



Atomic carbon growth on yttrium clusters: Relativistic density functional theory investigations



Hui-Lin Jia^a, Bao-Ru Wang^b, Qing-Min Ma^a, Zun Xie^{a,*}

^a Department of Physics and Hebei Advanced Thin Film Laboratory, Hebei Normal University, Shijiazhuang 050024, Hebei, China

^b College of Science, Hebei University of Science and Technology, Shijiazhuang 050018, Hebei, China

ARTICLE INFO

Article history:

Received 4 February 2016

Received in revised form 11 March 2016

Accepted 15 March 2016

Available online 16 March 2016

Keywords:

Relativistic density-functional theory

C@Y₆ sub-cluster

Relative stability

Closed electron shell

ABSTRACT

The geometries, stabilities, and electromagnetic characteristics of CY_n ($n = 1-14$) clusters have been systematically investigated using relativistic density functional theory with the generalized gradient approximation. The growth process of CY_n ($n = 1-14$) clusters can be divided into three phases. First, the C atom replaces a surface atom of Y_{n+1} cluster when $n < 6$. For the cluster with $n = 6$, the C atom goes into the center of a tetragonal bipyramid and the C@Y₆ cluster is formed. Over the range from $n = 7$ to 14, Y atoms are successively capped onto the C@Y₆ sub-cluster. Due to the C doping, the stability of clusters is enhanced and the magnetic moments are reduced compared to the corresponding pure yttrium clusters. In particular, doping with a carbon atom whether at the surface or in the subsurface can make some clusters transition from an open electronic shell to a closed electron shell.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Due to the exchange splitting of 4d electrons, many non-magnetic transition metal (TM) or rare earth metal clusters are found to carry an appreciable magnetic moment [1–4]. The first 4d element yttrium is non-magnetic and yttrium clusters is a subject investigated extensively for its quite intriguing electronic and magnetic properties [4–9]. Both Stern–Gerlach molecular-beam deflection experiment on Y_n ($n = 5-20$) [7] and calculations of magnetic moments for Y_n ($n = 2-17$) clusters [8] based on DFT suggest that the magic cluster Y₁₃ possesses exceptionally high magnetic moment. Neither the photoionization spectra of yttrium clusters Y_n ($n = 2-31$) [4] nor the vertical ionization potentials (VIPs) as calculated within the conducting spherical droplet model [5] show electronic shell-filling behavior.

On the basis of pure Y_n cluster, many researchers involve in doped Y_n clusters in order to control the physical properties of clusters. The yttrium monoxides clusters have been explored experimentally [4] and theoretically [10]. The DFT calculations for Y_nO ($n = 2-14$) clusters indicate that the oxygen atom occupies an outer site of clusters for small clusters, and then at $n = 12$ falls into the center of the cluster of Y atoms, finally for larger clusters, prefers a subsurface site [10]. There are also theoretical reports regarding Al- [11], Mn- [12], and Si- [13] doped yttrium clusters.

The growth pattern of AlY_n ($n = 1-14$) and SiY_n ($n = 1-14$) clusters retains a framework similar to that of the most stable Y_{n+1} clusters with the impurity atom substituting for a surface atom in small Y_{n+1} clusters, then falling into the center of larger yttrium clusters. The MnY_n clusters ($n = 2-13$) have octahedron structures with the Mn atom occupying the center [12]. The doping atoms all enhance the stabilities but reduce the magnetic moments of the yttrium clusters. In the case of Y₁₃, different encapsulated atoms (Na, Mg, Al, Si, P) result in different changes to the magnetic properties of the host Y₁₃ clusters, but closed electronic shells do not occur as they do in doped icosahedron and decahedron La₁₃ clusters with C and Si atoms [14]. To date, there have been no systematic investigations of C-doped yttrium clusters. To determine the structural patterns arising with yttrium clusters and C atoms and understand the effects of the C atom on the electromagnetic properties of CY_n clusters, we present spin-polarized DFT study of CY_n clusters up to $n = 14$. Here we show that doping with one tetravalent carbon impurity endows some clusters with closed electronic shell.

