RESEARCH ARTICLE

Cage Structure Formation of Singly Doped Aluminum Cluster Cations Al_nTM^+ ($\text{TM} = \text{Ti}, \text{V}, \text{Cr}$)

Sandra M. Lang,^{1,2} Pieterjan Claes,¹ Sven Neukermans,¹ Ewald Janssens¹

¹Laboratory of Solid State Physics and Magnetism, Katholieke Universiteit Leuven, B-3001 Leuven, Belgium

²Institute of Surface Chemistry and Catalysis, University of Ulm, 89069 Ulm, Germany

Abstract

Structural information on free transition metal doped aluminum clusters, Al_nTM^+ ($\text{TM} = \text{Ti}, \text{V}, \text{Cr}$), was obtained by studying their ability for argon physisorption. Systematic size ($n = 5 - 35$) and temperature ($T = 145 - 300 \text{ K}$) dependent investigations reveal that bare Al_n^+ clusters are inert toward argon, while Al_nTM^+ clusters attach one argon atom up to a critical cluster size. This size is interpreted as the geometrical transition from surface-located dopant atoms to endohedrally doped aluminum clusters with the transition metal atom residing in an aluminum cage. The critical size, n_{crit} , is found to be surprisingly large, namely $n_{\text{crit}} = 16$ and $n_{\text{crit}} = 19 - 21$ for $\text{TM} = \text{V}, \text{Cr}$, and $\text{TM} = \text{Ti}$, respectively. Experimental cluster–argon bond dissociation energies have been derived as function of cluster size from equilibrium mass spectra and are in the 0.1–0.3 eV range.

Key words: Metal clusters, Rare gas complexes, Photofragmentation, Endohedral clusters, Van't Hoff plot

Introduction

The desire for a basic understanding of the size dependent physical and chemical properties emerging for simple metal clusters aroused intensive research on small aluminum particles. The trivalent aluminum ($\text{Al} = [\text{Ne}] 3s^2 3p^1$) is a suitable material to apply the shell model for metal clusters [1] in order to account for cluster size dependent electronic effects since its valence electrons exhibit free-electron-like character [2]. In particular, the search for ‘magic’ structures with enhanced stability against dissociation that could be used as building blocks in cluster-assembled materials drew considerable attention to the 13-atomic anionic aluminum cluster. Al_{13}^- has 40 valence electrons, which corresponds to a closed shell system within the phenomenological shell model for metal clusters and, thus, is especially stable. Using reactivity studies it was shown that Al_{13} has superhalogen character and behaves like a single iodine atom, while Al_{14} is similar to an alkaline earth atom [3, 4]. Furthermore, theoretical calculations demonstrated that Al_{13}^- is addition-

ally stabilized by a high symmetric icosahedral geometry [3, 5–10]. In contrast, neutral Al_{13} has one electron less than needed for shell closing and was predicted to exhibit either a highly symmetric [6, 11–14] or Jahn-Teller distorted [5, 9, 12] decahedral or icosahedral structure.

In order to electronically and geometrically stabilize Al_{13} , the substitution of one Al atom by tetravalent atoms like C, Si, Ge, Sn, or Pb has been proposed [8, 10, 15, 16]. Doping aluminum clusters with transition metal (TM) atoms provides additional flexibility to control the electronic and geometric properties of the clusters [7, 8, 13, 14, 17–20]. Varying the dopant material and thus the atomic radius and the number of valence d electrons allows for changing the electronic and eventually also the geometric structure in a controlled manner. For instance, a combined experimental and theoretical study showed that $\text{Al}_{12}\text{Cu}^-$ structurally resembles the icosahedral Al_{13}^- with the Cu atom occupying the central site while doping with gold yields a strongly distorted and opened structure caused by the large atomic radius of the Au atom [21].

The probability for argon physisorption is known to provide structural information. Already in 1991, it was proposed that the cluster-size-dependent Ar attachment to

Correspondence to: Ewald Janssens; e-mail: ewald.janssens@fys.kuleuven.be

small gas phase clusters is associated with changes in the cluster surface structure [22]. Later, the physisorption of Ar on clusters proved to be a successful structural probe (1) for the transition from exohedrally to endohedrally doped clusters [23], and (2) for the geometrical transition from 2D to 3D structures and the determination of cluster sizes with pronounced planar faces of monoatomic species [24]. Ar was shown to probe the formation of endohedral cage structures for Si_nTM^+ ($\text{TM}=\text{Ti}, \text{V}, \text{Cr}, \text{Co}, \text{Cu}$). Since Si_n^+ clusters are not able to attach Ar, the Ar must exclusively bind to the TM atom [23]. As a consequence, Ar can attach to the clusters as long as the dopant occupies an exohedral position. If the dopant resides in the interior of a cage, Ar can only interact with the Si surface atoms and is not adsorbed. The critical size for Ar attachment to Si_nTM^+ has been found to lie in the range of $7 \leq n_{\text{crit}} \leq 12$, depending on the size of the dopant atom, agreeing nicely with theoretically predicted cage structures [23].

