CALCULATED PROPERTIES OF NEUTRAL AND CHARGED Al_nCO_m CLUSTERS BY DENSITY FUNCTIONAL THEORY

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Density functional calculations are performed to study the structures and electronic properties of Al_nCo_m clusters with $n = 1$—7 and $m = 1, 2$. Frequency analysis is also performed after structural optimization to make sure that the calculated ground states are real minima. The corresponding total and binding energies, adiabatic electron affinities and ionization potentials are presented and discussed to aid the identification of our calculations. The BSSE correction is also considered in our calculation. Among Al_nCo_m, $Al_nCo_m^-$, and $Al_nCo_m^+$ clusters ($n = 1$—7 and $m = 1$—2), Al_4Co^-, Al_6Co^-, Al_2Co_2, and Al_6Co_2 are predicted to be more stable. Our results are consistent with the available experimental data.

K e y w o r d s: Al_nCo_m clusters, density functional theory, frequency analysis, structural properties.

INTRODUCTION

Bimetallic mixed clusters have recently been the topic of many experimental and theoretical studies based on their peculiar applications in many areas, such as catalytic chemistry and chemical engineering [1]. So in the last decades, a number of studies of bimetallic clusters have been performed. Among the candidate systems to be considered, the bimetallic aluminum cobalt clusters have been the topic of some experimental and theoretical studies [2—6]. A few years ago, Nonose et al. [7] studied the chemisorption reactivity of neutral Al_nCo_m ($n > m$) and Co_nAl_m ($n > m$) clusters toward H_2 using fast flow reactors. In the study, they found that the doping of Co_n clusters with only one Al atom reveals a remarkable increase in hydrogen chemisorption rates compared to pure Co_n clusters. In 1993, using laser photoionization mass spectrometry, Menezes et al. [8] reported the IP measurements for bimetallic aluminum-cobalt Al_nCo_m ($m > n$ and $m = 0$—7) clusters and investigated their electronic shell structure. Since the properties of the clusters are unique, it is expected that cluster-assembled materials can have uncommon properties. Studies on the electronic and geometric structures of clusters are necessary. Theoretical calculations have been performed on aluminum cobalt clusters by a number of methods. Recently, Guo [9] has reported theoretical structural and electronic properties of neutral and ionic Al_nCo ($n = 8$—17) clusters, and the result is consistent with all available experimental data on ionization energies and electron affinities.

In this paper, in order to investigate Al_nCo_m clusters systemically, theoretical calculations have been performed on neutral and charged Al_nCo_m ($n = 1$—7, $m = 1$—2) clusters using density-functional theory (DFT). We have calculated the equilibrium geometries and total energies of neutral and charged clusters at the CEP-121g level. We have also discussed the stability of the clusters and presented a range of calculated data as well as the experimental data to support our theoretical results.

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THEORETICAL METHOD

In the present study, the geometrical parameters for several different starting structural and electronic arrangements were optimized completely using DFT [10, 11]. The exchange and correlation potential contributions have been considered at the B3LYP level [12]. The compact effective potential (CEP) basis functions with the ECP triple-split basis, namely CEP-121G [13—15], have been used in the calculations.

Frequency analysis was also performed at the same theoretical level to check whether the optimized structures were the transition states or true minima on the potential energy surfaces of the corresponding clusters. In this paper, all the most stable Al_nCo_m, $Al_nCo_m^-$, and $Al_nCo_m^+$ clusters obtained were characterized as true minima without imaginary frequencies. Since one does not know a priori spin multiplicities of the clusters, the above calculations were repeated for different spin multiplicities of 1, 3, and 5… for even-electron clusters and 2, 4, and 6…for odd-electron clusters.

Furthermore, the basis set superposition error (BSSE) is considered to be one of the sources of calculation errors. The counterpoise correction (CP), which was first proposed by Boys and Bernardi [16], was carried out to correct the energy in the calculations.

All calculations were carried out using the Gaussian 03 program [17] on a PC.

RESULTS AND DISCUSSION

Geometry. The starting point in any description of cluster properties is its geometrical structure. The ground state and substate geometric sketch figures of Al_nCo_m ($n = 1$—7; $m = 1$—2) optimized by the B3LYP method are shown in Figs. 1 and 2 respectively. The relative energy of a structural isomer from the ground state is also labeled below the structural plots. Meanwhile, we give a clear indication of the geometry symmetry and multiplicity of each isomer. The corresponding energy and symmetry of the most stable neutral anionic and cationic clusters are listed in Table 1.

AlCo, AlCo⁻, AND AlCo⁺

AlCo, AlCo⁻, and AlCo⁺. Neutral AlCo can adopt $C_{\infty V}$ symmetry, and the structure with electron spins of 3 is more stable. The length of the optimized Al—Co bond in the metastable state is 2.4373 Å. Anionic AlCo clusters have the same symmetry. The addition of one electron to the $C_{\infty V}$ isomer results in a decrease in the Al—Co bond with respect to the neutral cluster. The Al—Co bond length is shorter by about 1.5 % in Al_nCo^- than that in the neutral cluster. For the cationic case, the ionized electron comes out from a bonding orbital predicting its instability relative to the neutral monomer by 6.69 eV. It is also manifested in an increase in the internuclear distance (2.5252 Å) indicating that the bond is weaker in the cationic state than the corresponding one in the neutral structure.

