J. Phys. Chem. A **2007,** *111,* 8659−8662

Al_7Ag and Al_7Au Clusters with Large Highest Occupied Molecular Orbital−Lowest Unoccupied Molecular Orbital Gap

Ming-Xing Chen,[†,‡] X. H. Yan,[*,†] and S.H. Wei[§]

College of Science, Nanjing University of Aeronautics and Astronautics, Jiangsu-210016, People's Republic of China, Department of Physics, Xiangtan University, Hunan-411105, People's Republic of China, and College of Science, Ningbo University, Zhejiang-315211, People's Republic of China

Received: October 16, 2006; In Final Form: June 27, 2007

The candidate structures for the ground-state geometry of the Al_7M (M = Li, Cu, Ag, and Au) clusters are obtained within the spin-polarized density functional theory. Absorption energy, vertical ionization potential, vertical electron affinity, and the energy gap between the highest occupied molecular orbital (HOMO) level and the lowest unoccupied molecular orbital (LUMO) level have been calculated to investigate the effects of doping. Doping with Ag or Au can lead to a large HOMO−LUMO gap, low electron affinity, and increased ionization potential of Al_7 cluster. In the lowest-energy structure of the Al_7Au cluster, the Al atom binding to the Al_6Au acts monovalent and the other six Al atoms are trivalent. Thus, the Al_7Au cluster has 20 valence electrons, and its enhanced stability may be due to the electronic shell closure effect.

1. Introduction

Doping of clusters has been used in an important way to stabilize certain clusters so that there is electronic shell closing. This is interesting because it could lead to symmetry breaking and could produce new kinds of compound clusters with higher stability.[1] Over the past few years, aluminum clusters doped with a metal or nonmetal atom have received much attention.[2−28] Because the trivalency of the Al atom gives most of its clusters an incomplete electronic shell in the jellium picture, doping the Al clusters with a suitable impurity atom could lead to clusters with a closed electronic shell. For example, doping Al_{12} cluster with a tetravalent atom[2−5] or doping Al_{13} clusters with a monovalent atom[6−11] can give rise to an closed electronic shell corresponding to 40 valence electrons. These clusters are found to have a large highest occupied molecular orbital−lowest unoccupied molecular orbital (HOMO−LUMO) gap. Consequently, they are very stable and can serve as building blocks for cluster-assembled materials.

Cu, Ag, and Au atoms lie at the end of the 3d, 4d, and 5d periods, respectively. The d shell is filled with 10 electrons, and the valence shell contains a single s electron. These lead one to expect some similarities between small clusters of the noble metals and the clusters of the alkali elements. For noble metal-doped aluminum clusters, Thomas et al. reported that the magic numbers appear at $n = 6$, 13, 19, and 23 by observing the mass spectrum of $CuAl_n^-$ clusters.[13] M. Heinebrodt's experiment showed that gold−aluminum clusters exhibit electronic shell effects.[14] However, in the coinage metal atoms, the d electrons should play some role in structure, bonding, and electronic properties.[10] Moreover, relativistic effects in these series are found to be more and more significant as the nuclear charge increases. Thus, it is interesting to investigate the doping effect of a coinage metal atom on the structure, stability, and electronic properties of Al clusters and to compare the results with those of alkali-doped ones. In the present work, we carry out density functional theory (DFT) calculations of Al_7M (M = Li, Cu, Ag, and Au) clusters to show how the impurity atom affects the stability, geometric, and electronic structures. The Al_7Au cluster is found to be a compound of an aluminum atom and Al_6Au clusters and to be more stable than its neighboring clusters.

2. Computational Scheme

Our calculations on Al_7M (M = Li, Cu, Ag, and Au) are based upon the all electron relativistic (RE) spin-polarized DFT using the $DMol^3$ package.[30] A double numerical basis including a d-polarization function is used as the basis functions in our calculations. In addition, to facilitate comparison we have also carried out nonrelativistic (NR) calculations for Al_7X (X = Cu, Ag, and Au). The electron density functional is treated by the generalized gradient approximation with the exchange-correlation potential parametrized by Perdew and Wang (PW91).[31] Geometry optimizations are performed by the Broyden−Fletcher−Goldfarb−Shanno algorithm without any symmetry constraints. Self-consistent field procedures are done with a convergence criterion of 10^{-3} au on the gradient and displacement and 10^{-5} au on the total energy and electron density.