In this work we study the physisorption of argon on doped aluminum cluster cations, Al_nTM^+ ($\text{TM}=\text{Ti}, \text{V}, \text{Cr}$). Ar is used as a structural probe which is sensitive to the location of the TM atom in the cluster. In particular, the transition from exohedral structures with the TM atom residing at the surface of the aluminum cluster to endohedral geometries where the TM occupies a central position is observed. Experimentally obtained cluster–argon bond dissociation energies confirm the assumption that the Ar atom is only weakly bound and does not considerably influence the structure of the cluster. Furthermore, photofragmentation studies were performed on Al_nTi^+ and Al_nV^+ , corroborating the results of the Ar attachment experiments.

Method

Experimental Setup

The Al_nTM^+ clusters are formed in a dual-target dual-laser vaporization source described in detail elsewhere [25]. Two independent pulsed Nd:YAG lasers vaporize the surfaces of translating rectangular metal targets (Al and TM) while a short pulse of He gas is introduced into the source. This gas cools the hot metal plasma and initiates the cluster formation process before the material enters the thermalization room. The temperature of the thermalization room can be controlled in the 80–320 K range by a combination of liquid nitrogen cooling and resistive heating, facilitating the production of clusters at different temperatures. Cluster–argon complexes are formed by adding a small amount of Ar to the He carrier gas (2%–3% Ar in He). The thus created mixture of He gas, neutral and charged atoms, clusters and their Ar complexes is expanded into the vacuum. After passing through a skimmer that serves to define a narrow cluster beam, the cluster ion distribution is analyzed by a reflectron time-of-flight mass spectrometer (RTOF).

In the photofragmentation studies the clusters are irradiated by a high fluence ArF excimer laser beam ($\lambda=193$ nm,

2 mJ/cm²) prior to mass separation in the RTOF. The absorption of multiple photons leads to internal heating of the cluster and subsequent rapid evaporation of atoms with the tendency to terminate at cluster sizes with an enhanced stability relative to adjacent sizes [26, 27]. The photofragments are then mass-analyzed in the RTOF.

Data Analysis

To investigate the Ar complex formation as a function of cluster size and source temperature it is suitable to define the fraction of formed Ar complexes, F_{Ar} :

$$F_{\text{Ar}} = \frac{I(\text{Al}_n\text{TM}^+ \cdot \text{Ar})}{I(\text{Al}_n\text{TM}^+) + I(\text{Al}_n\text{TM}^+ \cdot \text{Ar})} \quad (1)$$

with $I(\text{Al}_n\text{TM}^+)$ and $I(\text{Al}_n\text{TM}^+ \cdot \text{Ar})$ representing the integrated ion intensities of the cluster and its Ar complex, respectively, which are directly extracted from the recorded mass spectra. The temperature dependent integrated ion intensities can serve for a quantitative determination of the cluster–argon bond. Under the assumption of equilibrium between the clusters and the Ar complexes in the thermalization room of the cluster source, which is frozen out afterwards [23], the attachment of an Ar atom to the cluster can be described by:

The corresponding equilibrium rate constant K_{eq}^0 is directly calculated from the integrated ion intensities:

$$K_{\text{eq}}^0 = \frac{I(\text{Al}_n\text{TM}^+ \cdot \text{Ar})p_0}{I(\text{Al}_n\text{TM}^+)p(\text{Ar})} \quad (3)$$

with p_0 the standard pressure and $p(\text{Ar})$ the partial Ar pressure in the cluster source that cannot be directly measured but is roughly estimated from the He backing pressure and the known Ar concentration in the gas mixture. Furthermore, the gas is assumed to behave ideally and $p(\text{Ar})$ depends linearly on the temperature. The equilibrium rate constant K_{eq}^0 is then used to calculate the standard enthalpy ΔH^0 and standard entropy change ΔS^0 of the reaction

$$\ln(K_{\text{eq}}^0) = -\frac{\Delta H^0}{R} \frac{1}{T} + \frac{\Delta S^0}{R} \quad (4)$$

Plotting the experimental $\ln(K_{\text{eq}}^0)$ values versus the inverse temperature $1/T$ (van't Hoff plot) reveals approximately a linear relation. Thus any temperature dependence of ΔH^0 can be neglected in the investigated temperature range and Equation (4) allows to determine $-\Delta H^0$, which is equivalent to the cluster–argon bond dissociation energy E_0 . This method is based on the assumption that the cluster temperature equals the source temperature. Exact determination of ΔS^0 is not reliable because of the uncertainty on $p(\text{Ar})$.