Al_2Co, Al_2Co^-, and Al_2Co^+. The geometric sketches show that the ground states of Al_2Co, Al_2Co^-, and Al_2Co^+ have similar structures of isosceles triangles (C_{2V}). The Al—Co bond lengths are 2.4917 Å, 2.5527 Å, and 2.6423 Å respectively. Their substates have the same symmetry as the corresponding ground states, but different electron spins.

Al_3Co, Al_3Co^-, and Al_3Co^+. In our calculation, the structures of Al_3Co, Al_3Co^-, and Al_3Co^+ look alike, but have different symmetry. The ground state of neutral Al_3Co is a pyramidal C_s structure. The lengths of Al—Co are 2.4845 Å and 2.5996 Å. Its metastable state (C_{3V}) is calculated to be only by 0.33 eV higher than the lowest energy state. Al_3Co^- and its metastable state cluster have the same pyramidal C_{3v} symmetry. The ground state of Al_3Co^+ ($^2A'$) has the same symmetry as the neutral cluster, but is less stable than Al_3Co and Al_3Co^- in energy. Its metastable state has the same C_s symmetry as the ground state, but is higher by 0.24 eV in energy.

Al_4Co, Al_4Co^-, and Al_4Co^+. It is shown that a structure ($^2B_1$) with C_{4v} symmetry is the ground state, and it is a square pyramid. The metastable structure ($^4A_2$) of neutral Al_4Co has the same structure as the ground state. The length of Al—Co is 2.5521 Å. The anionic cluster has the same square pyramidal C_{4V} structure ($^3B_1$) as the neutral cluster. With the addition of an extra electron to Al_4Co to form Al_4Co^-, the bond distances and bond angles slightly changed. The ground state of the anionic
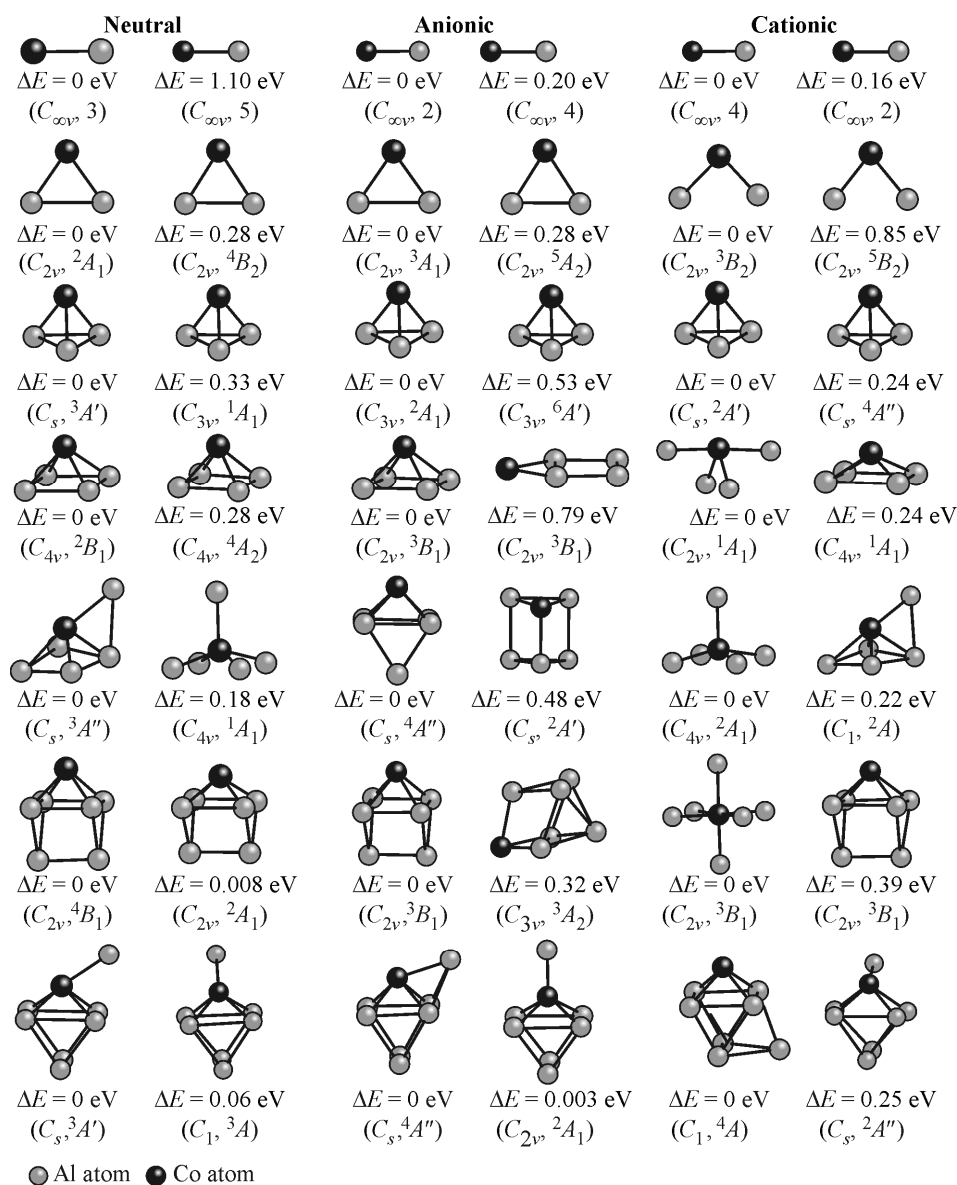
Fig. 1. Equilibrium geometries and metastable structures of AlnCo ($n = 1$—7) clusters. The symmetry and electronic state of each size are given in parentheses