3. Results and Discussion

A. Structural Properties. We have considered a number of possible structural candidates for Al_7M (M = Li, Cu, Ag, and Au) clusters to search the lowest-energy configurations. The typical stable isomers are presented in Figure 1 where the impurity atom is shown in a black sphere. The differences of the total energies between an isomer and the lowest-energy structure are also given.

For Al_7Li cluster, the obtained most stable structure, which is consistent with previous work,[15] can be constructed by

---

[*] To whom correspondence should be addressed. E-mail: xhyan@nuaa.edu.cn.
[†] Nanjing University of Aeronautics and Astronautics.
[‡] Xiangtan University.
[§] Ningbo University.

10.1021/jp066782l CCC: $37.00

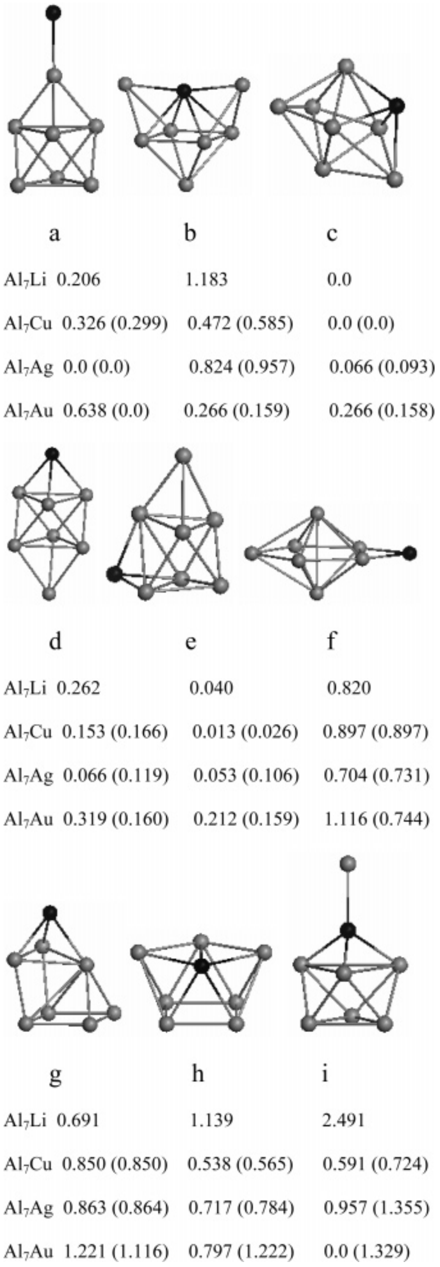

Figure 1. Schematic drawing of structures for the Al_7M (M = Li, Cu, Ag, and Au) clusters. The gray spheres represent Al atoms, and black spheres represent M atoms. The differences of total binding energies (in eV) of an isomer from the most favorable isomer are given below the structure for each size. The results obtained from NR DFT calculations are given in brackets.

capping a Li atom on a face of the Al_7 cluster. For Al_7Cu cluster, we obtained the same lowest-energy structure under both NR and RE calculations, which is similar to that of Al_7Li cluster. A metastable isomer (Figure 1e) is above the lowest-energy geometry by only 0.013 eV. As shown in Figure 1, for the Al_7Ag cluster the relativistic effects play a role on the energy difference between the ground-state structure and low-lying energy isomers. The lowest-energy structure (Figure 1a) of Al_7Ag is similar to those of Al_7H[18] and Al_7I[20,21] in which the impurity atoms prefer to bind to a single Al atom and occupy the on-top site of Al_7. Three isomers (Figure 1c−e) are in competition with the ground-state geometry, and the relative energies are 0.066, 0.066, and 0.053 eV, respectively. For Al_7Au cluster, it can be seen that the relativistic effects have a significant effect on the structure. The geometry of the most stable structure-obtained NR calculations is the same as that of Al_7Ag; however, this structure is higher in energy by $\Delta E = 0.638$ eV than the lowest-energy structure (Figure 1i) by RE calculations. The most stable structure of Al_7Au in which a Al atom just binds to the Au atom can be viewed as the combination of a Al atom and Al_6Au cluster.[32] To check the functional effects on the obtained results, we recalculated all the considered structures by adopting the Becke exchange functional and Lee−Yang−Parr correlation functional.[33,34] We obtained the same lowest-energy structure for the corresponding cluster.