However, possible systematic errors in the assumptions made and the rough estimate of $p(\text{Ar})$ do not affect the slope of the fit significantly, which determines E_0 . Consequently, the uncertainty on E_0 is derived from the fit quality and the number of data points.

Results

Figure 1 illustrates the mass distribution for bare Al_n^+ and vanadium doped Al_nV^+ clusters produced at a source temperature of 170 K using a 2% Ar in He mixture as carrier gas. The source parameters (vaporization laser powers, firing times of the lasers, backing gas pressure, and source geometry) are optimized to produce clusters containing only one dopant atom. The addition of Ar to the carrier gas does not affect the pure Al_n^+ cluster distribution. In contrast, the bimetallic Al_nV^+ clusters with $n < 16$ form Ar complexes, $\text{Al}_n\text{V}^+\cdot\text{Ar}$ (solid red lines in Figure 1), leading to almost complete disappearance of the Al_nV^+ with $n < 16$ cluster signal (dotted blue lines in Figure 1). About half of the Al_{16}V^+ clusters form Ar complexes under the given experimental conditions, while Al_nV^+ with $n > 16$ do not attach Ar at all. This cluster-size-dependent Ar physisorption shows that there is a critical number of Al atoms, n_{crit} , above which Ar attachment is very improbable. Similar size dependent Ar attachment is also observed in the mass spectra of Al_nTi^+ and Al_nCr^+ . It should be noted that under the present experimental conditions, complexes containing

more than one Ar atom have not been observed for any cluster size.

The cluster size dependence is even more pronounced when plotting the fraction of $\text{Al}_n\text{TM}^+\cdot\text{Ar}$ complexes, F_{Ar} (cf. Equation (1)), as a function of the number of aluminum atoms as is shown in Figure 2 for $\text{Al}_n\text{Ti}^+\cdot\text{Ar}$ (panel a), $\text{Al}_n\text{V}^+\cdot\text{Ar}$ (panel b), and $\text{Al}_n\text{Cr}^+\cdot\text{Ar}$ (panel c) at two different source temperatures of 183 K (black squares) and 163 K (red circles). For Al_nTi^+ the F_{Ar} fraction obtained at 148 K (green triangles) is additionally shown.

Ar attachment has been investigated in a broad temperature range between 300 and 145 K. Under the given pressure conditions, Ar attachment was found at temperatures below about 210 K for all studied Al_nTM^+ clusters. Measurements below 145 K were not possible due to the enhanced argon adsorption on the atomic Al^+ and TM^+ cations, completely inhibiting the cluster formation.

From Figure 2 it is apparent that F_{Ar} exhibits a sharp drop for Al_nV^+ and Al_nCr^+ yielding a critical size for Ar attachment at $n_{\text{crit}}=16$, independent of the source temperature. In contrast, for Al_nTi^+ the critical size appears to be temperature-dependent and shifting to larger n with decreasing temperature ($n_{\text{crit}}=19$ for $T=183$ K and $n_{\text{crit}}=21$ for $T=148$ K). Other remarkable size-dependent behavior is observed for the Ti and Cr doped Al cationic clusters, where $\text{Al}_{23}\text{Ti}^+$ and $\text{Al}_{14}\text{Cr}^+$ show exceptionally high and low Ar attachment probabilities, respectively, relative to clusters containing one Al atom more or less.

Figure 1. Mass distribution for bare Al_n^+ and vanadium doped Al_nV^+ clusters formed at a source temperature of 170 K using a 2% Ar in He carrier gas mixture. Al_nV^+ clusters are marked by dotted blue lines and the corresponding Ar complexes by solid red lines. Bare Al_n^+ clusters do not form Ar complexes under the present experimental conditions. Additional peaks, which are not labeled, are due to oxygen contaminants

Figure 2. Cluster size dependent fraction of Ar complexes, F_{Ar} , for (a) Al_nTi^+ , (b) Al_nV^+ , and (c) Al_nCr^+ formed at a cluster source temperature of 183 K (black squares) and 163 K (red circles), respectively. The fraction of $Al_nTi^+ \cdot Ar$ complexes is additionally shown at 148 K (green triangles)

