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Structural, electronic and magnetic properties of Co_nRh ($n=1$–8) clusters from density functional calculations

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ABSTRACT

The geometries, stabilities, electronic and magnetic properties of Co_nRh ($n=1$–8) clusters have been investigated systematically within the framework of the generalized gradient approximation density-functional theory. The results indicate that the most stable structures of Co_nRh ($n=1$–8) clusters are all similar to those of corresponding Co_{n+1} clusters. Maximum peaks of second-order energy difference are found at $n=2$, 4 and 7, indicating that these clusters possess relatively higher stability than their respective neighbors. The magnetism of the ground state of alloy clusters all displays ferromagnetic coupling except for Co_3Rh. In addition, the doped Rh atom exhibits an important influence on the magnetism of alloy clusters, e.g., compared with corresponding pure Co_n clusters, the local moment of Co atom is noticeably enhanced in Co_nRh alloy clusters at $n=1$, 2, 5, 6, 7 and 8, while reduced at $n=3$ and 4. Further analysis based on the average bond length, the charge transfer and the spin polarization has been made to clarify the different magnetic responses to Rh doping.

1. Introduction

During the past two decades, much attention has been paid to transition metal (TM) clusters due to its fundamental importance in basic science and promising applications of new functional materials and devices [1–3]. In particular, small TM clusters are shown to display rich structural, electronic, optical and magnetic properties that differ quite from the individual atoms, molecules or bulk matter [4–27]. These properties can be tailored by doping or mixing the clusters with other species, and as a result, adjusting the species of doping element as well as the size of alloy clusters, aiming at their exotic physical and chemical properties has become one of the most active research subjects in the field of cluster physics [28].

Among the numerous research works, the bimetallic Co/M ($M=$Mn, V, Rh, Fe, Ru, Pd and Nb) clusters are the most promising species in the filed of magnetic materials [29–44]. Experimentally, based on Stern–Gerlach (SG) molecular beam deflection experiment, Hihara et al. [29] performed magnetic deflection studies of Co_nBi_m clusters and found that segregated structures consisting of ferromagnetic Co_n "core" were surrounded by Bi atoms. Recently, Yin et al. [28] firstly measured the magnetic moment of Co_nMn_m, and Co_nV_m ($n \leq 60$, $m \leq n/3$) and found significant magnetic moment enhancement with doped Mn and reduction with doped V. Knickelbein [30] studied the magnetic properties of medium-sized Co_nMn_m ($n+m=11$–29) and observed that the magnetic moments of Co_mMn_n clusters are generally similar to those of Co_n clusters containing the same total number of atom, and higher in some cases (e.g, $n+m=11$–14). Notably, Zitoun et al. [39] synthesized CoRh nanoparticles using the classical chemical method, and observed that the CoRh nanoparticles exhibited an enhanced magnetism in experiment, up to twice the value of the bulk alloy. So far, the available experiment data on magnetism are also only limited above for the cobalt-based alloy clusters. Theoretically, inspired by these experiment results, much attention has been focused on the CoMn and CoV alloy clusters aiming at the Co cluster doped Mn and V with tunable magnetic properties [31–35]. More recently, using density functional theory, Xie et al. [36] studied the geometries, electronic structures and magnetism of small Bi_mCo_n clusters and found that the magnetic moments of its derives mainly from the Co atoms. In the light of the CoRh alloy clusters, Dennler et al. [40] confirmed that the introduction of Co in Rh_n ($n<4$) gave rise to a significant increase of magnetic moment. Sondón and Guevara [41] suggested that the 55-atom CoRh clusters showed enhanced magnetic moments in the whole range of constant magnetic concentration. Berlanga-Ramírez et al. [42] studied the structural and magnetic properties of Co_nRh_m clusters ($N=n+m=110$, and $n \approx m$) and indicated that Rh atoms close to Co displayed a noticeable spin polarization induced by the magnetic moment of the surrounding Co atoms. Aguilera-Granja et al. studied the structural and magnetic properties of the binary clusters of $X_{12}Y$ (X, Y$=$Fe, Co, Ni, Ru, Rh, Pd and Pt) and indicated that the $Co_{12}Rh$ still retain bilayer hcp (hexagonal closest packing) structure of the Co_{13} cluster, moreover, an appropriate doping of TM clusters by impurity

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atoms is crucial to increase their binding energies and/or to enhance their magnetic performance [43]. In our previous study, we also found that the local moment of Co atom exhibited a prominent enhancement in $(\mathrm{CoRh})_n$ ($n \le 5$) with respect to the corresponding pure Co clusters [44].

It is well-known that the CoRh cluster is a kind of important 3d-4d TM alloy clusters with much high saturation magnetization and is suggested to be the good candidate for highly stable magnetic clusters [39]. All the aforementioned investigations provide good insights to the novel magnetic phenomenon of CoRh nanoparticles, however, it is still far from completely understanding the magnetism behavior of $\mathrm{Co}_n\mathrm{Rh}_m$ clusters due to their complex geometrical arrangements, electronic structure and magnetic ordering of alloy system. In this paper, we propose to perform a systematical study on the structures, electronic and magnetic properties of $\mathrm{Co}_n\mathrm{Rh}$ ($n=1$–8) clusters based on the density function theory. Our main objective is to identify the optimal doping site of the Rh atom to Co_n clusters and their magnetism coupling nature, and thus to explore how the doped Rh atom impacts upon the magnetic behavior of Co_n clusters.