TABLE 1: The AE(M) on Al_7 Cluster, Values of Vertical IPs, Vertical EA, and the HOMO−LUMO Gap of Al_7 and Al_7M (M = Li, Cu, Ag, and Au) in eV

system	AE(M) (eV)	IP (eV)	EA (eV)	gap (eV)
Al_7		5.772	2.022	0.789
Al_7Li	1.811	5.578	1.850 (1.800)[a]	0.470
Al_7Cu	2.854	5.895	2.012 (2.140)[b]	0.540
Al_7Ag	2.191	6.598	1.924	1.653
Al_7Au	3.990	6.272	1.620	1.493

[a] Ref 11. [b] Ref 12.

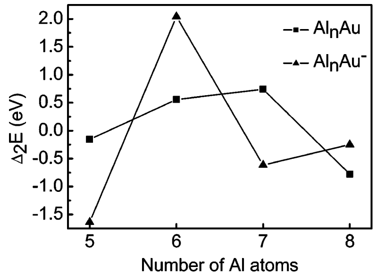

Figure 2. The second-order difference in energy (in eV) for the neutral and anionic Al_nAu ($n = 4-9$) clusters as a function of the number of Al atoms.

B. Electronic Properties. The absorption energy (AE(M)) of impurity atoms on Al_7 cluster, vertical ionization potential (IP), vertical electron affinity (EA), and the HOMO−LUMO gap calculated for Al_7M (M = Li, Cu, Ag, and Au) are given in Table 1. The absorption energy of impurity atoms is defined as $AE(M) = E(Al_7) + E(M) - E(Al_7M)$, where E is the total energy. It can be seen that the absorption energies of noble metal atoms are larger that of Li atom. This may be attributed to the d shell of noble metal atoms, which participates in the chemical bonding. The Ag atom has a weaker interaction with Al_7 than Cu and Au for its smaller absorption energy. This may be due to its peculiar structure in which there is only an Ag−Al bond. As can be seen from Table 1, the IPs of Al_7Cu, Al_7Ag, and Al_7Au are larger than that of Al_7 cluster by 0.12, 0.83, and 0.50 eV, respectively. The effect of doping Al_7 with a noble atom upon the IP is different from doping it with alkali atom, which the ionization potentials of aluminum clusters decrease with the addition of alkali atom.[15,35] Al_7Li and Al_7Cu have smaller HOMO−LUMO gaps than the Al_7 cluster. In contrast, significantly large gaps, which are one of characteristics for the magic clusters, have been observed for Al_7Ag and Al_7Au clusters and are comparable with those of magic clusters Al_7H[18] and Al_7I,[20,21] for which the gaps are 1.716 and 1.768 eV, respectively.

To investigate the stability of the Al_7Au cluster, in Figure 2 for Al_nAu and Al_nAu^- ($n = 4-9$) clusters we present the second-order difference of total energies ($E(n)$) defined by $\Delta_2E = E(n+1) + E(n-1) - 2E(n)$, which is a sensitive quantity that characterizes relative stability of atomic clusters. A noticeable peak is found at $n = 6$ for anion $AuAl_n$ clusters, and a maximum is seen in Δ_2E at $n = 7$ for neutral clusters. These