The Ar bond dissociation energies (BDE) of a variety of observed complexes derived according to Equations (2–4) are summarized in Table 1. The obtained values range between $E_0 = 0.11 \pm 0.02$ eV and $E_0 = 0.34 \pm 0.07$ eV indicating a rather weak argon-cluster interaction, which confirms the assumption that Ar is a suitable structural probe that does not noticeably influence the cluster structure [23, 28, 29]. The obtained BDEs are in agreement with typical BDEs of physisorbed argon atoms on small clusters and metal surfaces [23, 30, 31]. The BDEs of Al_nV^+ ($n=7-11$) are 0.19–0.28 eV and, thus, larger than the BDEs of Ar physisorbed on Si_nV^+ ($n=7-11$) of 0.12–0.16 eV, obtained using the same method. The different BDE of Ar on Al_nV^+ and Si_nV^+ may reflect a different charge density on the dopant atom or a different polarizability of the host aluminum and silicon clusters. Due to the large F_{Ar} value

Table 1. Experimentally Obtained Cluster–Argon Bond Dissociation Energies E_0 of the First Physisorbed Ar Atom to Transition Metal Doped Aluminum Clusters Al_nTM^+

$Al_nTM^+ \cdot Ar$	E_0/eV	$Al_nTM^+ \cdot Ar$	E_0/eV
$Al_6V^+ \cdot Ar$	0.23 ± 0.03	$Al_9Ti^+ \cdot Ar$	0.25 ± 0.05
$Al_7V^+ \cdot Ar$	0.28 ± 0.04	$Al_{11}Ti^+ \cdot Ar$	0.34 ± 0.07
$Al_8V^+ \cdot Ar$	0.19 ± 0.04	$Al_{12}Ti^+ \cdot Ar$	0.30 ± 0.07
$Al_9V^+ \cdot Ar$	0.24 ± 0.03	$Al_{16}Ti^+ \cdot Ar$	0.24 ± 0.06
$Al_{10}V^+ \cdot Ar$	0.25 ± 0.03	$Al_{17}Ti^+ \cdot Ar$	0.26 ± 0.06
$Al_{11}V^+ \cdot Ar$	0.20 ± 0.02	$Al_{19}Ti^+ \cdot Ar$	0.18 ± 0.02
$Al_{12}V^+ \cdot Ar$	0.17 ± 0.02	$Al_{20}Ti^+ \cdot Ar$	0.22 ± 0.03
$Al_{13}V^+ \cdot Ar$	0.21 ± 0.02		
$Al_{14}V^+ \cdot Ar$	0.21 ± 0.03		
$Al_{16}V^+ \cdot Ar$	0.11 ± 0.02	$Al_6Cr^+ \cdot Ar$	0.23 ± 0.03
		$Al_7Cr^+ \cdot Ar$	0.28 ± 0.04
		$Al_8Cr^+ \cdot Ar$	0.19 ± 0.04
		$Al_9Cr^+ \cdot Ar$	0.25 ± 0.04
		$Al_{14}Cr^+ \cdot Ar$	0.21 ± 0.03

and a rather small temperature dependence of Ar attachment for some cluster sizes (for $n < n_{\text{crit}}$) the determination of reliable BDEs was not possible for all observed cluster-argon complexes.

To gain further insight into the geometric structure of doped aluminum clusters, photofragmentation experiments were performed on Al_nTi^+ and Al_nV^+ as displayed in Figure 3. The photofragmentation spectra exhibit a rather smooth cluster distribution showing only a slightly enhanced abundance for $\text{Al}_{13}\text{TM}^+$ ($\text{TM}=\text{Ti}, \text{V}$). The stability of the 14-atomic cluster might arise from a 40-electron shell closure if each Al atom delocalizes its three sp hybridized electrons, the TM dopant only donates its two s valence electrons and one electron is removed for the cationic state ($3 \times 13 + 2 - 1 = 40$). However, the 14-atomic clusters cannot have high symmetric icosahedral geometries [5, 13, 18]. Consequently, these experiments do not indicate the existence or the formation of particularly stable geometric structures of Al_nTi^+ and Al_nV^+ after photofragmentation of neutral Al_nTi and Al_nV clusters.

Discussion

The structural 2D $\rightarrow$ 3D transition for Al_n^+ has theoretically been predicted to occur at $n=5\rightarrow6$ [5, 6, 32]. Computations on cationic transition metal doped aluminum clusters have only been performed for Al_nBi^+ exhibiting the 2D $\rightarrow$ 3D

transition at $n+1=4\rightarrow5$ [33], while for neutral Al_nZn clusters the transition was predicted to occur at $n+1=5\rightarrow6$ [34] and for neutral Al_nY_m at sizes between $n+1=3\rightarrow4$ and $n+1=5\rightarrow6$, depending on the yttrium content [17]. Therefore, it can be assumed that also for the doped aluminum clusters Al_nTi^+ , Al_nV^+ , and Al_nCr^+ the structural 2D $\rightarrow$ 3D transition occurs at very small cluster sizes, even smaller than the smallest size for which we see Ar-complex formation in the current experiment. Consequently, a 2D $\rightarrow$ 3D transition does not explain the observed size dependent Ar attachment behavior of Al_nTM^+ .