2. Computational details

All calculations were performed at the DFT level with the DMol^3 package in the Materials Studio of Accelrys Inc [45]. The exchange–correlation interaction was treated within the GGA using PW91 function (GGA-PW91) [46]. The double numerical basis set augmented with *d*-polarization functions (DND) was utilized. For the numerical integration, a Fine quality mesh size was used, and the real space cutoff of the atomic orbital was set at 5.5 Å. The convergence criteria for structure optimization and energy calculations were set to Fine with the tolerance for density convergence in SCF, energy, gradient and displacement 1×10^{-6} e/Å^3, 1.0×10^{-5} a.u., 0.002 Hartree/Å and 0.005 Å, respectively. In the optimization of all structures and the calculation of energy and magnetism, a 5.0×10^{-4} Hartree of smearing was applied to the orbital occupation. In the geometry optimization procedure, we considered a number of initial structures including linear chains, planar and three-dimensional structures in this work to maximize our chance to find the ground state configurations of the alloy clusters. First, we identify the low-lying structures of pure Co_n clusters based on earlier theoretical works on cobalt and other TM clusters, and choose these low-lying structures as various reasonable initial structures. Second, based on these initial structures, we try to substitute the Co atom with the Rh atom in different positions of Co_{n+1} cluster as well as to place the Rh atom on each possible site of Co_n cluster, and some structures making reference to $\mathrm{Co}_n\mathrm{Mn}$, $\mathrm{Co}_n\mathrm{V}$, $\mathrm{Sc}_n\mathrm{Al}$ and $\mathrm{Fe}_n\mathrm{Mn}$ clusters are also tested [32,33,47,48]. In this way, we have considered more than 200 candidates altogether. Moreover, without any symmetry constrains, we relax the geometric structure to find out the true ground state. Third, for each geometry structure, the magnetic moment is firstly allowed to optimize automatically to the favored state (S_z) in DMol^3, then, we consider the neighboring spin state ($S_z \pm 2$) or more range spin and optimize them by fixing spin state. The calculations are implemented until the minimum energy is reached. In the end, we implement frequency analysis on the obtained possible low-lying isomers to make sure that they are indeed stable structures. In addition, the net charge and the magnetic moments were evaluated via the Mulliken population analysis.

To check the validity of the computational method in our work, we first perform the calculation on the Co_2 and Rh_2 dimers. As listed in Table 1, For Co_2, the bond length of 2.125 Å we obtained is very close to the experimental 2.310 Å [9], and previous theoretical data of 2.123 Å [8] and 2.130 Å [17]. Meanwhile, the binding energy per atom (2.77 eV), average magnetic moment (2 μ_B), vibration frequency (344.5 cm^{-1}) and the ionization potential (6.98 eV) are also in good agreement with the previous theoretical and experimental values of 2.74 eV [8], 2 μ_B [8–11,17], 280 ± 20 cm^{-1} [13] and 6.26 ± 0.16 eV [14], respectively. Similarly, for Rh_2 our calculated bond length (2.340 Å) and magnetic moment (2 μ_B) are also entirely consistent with the previous theoretical values (2.340 Å, 2 μ_B,) [20]. The vibration frequency (272.8 cm^{-1}) and bond length (2.340 Å) are all in good agreement with the experimental values (267 cm^{-1}, 2.280 Å) [22], and the ionization potential (7.29 eV) also well accords with the previous theoretical calculation (7.86 eV) [23]. All these results validate that our approach provides an efficient way to study small $\mathrm{Co}_n\mathrm{Rh}$ ($n=1$–8) clusters.

3. Results and discussion

3.1. Structure of the $\mathrm{Co}_n\mathrm{Rh}$ ($n=1$–8) clusters

Using the computation scheme described in Section 2, we have explored a number of low-lying isomers and determined the lowest-energy structures for $\mathrm{Co}_n\mathrm{Rh}$ ($n=1$–8) clusters. The obtained ground-state structures and some low-lying energy isomers are shown in Figs. 1 and 2.

The bond length of the CoRh is 2.163 Å, which lies between that of Co_2 (2.123 Å) and Rh_2 (2.340 Å). In the case of the $\mathrm{Co}_2\mathrm{Rh}$ cluster, the lowest-energy structure is an isosceles triangle (C_{2v}) with the Rh atom located at the apex, in which the Co–Co distance (2.311 Å) is 0.2 Å longer than that of the Co_2 dimer. This structure has a total magnetic moment of 5 μ_B. Its metastable state (5 μ_B) and the third stable state (7 μ_B) share the same geometric structure with the ground state and are 0.146 eV and 0.370 eV less stable, respectively.

As cluster size increases, the three-dimensional (3D) structures prevail and become the ground states of $\mathrm{Co}_n\mathrm{Rh}$ ($n=3$–8) clusters, completely similar to pure Co clusters. Our results show that the ground state of Co_4 is a distorted tetrahedron structure (C_{2v}) with 10 μ_B of total magnetism, in good agreement with the theoretical results of Datta et al. [11]. The replacement one Co with Rh leads to a more distorted tetrahedron of $\mathrm{Co}_3\mathrm{Rh}$ (C_s) and

Table 1
Calculated bond length, binding energy per atom, averaged magnetic moment, vibrational frequencies and ionization potential; the experimental results and previous theoretical studies.

	Co_2			Rh_2		
	Our work	Theoretical	Experimental	Our work	Theoretical	Experimental
Bond length (Å)	2.125	2.123 [8] 2.130 [17]	2.310 [9]	2.340	2.340 [20] 2.331Å [21]	2.280 [22]
E_b (eV/atom)	2.77	2.74 [8]	1.72 [9]	2.03	2.04 [24]	1.46 ± 0.11[22]
μ (μ_B/atom)	2	2 [8,10,11,17]	2 [9]	2	2 [20,21,24]	2 [22]
ω (cm^{-1})	344.5	342 [12]	280 ± 20 [13]	272.8	282 [21]	267 [22]
IP (eV)	6.98	7.48 [12]	6.26 ± 0.16 [14]	7.29	7.86 [23]	