluster the charge configurations remain close to Al_{13}^- and K^+, thus a bonding scheme that is very close to being ionic.

The electronic structure of $Al_{13}Cu$, on the other hand, is very different. The occupied molecular energy levels of $Al_{13}Cu$ contain a lot more states than those in Al_{13}^- and $Al_{13}K$. An analysis of the angular character of the occupied energy levels of $Al_{13}Cu$ indicates that the states near energies of -0.49 and -0.28 a.u. are derived primarily from $3d^{10}$ and $4s^1$ electrons of Cu. This strong admixture of the Cu $3d$ and $4s$ electrons with $3s$ and $3p$ electrons of aluminum results because of the high ionization potential of Cu that makes transferring its $4s^1$ electron to Al_{13} (as found for $Al_{13}K$) energetically difficult. Consequently, the bonding between Cu and Al_{13} is more due to charge sharing than due to charge transfer. This is why Cu prefers to be inside the Al_{13} cage so that it can form more bonds with Al. On the other hand, the low ionization potential of K (4.34 eV) makes it easier for it to transfer its electron to Al_{13} and makes an ionic bond. The strong hybridization of Cu $3d$ and $4s$ with Al_{13} valence electrons modifies the simple Jellium-like energy levels of Al_{13}^-. The total number of ''valence'' electrons in the $Al_{13}Cu$ neutral cluster is 50, of which 10 electrons belong to the Cu $3d$ states. Thus, the $Al_{13}Cu$ cluster still adheres to electronic shell closing although not in the same spirit as the jellium model. Note that there exists a large gap (1.53 eV) between the HOMO and LUMO of $Al_{13}Cu$ in spite of the strong hybridization.

In Table II we also list the calculated adiabatic and vertical electron affinities and compare them with available experimental result. Note that the magnitude of the difference between vertical and adiabatic electron affinities is an indication of the difference in the geometry between the ground states of the anion and neutral cluster. These energy differences are about 0.2 eV or less with the exception of $Al_{13}Cu$ where structural relaxation following electron detachment from the anion lowers the energy by about 0.4 eV. This should give rise to a broadened photodetachment peak in $Al_{13}Cu$ compared to neighboring clusters, and this is, indeed, the case.[6] We also note that the electron affinity (and HOMO–LUMO gap) of $Al_{13}Cu$ is smaller (larger) than those

of its neighbors—another indication that $Al_{13}Cu$ is a closed shell system. We also calculated the vertical ionization potentials (VIPs) of the neutral clusters. These represent the energy it takes to remove an electron from the neutral cluster without relaxing the geometry. Note that both $Al_{12}Cu$ and $Al_{13}Cu$ have relatively high VIPs. No experimental data are available for comparison.

IV. CONCLUSIONS

The present work brings out a fundamental difference between the shell closure in Al_{13}^-, $Al_{13}K$, and $Al_{13}Cu$ clusters. They all have 40 valence electrons (if we do not include the 10 d-electrons of Cu) and correspond to filled electronic shells in a jellium model. However, the key is to realize that the stability of small clusters is governed not only by the electronic but also by the geometric shell closings.[15] For Al_n^- clusters, the geometric and electronic shell closings occur at Al_{13}^- and the mass spectrum of the anionic clusters shows an unusually marked peak. For Al_nK clusters, the ionization potential of K is low, the size of the K atom is bigger than Al, and the AlK dimer bond is not strong. Consequently, the K atom in an $Al_{13}K$ cluster occupies an external site and donates an electron to the Al_{13} motif. The stability of Al_nK is then similar to those of the Al_n^- clusters and the recent experiments[5] indeed confirm the stability of $Al_{13}K$ in the mass spectrum of Al_nK clusters. The case of Cu is however different. The size of the Cu atom is comparable to Al, the ionization potential of Cu is high, and the AlCu dimer bond is strong with a bond strength higher than even the Al_2 bond. The Cu atom then occupies an interior site and there is considerable mixing between the electronic states of Cu and Al. This leads to a strange situation in Al_nCu clusters. While the geometric shell closure occurs at $Al_{12}Cu$, the electronic shell closure occurs at $Al_{13}Cu$. This is the reason that in anionic clusters, $Al_{12}Cu^-$ has a higher ΔE (Table II) than $Al_{13}Cu^-$. On the other hand, in neutral clusters, the electronic shell closure leads to a higher ΔE for $Al_{13}Cu$ than for $Al_{12}Cu$. This interplay between geometric and electronic closings is most transparent in the ionization where $Al_{12}Cu$ and $Al_{13}Cu$ both have a high VIP. It would be interesting to carry out experiments on other Al_nX clusters with atoms belonging to the same column of the periodic table to see how the size would affect the stability of the clusters.

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