In line with an earlier experiment on transition metal doped silicon clusters, Si_nTM^+ ($\text{TM}=\text{Ti}, \text{V}, \text{Cr}, \text{Co}, \text{Cu}$) [23], the critical size for Ar attachment is believed to probe the onset of endohedral cage formation. Si_n^+ clusters are not able to attach Ar. Consequently, Ar can only attach to Si_nTM^+ as long as the TM dopant assumes an exohedral position on the clusters [23]. Similarly to Si_n^+ , Ar attachment to elemental Al_n clusters is inhibited as shown in Figure 1. We argue that also for the here investigated Al_nTM^+ systems the Ar complex formation is possible only if the dopant resides at an exohedral position. The formation of such exohedrally doped Al_nTM^+ clusters is confirmed by the finding that at maximum one Ar atom can be attached (cf. Figure 1). This would correspond to one active Ar adsorption site on the cluster, namely the TM atom. In contrast, under alike experimental conditions the binding of multiple Ar atoms has been

Figure 3. Mass abundance spectra of (a) Al_nTi^+ and (b) Al_nV^+ after photofragmentation. The highest peaks in the spectra correspond to pure Al_n^+ clusters while peaks corresponding to Al_nTM^+ are connected by solid lines

observed for clusters consisting of materials that are not inert toward Ar, like Au_n^+ and $Au_nCu_m^+$ (unpublished work). Analog adsorption behavior has previously been demonstrated in N_2 saturation measurements on neutral Al_nNi_m ($n+m=12, 13, 14$) clusters yielding cluster-nitrogen complexes comprising a maximum number of N_2 molecules that is determined by the number of available Ni atoms on the surface of the cluster, while nickel atoms that are located in the interior of a cage structure are not accessible for N_2 adsorption [13].

Consequently, our observations indicate that the TM atoms reside on the surface of the Al_nTM^+ clusters up to $n_{crit}=16$ (Al_nV^+ and Al_nCr^+) and $n_{crit}=19-21$ (Al_nTi^+), respectively, while for larger clusters the TM atom is embedded into a cage of Al atoms. These observed critical cluster sizes for Al_nTM^+ clusters are, however, surprisingly large compared with $n_{crit}=7-12$ that mark the onset of endohedral structures for Si_nTM^+ [23].

For Al_nV^+ and Al_nCr^+ a sharp transition in F_{Ar} is observed pointing toward a sudden structural transition at the critical size, while for Al_nTi^+ the critical size depends on the cluster temperature. This rather unexpected behavior might be attributed to a particular geometry of the clusters in which the TM atom is still at an exohedral position but gets more and more covered by Al atoms with increasing cluster size leading to decreasing Ar adsorption behavior that can only be compensated by decreasing the temperature. Alternatively, it is also feasible that different but energetically similar isomers are present, exhibiting different Ar adsorption behavior due to different geometries. The exceptionally high and low Ar attachment probabilities of $Al_{23}Ti^+$ and $Al_{14}Cr^+$, respectively, relative to neighboring sizes, can be explained on the basis of analogous arguments. Since Ar attachment to these cluster sizes is only achieved at sufficiently low temperature (cf. Figure 2a and c) it can be concluded that both clusters exhibit a geometrical structure with the TM atom located at a position that is partially covered by Al atoms and, thus, less accessible for Ar attachment compared to an exposed exohedral position but more accessible for Ar attachment than an endohedral position.

To our knowledge, no structural computations have been reported on Al_nTM^+ ($TM=Ti, V, Cr$) in the critical size range. However, some minimum energy structures for neutral doped aluminum clusters have been predicted. Most of the theoretical investigations are limited to doped aluminum clusters containing around 13 atoms as the neutral Al_{13} might exhibit a symmetric icosahedral structure. While these studies predicted a caged structure with the TM atom occupying the central position for $Al_{11}TM$ ($TM=Ni, Cu$) [13, 19], $Al_{12}TM$ ($TM=Co, Ni, Cu$) [13, 14, 19], $Al_{13}TM$ ($TM=Cu, Au, Ni$) [13, 18, 19], and $Al_{14}TM$ ($TM=Cu$) [19], as well as for anionic Al_nCu^- ($n=11-14$) [19, 21] and Al_nAu^- ($n=12$) [21], minimum energy structures with the TM atom residing on the cluster surface were found for $Al_{12}TM$ ($TM=Cr, Mn, Fe, Cu, Ag, Au$) [14, 18] and $Al_{13}Ag$ [18]. The

different positions of the TM atom have been explained in terms of the ionization potential [19] and atomic radius [14, 19] of the dopant atom. The latter has also been found to play an important role for the critical sizes of cage formation observed for Si_nTM^+ [23].