cluster has shorter Al—Co bonds than those in the ground state of the neutral cluster. The metastable structure ($^3B_1$) of Al$_4$Co$^-$ has a planar structure with C_{2v} symmetry. The structure ($^1A_1$, C_{2v}) of the ground state for Al$_4$Co$^+$ is quite different from the others. Our present substate of cationic Al$_4$Co$^+$ has the same symmetry with the most stable structure of the anionic cluster but different electron spin.

Al$_5$Co, Al$_5$Co$^-$, and Al$_5$Co$^+$. The Al$_5$Co ground state has C_s symmetry, which can be obtained by capping an Al atom over the atoms (3, 4) in the ground state of Al$_4$Co. The C_{4v} symmetry structure ($^1A_1$) of Al$_5$Co is metastable and lies higher only by 0.18 eV in energy than the ground state. The lengths of Al—Co are 2.2447 Å and 2.4232 Å. The Al$_5$Co$^-$ cluster ($^4A''$, C_s) can be viewed as capping an additional Al atom between two adjacent Al atoms in the ground state of Al$_4$Co$^-$. The next structure ($^2A'$) in the energy ordering is a C_s isomer lying only 0.48 eV above the ground state. It is a slightly distorted triangle prism. Cationic Al$_5$Co$^+$ clusters can adopt C_{4v} ($^2A_1$) and C_1 (^2A) structures. They are similar to the neutral cluster, but the energy ordering is reversed. The C_{4v} isomer is predicted to be more stable than the other one.
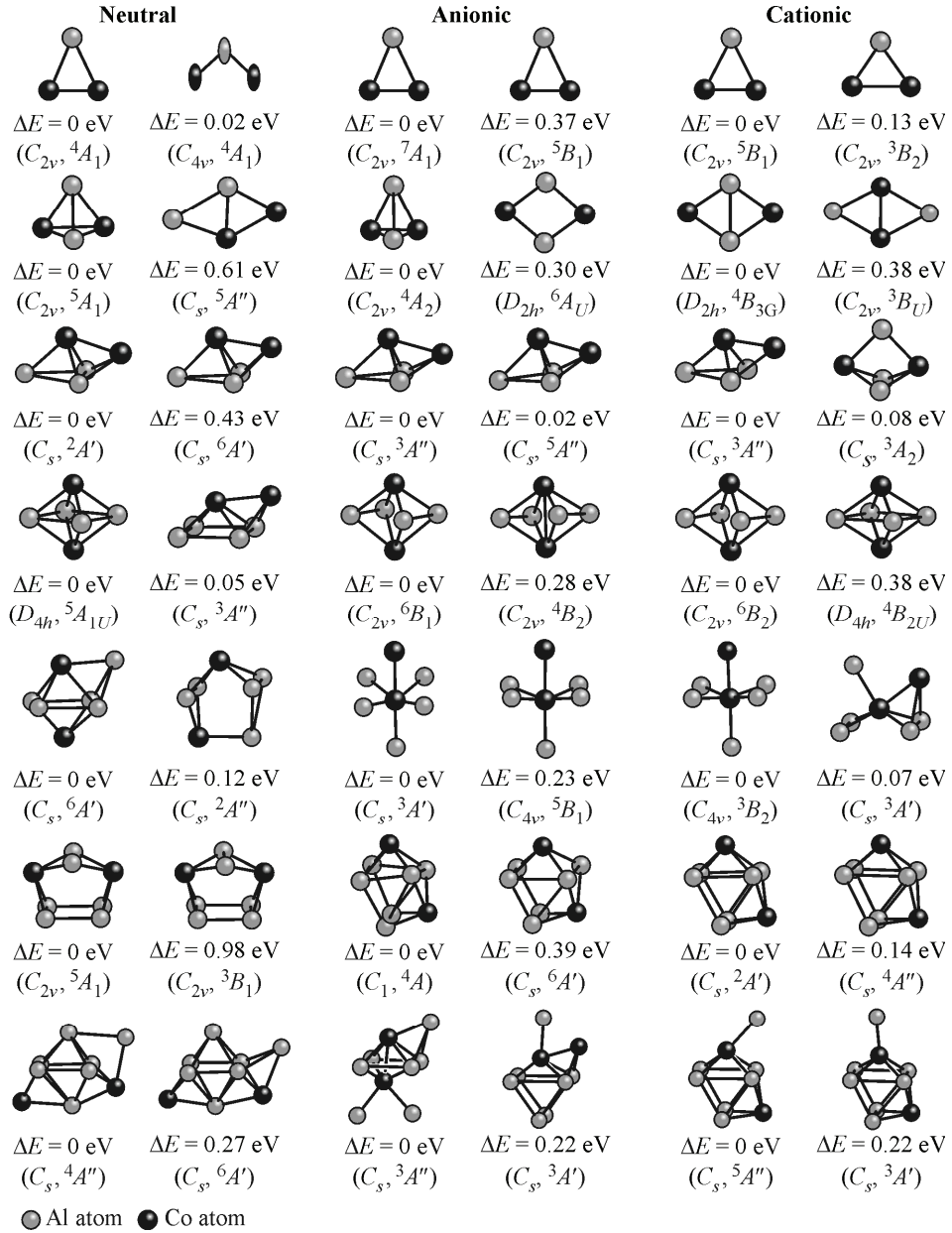
Neutral		Anionic		Cationic	

