Computational Materials Science 79 (2013) 599–610

Contents lists available at SciVerse ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Evolution of the electronic structure and properties of charged titanium doped aluminum nanoclusters

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ARTICLE INFO

Article history:
Received 10 December 2012
Received in revised form 1 July 2013
Accepted 5 July 2013
Available online 7 August 2013

Keywords:
Charged aluminum clusters
Titanium doping
DFT calculations
Relative energy
Structural stability
Electron affinities and ionization potential

ABSTRACT

A systematic study of the titanium doped aluminum clusters with various spin multiplicities have been performed by using Density Functional Theory calculations at the B3LYP/6-311++G(d,p) level. The HOMO–LUMO energy gap, ionization potential (IP), electron affinity (EA), Adiabatic Electron Affinity (AEA), Vertical Electron Affinity (VDE) and vertical detachment energy (VDE) are also computed for the most stable isomer of each cluster.

1. Introduction

Investigations of the geometries, electronic structures, energetic and reactivities of atomic clusters have attracted significant interest in recent years. One of the principal goals of these research activities is to explore the size evolutionary patterns of the properties of material aggregates from the molecular to condensed phase regime. Clusters play an important role in understanding the transition from microscopic to macroscopic structures of matter [1]. Thus, by studying the properties of clusters as a function of size, one hopes to learn how the bulk properties evolve. During the last few years, studies of transition metal clusters have attracted a lot of interests. In addition to, atomic clusters may have unique size specific properties that differ from their bulk systems. Consequently, materials synthesized by assembling clusters may be technologically important.

Among the group III elements aluminum, gallium and indium are the favorite metallic elements for cluster studies. Aluminum is a very common metal and has found many uses in everyday life. Small clusters composed of aluminum atom have naturally been the subjects of intensive studies for the last two decades. A large number of studies of aluminum cluster; both theoretical [3,15–19] as well as experimental [2–13] have been reported. In recent years, a number of series of experimental and theoretical works have been performed to study the structure, energetic stability, ionization potentials (IP), and electron affinities (EA) of the gas-phase elemental Al_n [14,3,16–17] and doped aluminum clusters AlnC [18], AlnSi [19], AlnP [20], AlnZn [21], AlnCr [22], AlnMn [22], AlnFe [22], AlnCo [22], AlnNi [22] and AlnBe [23] n varying from 2 to 23, and also the family of icosahedral XAl12 clusters with inserted heteroatoms X from the third and fourth main groups [24]. In addition, the dissociative chemisorption of molecular hydrogen on charged and neutral aluminum clusters $Al_{12}X$ (X = Mg, Al, Si) was investigated using DFT by Henry et al. [25]. Henry et al. [26] reported that the structure and bonding in charged and doped aluminum clusters have been investigated using Regional Density Functional Theory (RDFT). The structural electronic and other properties of the XAl12 type clusters was performed by Charkin et al. [27–29].

In this work, DFT-B3LYP at 6-311++G(d,p) [30,31] level is employed via the Gaussian 09 program [32] to optimize the structures of the Al_n (±) and $Al_{n-1}Ti$ (±) ($n \leqslant 7$) clusters. The analysis of the energetic and structural stability of these clusters depends on the various isomers that are presented. The HOMO–LUMO energy gaps, vertical detachment energy, vertical and Adiabatic Electron Affinity and adiabatic ionization potentials have been determined.

2. Method of calculation

The lowest-energy geometries of charged pure and the titanium doped aluminum clusters in the range of 1–7 derived from

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http://dx.doi.org/10.1016/j.commatsci.2013.07.010