The Ar physisorption and photofragmentation experiments presented above, demonstrate that $Al_{12}TM^+$ ($TM=Ti, V, Cr$) does not form a particularly stable icosahedral geometry with the TM atom residing in the interior of an aluminum cage (cf. Figures 2 and 3), which is most likely caused by the relatively large atomic radii of Ti, V, and Cr [35]. Dopants exhibiting sufficiently small atomic radii tend to occupy endohedral positions while with increasing size the dopant prefers exohedral positions. Thus, in the case of cationic clusters, it was shown that $Al_{12}X^+$ forms icosahedral structures of I_h symmetry when doped with small atoms such as P, Si, and Ge but yields icosahedral-like motifs with the dopant located at the surface and lowered to C_{5v} symmetry for the larger dopants Sn and Pb [10, 36]. Similar results recently were found for neutral and anionic doped aluminum clusters [8, 14, 18]. Differences in the atomic radii also might cause the larger value of n_{crit} for Al_nTi^+ compared with Al_nV^+ and Al_nCr^+ . However, the values of the radii are not sufficient to explain the general observation of endohedral cluster formation at rather large cluster sizes comprising 16 ($TM=V, Cr$) and 19–21 ($TM=Ti$) Al atoms, suggesting that also other factors are crucial. In a theoretical study of bare aluminum clusters, Fournier showed that neutral and anionic clusters exhibit very similar compact and symmetric geometries while the structures of cationic clusters differ considerably and adopt, for several sizes, more open structures [6]. This kind of structures might explain the experimental observation (1) that the TM atom resides on the surface of the cluster up to surprisingly large cluster sizes and (2) that the photofragmentation experiments exhibit a rather smooth cluster distribution not indicating the formation of particularly stable and highly symmetric geometric structures. Furthermore, incorporating a single TM atom and the accompanying interactions between the dopant d-electrons with the Al sp electrons might completely change the structure of the cluster.

Summary

In this contribution, Ar physisorption was used as a structural probe for the location of the TM dopant atom in aluminum cluster cations, Al_nTM^+ ($TM=Ti, V, Cr$). Experimentally obtained Ar-cluster bond dissociation energies indicate a weak interaction between the rare gas atom and the cluster cations leading to the conclusion that the Ar probe does not considerably influence the cluster structure. Ar attachment to doped clusters has been observed up to a critical cluster size $n_{crit}=16$ for Al_nV^+ and Al_nCr^+ and $n_{crit}=19-21$ for Al_nTi^+ , respectively. Since elemental Al_n^+ clusters are inert toward Ar under the present experimental conditions, it can be concluded that Ar attaches to the TM as long as the TM atom resides on an

exohedral position in the cluster that is easily accessible for the Ar atom. As a result, the lack of Ar complexes for $n > n_{\text{crit}}$ determines the cluster size for which the TM atom is located in the interior of an Al_n cage. Complementary photofragmentation experiments on Al_nTi^+ and Al_nV^+ provide supporting evidence that $\text{Al}_{12}\text{TM}^+$ do not form highly symmetric icosahedral structures with the TM occupying an endohedral position. This finding is in agreement with previous theoretical studies demonstrating that I_h symmetry structures can only be formed for sufficiently small dopants such as P, Si, and Ge. Differences in the atomic radii of Ti, V, and Cr also explain observed differences in n_{crit} . The generally rather large n_{crit} has been attributed to asymmetric open geometrical structures of cationic aluminum clusters. To elucidate the decisive factors for the rather unexpected size dependent formation of endohedrally doped cationic aluminum clusters, detailed computational studies are indispensable. We hope that the present results will inspire further investigations of the structure of cationic transition metal doped aluminum clusters.

Acknowledgments

The authors acknowledge support for this work by the Research Foundation–Flanders (FWO), the K.U. Leuven Research Council (GOA program), and the Belgian Interuniversity Attraction Poles (IAP) research program. In particular, S.M.L. is grateful for support from the FWO; P.C. acknowledges the Institute for the Promotion of Innovation through Science and Technology in Flanders (IWT-Vlaanderen).