$\Delta E = 0$ eV (C_{2v}, $^4A_1$) — $\Delta E = 0.02$ eV (C_{4v}, $^4A_1$) — $\Delta E = 0$ eV (C_{2v}, $^7A_1$) — $\Delta E = 0.37$ eV (C_{2v}, $^5B_1$) — $\Delta E = 0$ eV (C_{2v}, $^5B_1$) — $\Delta E = 0.13$ eV (C_{2v}, $^3B_2$)

$\Delta E = 0$ eV (C_{2v}, $^5A_1$) — $\Delta E = 0.61$ eV (C_s, $^5A''$) — $\Delta E = 0$ eV (C_{2v}, $^4A_2$) — $\Delta E = 0.30$ eV (D_{2h}, ^6A_U) — $\Delta E = 0$ eV (D_{2h}, $^4B_{3G}$) — $\Delta E = 0.38$ eV (C_{2v}, ^3B_U)

$\Delta E = 0$ eV (C_s, $^2A'$) — $\Delta E = 0.43$ eV (C_s, $^6A'$) — $\Delta E = 0$ eV (C_s, $^3A''$) — $\Delta E = 0.02$ eV (C_s, $^5A''$) — $\Delta E = 0$ eV (C_s, $^3A''$) — $\Delta E = 0.08$ eV (C_s, $^3A_2$)

$\Delta E = 0$ eV (D_{4h}, $^5A_{1U}$) — $\Delta E = 0.05$ eV (C_s, $^3A''$) — $\Delta E = 0$ eV (C_{2v}, $^6B_1$) — $\Delta E = 0.28$ eV (C_{2v}, $^4B_2$) — $\Delta E = 0$ eV (C_{2v}, $^6B_2$) — $\Delta E = 0.38$ eV (D_{4h}, $^4B_{2U}$)

$\Delta E = 0$ eV (C_s, $^6A'$) — $\Delta E = 0.12$ eV (C_s, $^2A''$) — $\Delta E = 0$ eV (C_s, $^3A'$) — $\Delta E = 0.23$ eV (C_{4v}, $^5B_1$) — $\Delta E = 0$ eV (C_{4v}, $^3B_2$) — $\Delta E = 0.07$ eV (C_s, $^3A'$)

$\Delta E = 0$ eV (C_{2v}, $^5A_1$) — $\Delta E = 0.98$ eV (C_{2v}, $^3B_1$) — $\Delta E = 0$ eV (C_1, ^4A) — $\Delta E = 0.39$ eV (C_s, $^6A'$) — $\Delta E = 0$ eV (C_s, $^2A'$) — $\Delta E = 0.14$ eV (C_s, $^4A''$)

$\Delta E = 0$ eV (C_s, $^4A''$) — $\Delta E = 0.27$ eV (C_s, $^6A'$) — $\Delta E = 0$ eV (C_s, $^3A''$) — $\Delta E = 0.22$ eV (C_s, $^3A'$) — $\Delta E = 0$ eV (C_s, $^5A''$) — $\Delta E = 0.22$ eV (C_s, $^3A'$)

○ Al atom ● Co atom

Fig. 2. Equilibrium geometries and metastable structures of AlnCo2 ($n = 1$—7) clusters. The symmetry and electronic state of each size are given in parentheses

Al$_6$Co, Al$_6$Co$^-$, and Al$_6$Co$^+$. The fully optimized ground state structure of Al$_6$Co ($^4B_1$) has the same C_{2v} symmetry as the Al$_6$Co$^-$ ($^3B_1$) cluster. They are both formed by capping an additional Co atom on the square face of the triangle Al$_6$ prism [18]. But in the ground state of Al$_6$Co, the Al(1)—Al(2) bond has been broken in the capping process as well as the bond between atoms 4 and 5. The next isomer in the energy ordering for Al$_6$Co has nearly the same configuration as the ground state, but different electron spin. We can find our present substate of Al$_6$Co$^-$ ($^3A_2$, C_{3v}) by capping an Al atom on the triangular face of Al$_6$. Its energy was calculated to be higher by 0.32 eV than the lowest energy state. The Al—Co bond length is 2.5167 Å and the Al—Al bonds are 2.7487 Å and 2.8500 Å. We regard the $^3B_1$ electronic state as the ground state of the Al$_6$Co$^+$ cluster. The second isomer ($^3B_1$) in the energy ordering is a C_{2v} symmetry isomer lying only 0.39 eV above the ground state, and the Al—Co bond length is 2.5012 Å.