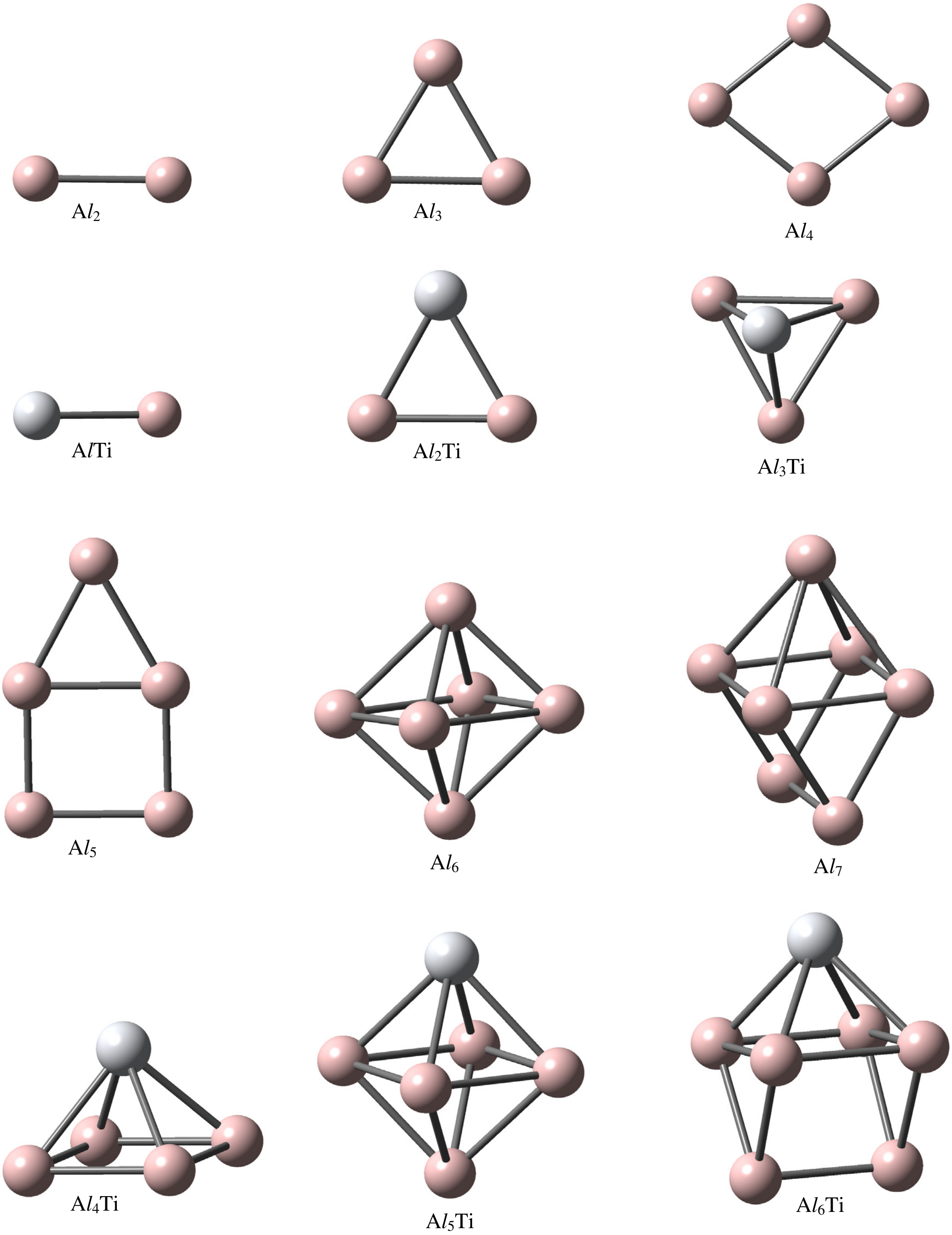

Fig. 1. Equilibrium geometries of anionic Al_n and $Al_{n-1}Ti$ ($n \leqslant 7$) type clusters.

Refs. [2–18,33–36] were verified using DFT calculations. Computationally we first searched for the global minimum of Al_n (±) and $Al_{n-1}Ti$(±) ($n \leqslant 7$) clusters using the B3LYP/6-311++G** level of theory. In total, this amounted to optimizing 190 separate geometries. Calculations are carried out without any symmetry restrictions for different starting geometries. Starting with the spin singlet configurations of even electron system and the spin doublet configuration of odd-electron system, the calculation procedure was repeated for various spin multiplicities for a given cluster size. In this work, we performed more than 500 geometric optimizations calculations. The calculations are continued until the minimum energy is reached. Frequency analysis is performed at the B3LYP/6-311++ G(d,p) level to check whether the optimized structures are transition states or true minima on the potential energy surfaces of corresponding clusters. The ground-state structures are obtained as actually equilibrium states without imaginary frequencies.

Secondly, to comparisons of these calculations to forthcoming experimental results, we was used the dunning's correlation consistent basis sets (cc-pVDZ and cc-pVTZ basis sets) for DFT