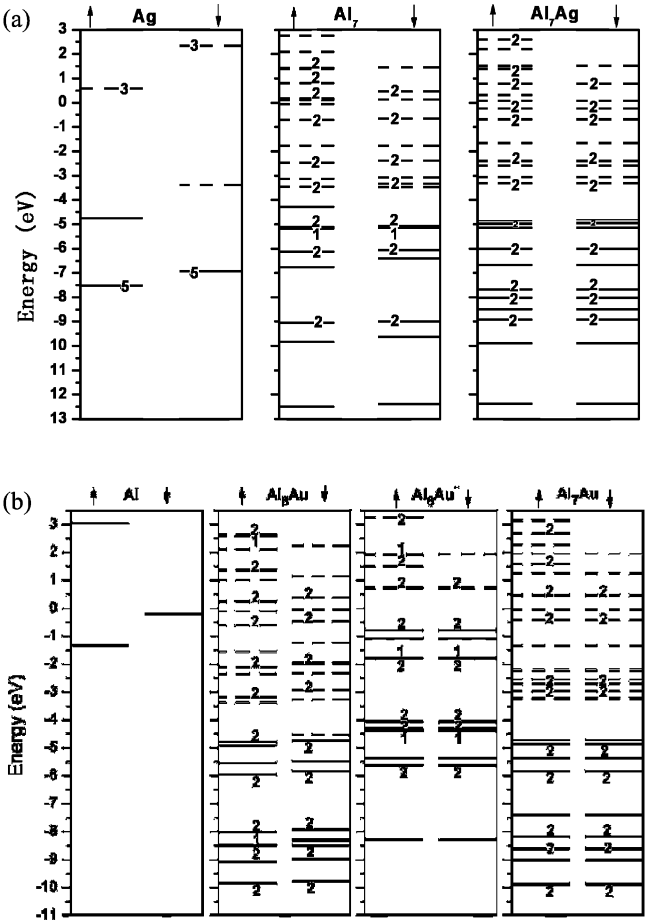

Figure 3. Electron energy levels for (a) Al, Al_7, and Al_7Ag, and (b) Al, Al_6Au, Al_7Au, and Al_6Au^-. Filled electron levels are indicated by solid lines, and dashed lines refer to unfilled levels. Numbers 1 and 2 indicate the degeneracy degree.

indicate that the $AuAl_6^-$ and $AuAl_7$ clusters should be more stable than the clusters with neighboring sizes.

It is interesting to note that the both the Al_7Ag and Al_7Au clusters have a large HOMO−LUMO gap. In the jellium picture, the Al_7 cluster has 21 valence electrons corresponding to an electronic configuration of $1s^2$ $1p^6$ $1d^{10}$ $2s^2$ 1f.[1] Mulliken population analysis indicates that there is a small amount of charge transfer (no more than 0.1 e) between Al_7 and the Ag atom, similar to the case of Al_7H.[18] To further understand the bonding nature in the Al_7Ag cluster, we plot in Figure 3a the energy levels in Ag, Al_7, and Al_7Ag. The arrows correspond to spin-up and -down states. The continuous lines correspond to the filled levels while the dashed lines represent the unfilled levels. The d state of the Ag atom is fivefold degenerate and very localized. Because of the interaction of Al_7, it is split into three states lying at the range of −8.495 to −7.682 eV in the $AgAl_7$ cluster. The interaction between Ag 5s and HOMO of Al_7 gives rise to a bonding state at around −4.9 eV and an antibonding state in the unoccupied region of the spectra. Both of the electrons occupy the bonding state and the HOMO−LUMO gap are enlarged due to the pairing of electrons.

The Al_6Au has 19 electrons, one less than the filled shell of 20 electrons corresponding to an electronic configuration of $1s^2$ $1p^6$ $1d^{10}$ $2s^1$ in the jellium picture. The anionic Al_6Au^- cluster therefore would have a closed electron shell and noticeable stability. The calculated vertical electron affinity (2.653 eV) of the lowest-energy clusters for Al_6Au is larger than that of the gold atom and comparable to that of the astatine atom (2.798 eV). The Mulliken population analysis indicates that there is a large charge transfer (0.239 e) from the Al-7 atom to the Al_6Au moiety. In Figure 3b, we plot the energy levels in Al, Al_6Au, Al_7Au, and Al_6Au^-. It can be seen that the Al_6Au cluster has a small HOMO−LUMO gap and a large gap between LUMO−LUMO + 1. For Al_6Au^-, the added electron would be local in the LUMO of Al_6Au, which enlarges the gap. The formation of Al_7Au proceeds by the interaction between the 3p state of Al and the 2s of Al_6Au. This interaction leads to the formation of a bonding and antibonding pair. The bonding state becomes the HOMO of Al_7Au while the antibonding state is raised in energy (around −2.5 eV). The bonding orbital (HOMO) is now filled with the single electron from the 3p orbital of Al and the 2s electrons of Al_6Au, which gives rise to a closed shell status for the Al_7Au. The displacement of the original LUMO orbital in Al_6Au in the formation of the compound results in an increase of the HOMO−LUMO gap to 1.493 eV.