*Symmetry, calculated electronic energies E (Hartree/ particle),
and the HOMO—LUMO gap (eV) for Al_nCo_m, $Al_nCo_m^-$, and $Al_nCo_m^+$ clusters*

Structure	Symmetry	E	E_{gap}, eV	Structure	Symmetry	E	E_{gap}, eV
AlCo	$C_{\infty V}$	–147.1302	2.61	$AlCo^-$	$C_{\infty V}$	–147.1528	1.51
Al_2Co	C_{2v}	–149.1299	1.77	Al_2Co^-	C_{2v}	–149.1668	2.14
Al_3Co	C_s	–151.1315	1.58	Al_3Co^-	C_{3v}	–151.1838	1.57
Al_4Co	C_{4v}	–153.1439	1.17	Al_4Co^-	C_{4v}	–153.2151	1.97
Al_5Co	C_s	–155.1340	1.50	Al_5Co^-	C_s	–155.2074	1.62
Al_6Co	C_{2v}	–157.1596	1.47	Al_6Co^-	C_{2v}	–157.2398	1.93
Al_7Co	C_s	–159.1742	1.94	Al_7Co^-	C_s	–159.2403	1.52
$AlCo_2$	C_{2v}	–292.2880	2.09	$AlCo_2^-$	C_{2v}	–292.3226	1.51
Al_2Co_2	C_{2v}	–294.3342	2.13	$Al_2Co_2^-$	C_{2v}	–294.3454	2.14
Al_3Co_2	C_s	–296.3313	2.00	$Al_3Co_2^-$	C_s	–296.3801	1.70
Al_4Co_2	D_{4h}	–298.3127	1.50	$Al_4Co_2^-$	C_{2v}	–298.3925	1.38
Al_5Co_2	C_s	–300.3438	1.58	$Al_5Co_2^-$	C_s	–300.4031	1.27
Al_6Co_2	C_{2v}	–302.3962	2.43	$Al_6Co_2^-$	C_1	–302.4596	1.87
Al_7Co_2	C_s	–304.3654	1.56	$Al_7Co_2^-$	C_s	–304.4387	1.24
Structure	Symmetry	E	E_{gap}, eV	Structure	Symmetry	E	E_{gap}, eV
$AlCo^+$	$C_{\infty V}$	–146.8852	2.70	$AlCo_2^+$	C_{2v}	–292.0521	2.04
Al_2Co^+	C_{2v}	–148.9016	2.27	$Al_2Co_2^+$	D_{2h}	–294.0885	1.88
Al_3Co^+	C_s	–150.9121	2.01	$Al_3Co_2^+$	C_s	–296.0965	2.23
Al_4Co^+	C_{2v}	–152.9085	2.14	$Al_4Co_2^+$	C_{2v}	–298.1063	1.43
Al_5Co^+	C_{4v}	–154.9256	1.40	$Al_5Co_2^+$	C_{4v}	–300.1311	1.62
Al_6Co^+	C_{2v}	–156.9354	1.08	$Al_6Co_2^+$	C_s	–302.1647	1.62
Al_7Co^+	C_1	–158.9485	1.67	$Al_7Co_2^+$	C_s	–304.1729	2.04

Al_7Co, Al_7Co^-, and Al_7Co^+. The ground state of the neutral cluster ($^3A'$, C_s) can be viewed as a result of adding yet another Al atom to the most stable structure of Al_6Co, and the added Al atom is located only over atom 7; the structure with low C_1 symmetry is one of the metastable states. For the anionic cluster, we obtain the lowest energy geometry for Al_7Co^- ($^4A''$, C_s) by capping an additional Al atom on a triangular face of the ground state of the Al_6Co^- anionic cluster. The second isomer in the energy ordering is a C_{2v} ($^2A_1$) isomer lying only 0.003 eV above the ground state, and Al—Co bonds are shorter than those in its ground state. The lowest energy Al_7Co^+ isomer adopts C_1 symmetry.

Al_NCO_2, $Al_NCO_2^-$, AND $Al_NCO_2^+$

$AlCo_2$, $AlCo_2^-$, and $AlCo_2^+$. Our calculation shows that all of the ground states for neutral $AlCo_2$ and the corresponding charged clusters can adopt C_{2v} structures with comparable energy, and the Co—Co bond in $AlCo_2^-$ is the shortest of all. For the neutral cluster, the next structure ($^4A_1$) in the energy ordering has the same symmetry and electron spin as the ground state but higher by 0.02 eV in energy. The length of Al—Co (2.4505 Å) is shorter than that in the ground state. The substate for $AlCo_2^-$ and $AlCo_2^+$ are isosceles triangles, too. The Al—Co bond length in the substate of $AlCo_2^-$ is 2.5008 Å, and Co—Co is 2.0750 Å, while they are 2.6151 Å and 2.3747 Å in the substate of $AlCo_2^+$.