2. Computational details

The number of distinct initial geometries and the methods used to construct them are important as regards the reliability of the low-lying energy states obtained, for it is impossible to explore all possible structures. Based on our previous experience on TM cluster building and the results of Refs. [7,8,11,12,33], in the initial stages of this study, we investigated a number of geometries of

* Corresponding author.

E-mail address: zxie@hebtu.edu.cn (Z. Xie).

pure Y_{n+1} ($n = 1-14$) clusters. For those structures with higher symmetry and orbital electronic degeneracy, Jahn–Teller distortions [15–17] were used to lower the symmetry and remove the degeneracy of the highest occupied molecular orbital (HOMO). Based on the initial and optimized structures of the above Y_{n+1} ($n = 1-14$) clusters, we constructed a large number of candidate CY_n ($n = 1-14$) clusters by replacing one Y atom with a C atom on all non-equivalent sites of the Y_{n+1} cluster or by adding one Y (C) atom to the corresponding CY_{n-1} (Y_n) cluster.

The calculations were implemented using the DMOL method [18,19] based on DFT with the GGA, which is made available in the quantum chemistry package in Materials Studio. For the problem being investigated, the choice of the exchange and correlation and basis functions are crucial to the reliability of the final results. In the present work, a nonlocal Perdew–Burke–Ernzerhof (PBE) exchange and correlation function [20] and a double numerical basis plus polarized functions (DNP) were chosen. Relativistic effects in the heavy metal atom Y, were considered by using the DFT-based relativistic semi-core pseudo-potential (DSPP) [21] for the atomic core, which includes scalar relativistic effects and neglect spin–orbit interactions. To verify the effects of spin–orbit coupling (SOC) on Y_n and CY_n clusters, we employed the Vienna ab initio simulation package (VASP 5.3) to calculate the total energies and the total magnetic moments for the larger clusters Y_{n+1} and CY_n ($n = 7-14$). The GGA with PBE exchange and correlation function and the projector augmented-wave potential was used. The results show that the total energy difference between the calculations with and without SOC is about 0.045–0.049 eV/atom. Besides, the total magnetic moments without SOC are very closed to that on Z direction in the SOC calculations. The magnetic moments yielded on X-axis and Y-axis are not significant and can be neglected.

In the calculations of the electronic structure, the density mixing criteria were set to 0.2 for charge and 0.5 for spin. In the course of structural optimization without any symmetry constraints, the convergence criteria were set to 2×10^{-3} Hartree/Å for the forces, 5×10^{-3} Å for the atomic displacement and 10^{-5} Hartree for the energy change. Following the optimization, the stability of the lowest-energy structure obtained was further confirmed to be the minimum of the potential energy surface by investigating the harmonic vibrational frequencies and ensuring that there were no imaginary modes.

To evaluate the accuracy of the above computational scheme, we first performed test calculations on the dimers C_2 and Y_2 . The binding energies (E_b) are defined as the energy required for decomposing the cluster system into isolated atoms. The VIPs are defined as the difference between the total energy of the neutral and positively charged clusters in the same geometry. The results for the dimers are listed in Table 1 along with related references to the literature and available experimental data for comparison.

It is clear that the bond length and binding energy of Y_2 are consistent with previous theoretical values obtained using the DFT–GGA [8] and CASSCF–MRSDCI methods [6]. The VIP of the yttrium dimer is close to the experimental result [4]. Calculations for the C_2 dimer gave a bond length, average binding energy and vibrational frequency in agreement with the theoretical and

experimental values [22–25]. These benchmark calculations show that the well-designed PBE/DSPP/DNP computational scheme is suitable for studying CY_n clusters.