References

- de Heer, W.A.: The Physics of Simple Metal Clusters: Experimental Aspects and Simple Models. *Rev. Mod. Phys.* **65**, 611–676 (1993)
- Roach, P.J., Woodward, W.H., Reber, A.C., Khanna, S.N., Castleman, J.A.W.: Crystal Field Effects on the Reactivity of Aluminum-Copper Cluster Anions. *Phys. Rev. B* **81**, 195404 (2010)
- Bergeron, D.E., Castleman Jr., A.W., Morisato, T., Khanna, S.N.: Formation of Al_{13}F^- : Evidence for the Superhalogen Character of Al_{13} . *Science* **304**, 84–87 (2004)
- Bergeron, D.E., Roach, P.J., Castleman Jr., A.W., Jones, N.O., Khanna, S.N.: Al Cluster Superatoms as Halogens in Polyhalides and as Alkaline Earths in Iodide Salts. *Science* **307**, 231–235 (2005)
- Rao, B.K., Jena, P.: Evolution of the Electronic Structure and Properties of Neutral and Charged Aluminum Clusters: A Comprehensive Analysis. *J. Chem. Phys.* **111**, 1890–1904 (1999)
- Fournier, R.: Trends in Energies and Geometric Structures of Neutral and Charged Aluminum Clusters. *J. Chem. Theory Comput.* **3**, 921–929 (2007)
- Thomas, O.C., Zheng, W., Bowen, K.H.: Magic Numbers in Copper-Doped Aluminum Cluster Anions. *J. Chem. Phys.* **114**, 5514–5519 (2001)
- Li, S.F., Gong, X.G.: Neutral and Negatively Charged Al_{12}X ($\text{X}=\text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) Clusters Studied from First Principles. *Phys. Rev. B* **74**, 045432 (2006)
- Aguado, A., López, J.M.: Structures and Stabilities of Al_n^+ , Al_n , and Al_n^- ($n=13$ –34) Clusters. *J. Chem. Phys.* **130**, 064704 (2009)
- Akutsu, M., Koyasu, K., Atobe, J., Hosoya, N., Miyajima, K., Mitsui, M., Nakajima, A.: Experimental and Theoretical Characterization of Aluminum-Based Binary Superatoms of Al_{12}X and Their Cluster Salts. *J. Phys. Chem. A* **110**, 12073–12076 (2006)
- Lloyd, L.D., Johnston, R.L.: Modeling Aluminum Clusters with an Empirical Many-Body Potential. *Chem. Phys.* **236**, 107–121 (1998)
- Chuang, F.-C., Wang, C.-Z., Ho, K.H.: Structure of Neutral Aluminum Clusters Al_n ($2 \leq n \leq 23$): Genetic Algorithm Tight-Binding Calculations. *Phys. Rev. B* **73**, 125431 (2006)
- Rexer, E.F., Jellinek, J., Krissinel, E.B., Parks, E.K., Riley, S.J.: Theoretical and Experimental Studies of the Structures of 12-, 13-, and 14-Atom Bimetallic Nickel/Aluminum Clusters. *J. Chem. Phys.* **117**, 82–94 (2002)
- Wang, M., Huang, X., Du, Z., Li, Y.: Structural, Electronic, and Magnetic Properties of a Series of Aluminum Clusters Doped with Various Transition Metals. *Chem. Phys. Lett.* **480**, 258–264 (2009)
- Rao, B.K., Jena, P.: Energetics and Electronic Structure of Carbon Doped Aluminum Clusters. *J. Chem. Phys.* **115**, 778–783 (2001)
- Gong, X.G., Kumar, V.: Enhanced Stability of Magic Clusters: A Case Study of Icosahedral Al_{12}X , $\text{X}=\text{B}, \text{Al}, \text{Ga}, \text{C}, \text{Si}, \text{Ge}, \text{Ti}, \text{As}$. *Phys. Rev. Lett.* **70**, 2078–2081 (1993)
- Venkataramanan, N.S., Suvitha, A., Note, R., Kawazoe, Y.: Structures of Small Y_nAl_m Clusters ($n+m \leq 6$): A DFT Study. *J. Mol. Struct. THEOCHEM* **902**, 72–78 (2009)
- Zope, R.R., Baruah, T.: Conformers of Al_{13} , Al_{12}M , and Al_{13}M ($\text{M}=\text{Cu}, \text{Ag}, \text{and Au}$) Clusters and Their Energetics. *Phys. Rev. A* **64**, 053202 (2001)
- Khanna, S.N., Ashman, C., Rao, B.K., Jena, P.: Geometry, Electronic Structure, and Energetics of Copper-Doped Aluminum Clusters. *J. Chem. Phys.* **114**, 9792–9796 (2001)