Meanwhile the two substates are higher by 0.37 eV and 0.13 eV than their corresponding ground state. Above all, the ground state of the $AlCo_2^-$ cluster is the most stable configuration among the six structures.

Al_2Co_2, $Al_2Co_2^-$, and $Al_2Co_2^+$. The most stable configuration of Al_2Co_2 ($^5A_1$) is pyramidal C_{2v} structures that can be derived from Co substitution for an Al atom in the apical position in the ground state of Al_3Co. The second isomer ($^5A''$) in the energy ordering is a C_s planar structure lying 0.61 eV above the ground state. The ground state of the anionic cluster ($^4A_2$) adopts the same structure as the lowest state of the neutral cluster. One additional electron results in decreases in Al—Co and Co—Co bonds with respect to the neutral cluster, which reveals that the anionic cluster is more stable than the neutral one. The next in the energy ordering, located at 0.30 eV above the ground state, is a planar structure with D_{2h} (^6A_U) symmetry. The Al—Co bond length is 2.4851 Å. For the cationic cluster, both of the two minima adopt planar structures. The one ($^4B_{3G}$) with higher D_{2h} symmetry is more stable than the other (^4B_U, C_{2h}). The four equal Al—Co bond lengths in the ground state are 2.4551 Å, which is slighter contracted compared to the Al—Co bond length (2.7106 Å, 2.7184 Å) of the substate.

Al_3Co_2, $Al_3Co_2^-$, and $Al_3Co_2^+$. The fully optimized ground state ($^2A'$) of Al_3Co has the same C_s symmetry as the lowest lying isomers of Al_3Co^- ($^3A''$) and Al_3Co^+ ($^3A''$). All of them can be viewed as a result of capping an additional Co atom on the face of the ground state of Al_3Co. As to their corresponding substates, the geometries of Al_3Co_2 and $Al_3Co_2^-$ are very similar to their ground states, except for their different electron spins. But the next low-lying state ($^3A_2$, C_{2v}) of $Al_3Co_2^+$ is quite different from its ground state. It can be viewed as capping an additional Co atom on the face of a triangular pyramid that contains no Co atom on it. And there are no bonds among the Al atoms on the interface of the structure.

Al_4Co_2, $Al_4Co_2^-$, and $Al_4Co_2^+$. By capping an additional Co atom on a square face of the ground state structure of the neutral Al_4Co cluster, we obtain the lowest-energy geometry for Al_4Co_2. It has high D_{4h} symmetry. The following isomer (C_s, $^3A''$) lies only 0.05 eV above the ground state. It also can be viewed as a result of adding an additional Co atom on the ground state of the neutral Al_4Co cluster, and the Co atom is added on the triangular face. The Co—Co bond is about 2.5740 Å in this structure. Anionic $Al_4Co_2^-$ can adopt C_{2v} structures as the first two structures in the energy ordering. Both of them can be viewed as Co substitution for two apical Al atoms in the Al_6 octahedron. The less stable structure lies higher only by 0.28 eV than the ground state. The Al—Al bonds are longer in it, while the Co—Co bond and Al—Co bonds become shorter. The most stable configuration of $Al_4Co_2^+$ is an octahedron with C_{2v} ($^6B_2$) symmetry. The next structure in the energy ordering is the D_{3h} ($^4B_{2U}$) isomer lying 0.38 eV above the ground state.

Al_5Co_2, $Al_5Co_2^-$, and $Al_5Co_2^+$. Calculations on the Al_5Co_2 cluster indicate that the most stable neutral isomer is a C_s symmetry structure, which is derived from the ground state structure of Al_5Co by capping an additional Co atom over the square face. The C_s symmetry structure of the $^3A'$ ground state for the Al_5Co_2 anionic cluster is derived from the Co substitution for an Al atom in the apical position. The next structure of the $^5B_1$ metastable state has C_{4v} symmetry and lies 0.23 eV above the ground state. The Co—Co bond is shorter in the former structure. The ground state of the $Al_5Co_2^+$ cluster is similar to the most stable structure of the $Al_5Co_2^-$ cluster, but has higher C_{4v} symmetry. The following isomer can be viewed as a result of capping an additional Co atom on the triangular face of the ground state of the Al_5Co cluster. The Al (1)—Al (2) and Al (3)—Al (4) bonds have been broken in the capping process.

Al_6Co_2, $Al_6Co_2^-$, and $Al_6Co_2^+$. The C_{2v} symmetry structure of the $^5A_1$ ground state for neutral Al_6Co_2 is derived from capping two Co atoms on two of the square faces of a triangular prism. The next structure in the energy ordering is another C_{2v} ($^3B_1$) structure with a very small imaginary frequency, which is located 0.98 eV above the ground state. The fully optimized ground state structure of $Al_6Co_2^-$ is a distorted structure with low C_1 symmetry, which is obtained by adding a Co atom on the

square face of the Al_6Co neutral cluster. Next in the energy ordering, located at 0.39 eV above the ground state, is a C_s ($^6A'$) isomer. The $Al_6Co_2^+$ cationic cluster can adopt the same C_s symmetry structures. The isomer that has electron spin of 2 is more stable. They can be formed by adding an additional Co atom on the square face of the most stable structure of neutral Al_6Co, and Al—Co bonds are shorter in the metastable state than those in the ground state.