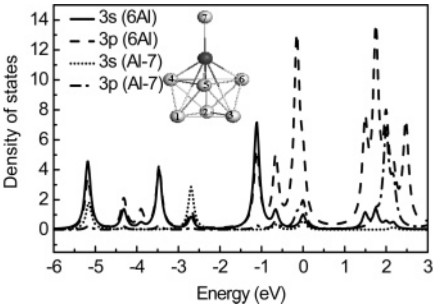

Figure 4. Calculated PDOS for the Al_7Au cluster. The Fermi level has been shift to zero. The Al atoms are labeled by Arabic numerals.

We show the partial density of states (PDOS) of Al 3s, 3p orbitals for the Al_7Au cluster in Figure 4. For the Al atom (Al-7) located at the top site, the 3p electron occupies the HOMO orbital, suggesting that the 3p electron is delocalized. However, the 3s levels lie at around −2.694 and −5.185 eV. One finds that there is a large gap between the 3s and 3p orbitals of Al-7, which suggests that the 3s and 3p orbitals are not hybridized. A previous study on the electronic structure of aluminum clusters shows that the Al atom behaves as a monovalent atom because of the large energy separation between the 3s and 3p orbitals and as a trivalent atom when the s- and p-bands start to overlap.[36] Therefore, in the case of Al_7Au, the 3s electrons of the Al-7 atom may behave more like core electrons and the Al-7 atom acts monovalent. For the other six Al atoms, one can see that the 3s orbital has hybridized with 3p orbital. It suggests that the 3s electrons of these Al atoms are delocalized, so these Al atoms are trivalent. Thus, the Al_7Au cluster may be viewed as having 20 valence electrons. Within a simple jellium picture, clusters containing 2, 8, 18, 20, 34, and 40 electrons that are closed electronic shells are particularly stable. The monovalent behavior of Al the atom is also observed in Al_{14}, in which the monovalent Al atom caps on the icosahedral structure of Al_{13}.[37]

4. Conclusions

In conclusion, based on DFT we investigate the geometric and electronic structures of Al_7M (M = Li, Cu, Ag, and Au) clusters. Relativistic effects have a significant effect on the structures of the Al_7Au cluster. Doping the Al_7 cluster with a noble metal atom increases its ionization potential. Al_7Ag and Al_7Au are found to have a large HOMO−LUMO gap. The structure of Al_7Au is a compound consisting of an aluminum atom and Al_6Au clusters that has a high-electron affinity, and it is determined that the Al on-top site acts monovalent. Accordingly, the increase in stability of the Al_7Au cluster may be rationalized with the help of the spherical jellium model.

Acknowledgment. M.X.C. especially thanks Professor X.G. Gong for help. This work was supported by the National Natural Science Foundation of China (Grant 10674070), the Program for New Century Excellent Talents in University (Grant NCET-04-0779), and the Program for Changjiang Scholars and Innovative Research Team in University (Grant IRT0534).

References and Notes

(1) Kawazoe, Y.; Kondow, T.; Ohno, K. *Clusters and Nanomaterials: Theory and Experiment*; Springer-Verlag: Heidelberg, Germany, 2002.

(2) Gong, X. G.; Kumar, V. *Phys. Rev. Lett.* **1993**, *70*, 2078.

(3) Kumar, V.; Sundararajan, V. *Phys. Rev. B* **1998**, *57*, 4939.

(4) Kumar, V.; Bhattacharjee, S.; Kawazoe, Y. *Phys. Rev. B* **2000**, *61*, 8541.

(5) Li, X.; Wang, L.-S. *Phys. Rev. B* **2002**, *65*, 153404.

(6) Rao, B. K.; Jena, P. *J. Chem. Phys.* **2001**, *115*, 778.

(7) Rao, B. K.; Khanna, S. N.; Jena, P. *Phys. Rev. B* **2000**, *62*, 4666.

(8) Khanna, S. N.; Rao, B. K.; Jena, P. *Phys. Rev. B* **2002**, *65*, 125105.

(9) Ashman, C.; Khanna, S. N.; Pederson, M. R. *Phys. Rev. B* **2002**, *66*, 193408.