3. Results and discussions

3.1. Geometrical evolution of different-sized carbon-doped yttrium clusters

The results for CY_n ($n = 1-14$) clusters are reported in what follows. The lowest-energy and low-lying geometries of CY_n ($n = 1-14$) clusters are shown in Figs. 1 and 2. The lowest-energy geometries of the Y_{n+1} ($n = 1-14$) clusters are also given for comparison.

By exploring the many configurations and employing Jahn–Teller distortions, the lowest-energy structures of Y_{n+1} ($n = 1-14$) clusters have been determined. The results for most of the pure clusters are in good agreement with previous work [8], i.e. the Y_{n+1} clusters up to $n = 14$ favor the icosahedral close packing growth pattern. However, the lowest-energy structures of Y_9 and Y_{10} are different from those of Ref. [8] while being very similar to the ground states mentioned in Refs. [11,12]. For Y_9 , all possible initial configurations based on capping different faces of the octahedron, pentagonal bipyramid, square prism, and antiprism structures were considered. We found that one capped tetragonal antiprism with C_s symmetry had the highest binding energy and a singlet HOMO state. This configuration was obtained by distorting the C_2 ground state structure given in Ref. [8] according to the Jahn–Teller effect. The lowest-energy state of Y_{10} was obtained by capping one atom onto the ground state of the Y_9 cluster.

The 13-atom cluster, which is “a magic cluster” for a number of elements, has been intensively studied [26–34]. Here, based on the Refs. [7,10,26–34] mentioned above, we have considered six potential modes: icosahedral (i), decahedral (d), cuboctahedral, anti-cuboctahedral [31], buckled biplanar [26] and biplanar hexagonal close-packed structures [33] as well as their Jahn–Teller distorted structures (that is, the icosahedron mode includes five structures, $i-I_h$ and its distorted structures $i-D_{5d}$, $i-D_{3d}$, $i-D_{2h}$ and $i-C_{5v}$). Of these modes, we find that the icosahedron is more stable than the others. This is consistent with the results of previous studies [8,10]. The optimization of the $i-D_{2h}$ structure, without any symmetry constraint, yielded the lowest-energy structure of Y_{13} , an icosahedron with C_1 symmetry, which is a little different from the $i-I_h$ in Refs. [7,8,11,12] and $i-C_{5v}$ icosahedrons in Ref. [10]. The total bonding energy of the lowest-energy icosahedron is higher by 0.010–0.406 eV than the other icosahedrons (I_h , $i-C_{5v}$, $i-D_{5d}$). In addition, the total spin magnetic moment of the lowest-energy icosahedron $13 \mu_B$ is closer to the experimental value $8.8 \pm 0.1 \mu_B$ [7] than is the second isomer $i-I_h$ with $19 \mu_B$.

To seek out the ground states of C-doped yttrium clusters, a broader search was made based on the above work on Y_{n+1} ($n = 1-14$) clusters. For small clusters with $n < 6$, the lowest-energy structures of CY_n could be obtained by directly replacing surface atoms of the lowest-energy Y_{n+1} clusters, which is the same pattern as seen with the doped atom in Al-, Mn-, and Si-doped yttrium clusters [11–13]. Only through careful comparative

Table 1
Calculated bond lengths (r) (Å), E_b (eV), vibrational frequencies (ω) (cm^{-1}), and the VIPs (eV) for Y_2 and C_2 in the ground states.

	Y_2			C_2		
	Our work	Theo.	Expt.	Our work	Theo.	Expt.
r	2.952	3.030 [6], 2.956 [8]	–	1.318	1.325 [22], 1.315 [23]	1.31 [24]
E_b	1.940	2.560 [6]	–	6.905	6.20 [22], 6.32 [23]	6.08 [24]
ω	174.0	185.5 [8]	184.4 [9]	1693.7	1703 [25]	1828 [24]
VIP	5.034	–	4.96 [4]	11.909	–	–

Download English Version:

<https://daneshyari.com/en/article/5392865>

Download Persian Version:

<https://daneshyari.com/article/5392865>

[Daneshyari.com](https://daneshyari.com)