Al_7Co_2, $Al_7Co_2^-$, and $Al_7Co_2^+$. Al_7Co_2 has the same C_s symmetry as its substate state. They can be viewed as result of capping additional atoms on the slightly distorted bipyramidal structures. Atom 1 in the ground state is bonded to atoms 2 and 3, while it is bonded to atoms 6, 7, and 9 in the other structure. The ground state structure of $Al_7Co_2^-$ is built by adding an Al atom on the minimum energy structure of Al_6Co_2. Its substate structure (C_s) is obtained by adding a Co atom on the substate of Al_7Co. $Al_7Co_2^+$ can be viewed as a result of capping an additional Co atom on the square face of the most stable structure of the neutral Al_7Co cluster. We can find that the bond between atoms 3 and 5 has been broken. Most Al—Co bonds are shorter in the substate than those in the ground state structure.
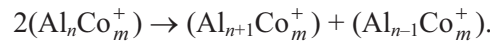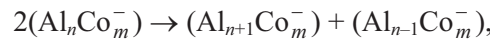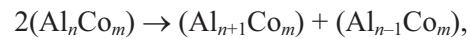
RELATIVE STABILITY

The total energies, HOMO-LUMO energy gap are listed in Table 1. The energy gap of the ground state structures is larger than that of their substable structures, which can be thought to be evidence that the ground state was correctly predicted.

An unambiguous insight into the relative stability of clusters can be gained by analyzing their energy. We first computed the binding energy per atom (E_b) of the neutral and charged clusters. This is defined by $E_b [Al_nCo_m] = \{nE[Al] + mE[Co] - E[Al_nCo_m]\}/(n + 1)$ in the neutral clusters and their corresponding charged clusters.

Eb is plotted as a function of the cluster size n in Fig. 3, *a*, *b*. We note that the binding energy of the neutral Al_nCo and Al_nCo^+ cationic clusters rises monotonically with the cluster size, which indicates that the clusters continue to gain energy during the growth process. It is found that the AlCo and AlCo$^+$ clusters are less stable. We can deduce that Al_4Co^- and Al_6Co^- are more stable in anionic clusters because of the major bump at $n = 4$ and 6. From Fig. 3, *b*, we can find that Al_2Co_2, Al_6Co_2, and $AlCo_2^-$ are more stable.

In order to test the relative stability of Al_nCo, Al_nCo_2, and their corresponding charged clusters further, the following energy variation of the reaction is considered:

$$2(Al_nCo_m) \rightarrow (Al_{n+1}Co_m) + (Al_{n-1}Co_m),$$

$$2(Al_nCo_m^-) \rightarrow (Al_{n+1}Co_m^-) + (Al_{n-1}Co_m^-),$$

$$2(Al_nCo_m^+) \rightarrow (Al_{n+1}Co_m^+) + (Al_{n-1}Co_m^+).$$

We define the energy variation in the formula as $\Delta^2E_n = E_{n+1} + E_{n-1} - 2E_n$, the second difference in energy for Al_nCo_m ($n = 1\sim7$, $m = 1, 2$) and their corresponding charged clusters. Hence, we obtain the curves shown in Fig. 4 corresponding to energy variations in the formula as the cluster size n. The larger the Δ^2E_n, the more stable the cluster corresponding to the size n is. Thereafter it is clear that Δ^2E_n is

Fig. 3. Relationships between E_b and the number of Al atoms for the ground state structures of Al_nCo, Al_nCo^-, Al_nCo^+; Al_nCo_2, $Al_nCo_2^-$, $Al_nCo_2^+$
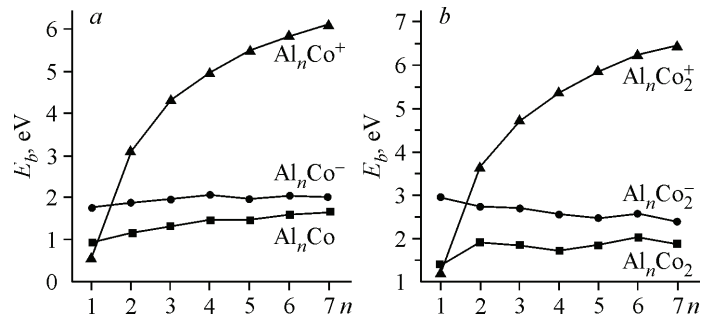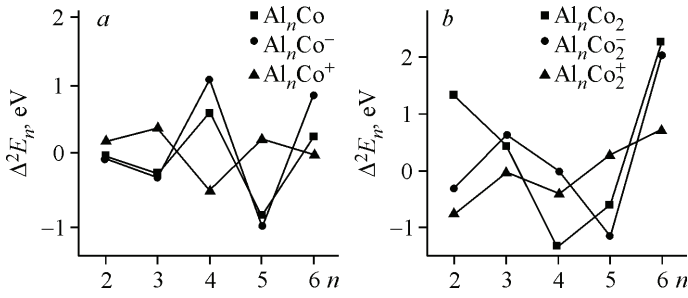
Fig. 4. Relationships between $\Delta^2 E_n$ and the number of Al atoms for the ground state structures of Al_nCo, Al_nCo^-, Al_nCo^+; Al_nCo_2, $Al_nCo_2^-$, $Al_nCo_2^+$