(10) Zope, R. R.; Baruah, T. *Phys. Rev. A* **2001**, *64*, 053202.

(11) Thomas, O. C.; Zheng, W.-J.; Lippa, T. P.; Xu, S.-J.; Lyapustina, S. A.; Bowen, K. H., Jr. *J. Chem. Phys.* **2001**, *114*, 9895.

(12) Kuznetsov, A. E.; Boldyrev, A. I.; Zhai, H.-J.; Li, X.; Wang, L.-S. *J. Am. Chem. Soc.* **2002**, *124*, 11791.

(13) Thomas, O. C.; Zheng, W.; Bowen, K. H., Jr. *J. Chem. Phys.* **2001**, *114*, 5514.

(14) Heinebrodt, M.; Malinowski, N.; Tast, F.; Branz, W.; Billas, I. M. L.; Martin, T. P. *J. Chem. Phys.* **1999**, *110*, 9915.

(15) Rao, B. K.; Jena, P. *J. Chem. Phys.* **2000**, *113*, 1508.

(16) Burkart, S.; Blessing, N.; Klipp, B.; Muller, J.; Gantefor, G.; Seifert, G. *Chem. Phys. Lett.* **1999**, *301*, 546.

(17) Han, Y.-K.; Jung, J.; Kim, K. H. *J. Chem. Phys.* **2005**, *122*, 124319.

(18) Kawamura, H.; Kumar, V.; Sun, Q.; Kawazoe, Y. *Phys. Rev. B* **2001**, *65*, 045406.

(19) Han, Y.-K.; Jung, J. *J. Chem. Phys.* **2004**, *121*, 8500.

(20) Ergeron, D. E.; Roach, P. J.; Castleman, A. W., Jr.; Jones, N. O.; Reveles, J. U.; Khanna, S. N. *J. Am. Chem. Soc.* **2005**, *127*, 16048.

(21) Wei, S. H.; Huang, L.; Ji, M.; Gong, X. G. *Chem. Phys. Lett.* **2006**, *420*, 125.

(22) Ashman, C.; Khanna, S. N.; Pederson, M. R. *Chem. Phys. Lett.* **2000**, *324*, 137.

(23) Leskiw, B. D.; Castleman, A. W., Jr. *Chem. Phys. Lett.* **2000**, *316*, 31.

(24) Zhao, J. J.; Liu, B. C.; Zhai, H. J.; Zhou, R. F.; Ni, G. Q.; Xu, Z. Z. *Solid State Commun.* **2002**, *122*, 543.

(25) Li, S. F.; Gong, X. G. *Phys. Rev. B* **2004**, *70*, 075404.

(26) Li, X.; Wang, L.-S. *Eur. Phys. J. D* **2005**, *34*, 9.

(27) Wang, B.; Zhao, J.; Shi, D.; Chen, X.; Wang, G. *Phys. Rev. A* **2005**, *72*, 023204.

(28) Averkiev, B. B.; Boldyrev, A. I.; Li, X.; Wang, L.-S. *J. Chem. Phys.* **2006**, *125*, 124305.

(29) Sun, J.; Lu, W. C.; Wang, H.; Li, Z.-S.; Sun, C.-C. *J. Phys. Chem. A* **2006**, *110*, 2729.

(30) Delley, B. *J. Chem. Phys.* **1990**, *92*, 508. $DMol^3$ is a DFT-based package with atomic basis, distributed by Accelrys, Inc. as a part of Materials Studio. http://www.accelrys.com.

(31) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.

(32) We have optimized the structures of neutral and anionic Al_6Au clusters. Both clusters possess a C_{3v} ground-state structure. The calculated vertical electron affinity of the lowest-energy clusters for Al_6Au is 2.653 eV in our calculation, which is comparable with the value of 2.830 eV by experiment (ref 12).

(33) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 786.

(34) Becke, A. D. *J. Chem. Phys.* **1988**, *88*, 2547.

(35) Nakajima, A.; Hoshino, K.; Naganuma, T.; Sone, Y.; Kaya, K. *J. Chem. Phys.* **1991**, *95*, 7061.

(36) Li, X.; Wang, L.-S. *Phys. Rev. Lett.* **1998**, *81*, 1909.

(37) Kumar, V. *Phys. Rev. B* **1998**, *57*, 8827.