- Calleja, M., Rey, C., Alemany, M. M. G., Gallego, L. J., Ordejón, P., Sánchez-Portal, D., Artacho, E., Soler, J. M.: Self-Consistent Density-Functional Calculations of the Geometries, Electronic Structures, and Magnetic Moments of Ni-Al Clusters. *Phys. Rev. B* **60**, 2020–2024 (1999)
- Pal, R., Cui, L.-F., Bulusu, S., Zhai, H.-J., Wang, L.-S., Wang, X.C.: Probing the Electronic and Structural Properties of Doped Aluminum Clusters: MAl_{12} ($\text{M}=\text{Li}, \text{Cu}, \text{and Au}$). *J. Chem. Phys.* **128**, 024305 (2008)
- Knickelbein, M.B., Menezes, W.J.C.: Metal Cluster-Rare Gas van der Waals Complexes: Nb_nAr_m and Fe_nKr_m . *Chem. Phys. Lett.* **184**, 433–438 (1991)
- Janssens, E., Gruene, P., Meijer, G., Wöste, L., Lievens, P., Fielicke, A.: Argon Physisorption as Structural Probe for Endohedrally Doped Silicon Clusters. *Phys. Rev. Lett.* **99**, 063401 (2007)
- Huang, W., Wang, L.-S.: Probing the 2D to 3D Structural Transition in Gold Cluster Anions Using Argon Tagging. *Phys. Rev. Lett.* **102**, 153401 (2009)
- Bouwen, W., Thoen, P., Vanhoutte, F., Bouckaert, S., Despa, F., Weidele, H., Silverans, R.E., Lievens, P.: Production of Bimetallic Clusters in a Dual-Target Dual-Laser Vaporization Source. *Rev. Sci. Instrum.* **71**, 54–58 (2000)
- Veldeman, N., Janssens, E., Hansen, K., De Haeck, J., Silverans, R. E., Lievens, P.: Stability and Dissociation Pathways of Doped Au_nX^+ Clusters ($\text{X}=\text{Y}, \text{Er}, \text{Nb}$). *Faraday Discuss.* **138**, 147–162 (2008)
- Neukermans, S., Janssens, E., Tanaka, H., Silverans, R.E., Lievens, P.: Element- and Size-Dependent Electron Delocalization in Au_nX^+ Clusters ($\text{X}=\text{Sc}, \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$). *Phys. Rev. Lett.* **90**, 033401 (2003)
- Knickelbein, M.B., Menezes, W.J.C.: Metal Cluster-Rare Gas van der Waals Complexes: Physisorption on a Microscopic Scale. *J. Phys. Chem.* **96**, 6611–6616 (1992)
- Fielicke, A., Kirilyuk, A., Ratsch, C., Behler, J., Scheffler, M., von Helden, G., Meijer, G.: Structure Determination of Isolated Metal Clusters Via Far-Infrared Spectroscopy. *Phys. Rev. Lett.* **93**, 023401 (2004)
- Bruck, L.W., Cole, M.W., Zaremba, E.: Physical Adsorption: Forces and Phenomena. Oxford University Press, Oxford (1997)
- Gehrke, R., Gruene, P., Fielicke, A., Meijer, G., Reuter, K.: Nature of Ar Bonding to Small Co_n^+ Clusters and its Effect on the Structure Determination by Far-Infrared Absorption Spectroscopy. *J. Chem. Phys.* **130**, 034306 (2009)
- Jones, R.O.: Simulated Annealing Study of Neutral and Charged Clusters: Al_n and Ga_n . *J. Chem. Phys.* **99**, 1194–1206 (1993)
- Jones, C.E., Clayborne, P.A., Reveles, J.U., Melko, J.J., Gupta, U., Khanna, S.N., Castleman Jr., A.W.: Al_nBi Clusters: Transition Between Aromatic and Jellium Stability. *J. Phys. Chem. A* **112**, 13316–13325 (2008)
- Ren, X.-J., Li, B.-X.: First-Principles Study on Stability and Magnetism of Al_nZn ($n=1$ –9) Clusters. *Physica B* **405**, 2344–2349 (2010)
- Cordero, B., Gómez, V., Platero-Prats, A. E., Revés, M., Echeverría, J., Cremades, E., Barragán, F., Alvarez, S.: Covalent Radii Revisited. *Dalton Trans.* 2832–2838 (2008)
- Chen, G., Kawazoe, Y.: Structural and Electronic Properties of Al_{12}X^+ ($\text{X}=\text{C}, \text{Si}, \text{Ge}, \text{Sn}, \text{and Pb}$) Clusters. *J. Chem. Phys.* **126**, 014703 (2007)