larger for even n and lower for odd n in Al_nCo neutral clusters and Al_nCo^- anionic clusters in Fig. 4, *a*. For Al_nCo clusters, conspicuous peaks exist in the position of Al_4Co, while for Al_nCo^- they exist in the position of Al_4Co^- and Al_6Co^- clusters. $\Delta^2 E_n$ is larger when the size number n is odd in Al_nCo^+, and Al_3Co^+ is more stable. In Fig. 4, *b*, we note that $\Delta^2 E_n$ is larger when n is an odd number for the charged clusters, while the pattern is quite different for the neutral clusters. Anyway, we can deduce that Al_2Co_2, Al_6Co_2 are more stable. This is consistent with the findings from the binding energy.

ADIABATIC IONIZATION POTENTIAL (AIP) AND ADIABATIC ELECTRON AFFINITY (AEA)

Let us discuss the adiabatic ionization potential (AIP) and the adiabatic electron affinity (AEA). The charged clusters have different configurations with their corresponding neutral clusters when mention to adiabatic energies. So AIP measures the energy difference between the ground state of the neutral and cationic clusters when the cationic clusters do not have exactly the same configurations as the ground state of the neutral one. Similarly, AEA is the difference in the total energy between the ground state of the anionic and neutral clusters provided that they have different structures. AIPs and AEAs of Al_nCo and Al_nCo_2 are shown in Fig. 5. The configurations are more stable when they have higher AIPs and lower AEAs, so we can deduce that Al_2Co_2, Al_6Co_2 are more stable structures, while Al_4Co_2 is less stable (Fig. 5). This is consistent with the findings from the relationship between $\Delta^2 E_n$ and the cluster size n.

The most detailed experiments on the ionization potential (IP) up to $n = 20$ and $m = 1—7$ were carried out by Menezes and co-workers [8] using laser photoionization mass spectrometry. Our calculated AIPs are presented in Table 2. As can be seen from the table, our calculated AIPs generally agree reasonably with the experimental ionization potentials.

CONCLUSIONS

We have investigated the structural and electronic properties of Al_nCo_m and their charged species using the B3LYP-DFT method in the ranges of $n = 1—7$, $m = 1—2$. The ground state geometrical structures of the clusters have been found in the calculation. The total energies, HOMO-LUMO energy gap, binding energy, $\Delta^2 E_n$, AIP and AEA have been calculated. We can conclude that BSSE is too large to be ignored. By the calculation and analysis we found some characteristic of the relative stability of the clusters. As for the neutral Al_nCo and Al_nCo^- clusters, they are stable when the cluster size n is even and less stable when n is odd. While Al_nCo^-, Al_4Co^-, and Al_6Co^- are more stable than their
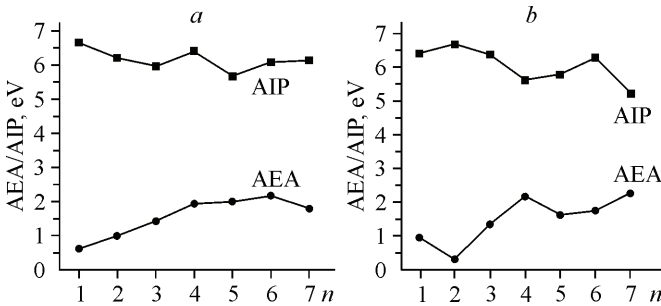

Fig. 5. Calculated AIPs and AEAs against the cluster size for Al_nCo^+ and Al_nCo_2

Calculated adiabatic ionization potentials (eV) *and experimental ionization potentials* (eV)

Al_nCo_m cluster	Calculated AIP/eV	Experiment IP/eV	Al_nCo_m cluster	Calculated AIP/eV	Experiment IP/eV
AlCo	6.67	6.99±0.17 [19]	Al_6Co	6.10	6.5
Al_2Co	6.21	6.5	Al_7Co	6.14	6.3
Al_3Co	5.97	6.15	Al_5Co_2	5.79	6.1
Al_4Co	6.41	5.8	Al_6Co_2	6.30	6.5
Al_5Co	5.67	6.0	Al_7Co_2	5.24	6.0

neighbors. However, Al_nCo^+ cationic clusters are more stable when the cluster size n is odd. As for the Al_nCo_2 clusters, Al_4Co_2 is less stable among the neutral clusters, while its corresponding $Al_4Co_2^-$ anionic cluster is quite stable. Al_2Co_2 and Al_6Co_2 are more stable configurations. Our theoretically calculated ionization potential values are in good agreement with the available experimental observations.

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