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Structural transition and magnetic properties of Co_mPt_n $(m+n=38)$ clusters

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Abstract

The ground state structures of Co_mPt_n $(m+n=38)$ clusters are obtained by a genetic algorithm with a Gupta-like many-body potential, and further optimized using the density functional theory. The structure of pure atomic clusters Co_{38} and Pt_{38} is truncated octahedron. For the clusters with $n=1$, 2 and 34–37, their structures are slightly distorted configuration of Co_{38} and Pt_{38}. The structures of all the other bimetallic clusters are defective pattern based on icosahedrons. Segregation effect can be seen in the ground structures of bimetallic clusters. The Pt atom prefers to locate on the surfaces of these clusters. The cluster with $n=3$, 5, 23, 29, 33, they are relatively more stable than their neighbors. The magnetic moment of Co_{38} is in agreement with experiment. The nonzero moment of Pt_{38} cluster is found. Compared with Co_{38}, the introduction of Pt atom dramatically reduces the total magnetic moments of Co_mPt_n clusters.

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Keywords: Bimetallic clusters; Structural transition; Magnetic properties

1. Introduction

One of the goals on the area of clusters is to understand the physical properties and structural evolve from an atom to molecule, to cluster, and to a bulk phase. Pure and mixed transition-metal clusters are very important in many fields such as the catalysis, surface sciences, as well as electromagnetic applications. They have received much theoretical and experimental interest and been widely studied in the past two decades [1]. They show the distinction of complexity in both geometrical structure and magnetism. Magnetism of clusters is closely related to their size and interatomic separation. The experimental results show that the monoatomic ferromagnetic clusters, such as Ni, Fe and Co, have the larger average magnetic moment per atom than the bulk value [2,3]. So far many studies have been conducted on homogeneous metallic clusters, but not on mixed or alloy clusters, particularly for transition-metal bimetallic clusters because of the complexity of their electronic structure [4–6]. There are some novel properties as a function of cluster size and concentration for bimetallic clusters. In the Letter, we should report the studies of the structures and the magnetic properties of mixed Co_mPt_n $(m+n=38)$ clusters.

2. Calculations

The primary lowest energy structures of Co_mPt_n clusters are obtained by a genetic algorithm (GA) with a Gupta-like many-body potential [7]. The GA procedure has been successfully applied to clusters in our previous work [8–13]. In the GA scheme, a number of random initial configurations are generated in the beginning. Then two candidates in the population can be chosen as parents to generate a child cluster by mating operation. The obtained child cluster is further locally relaxed by molecular dynamics (MD) quenching. The relaxed child can be selected to replace its parent, if it has lower binding energy but its configuration is different from any one in the population.

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The magnetism of clusters is very sensitive to their structures. Based on the results of GA method, we further optimize the lowest energy structures using the Dmol3 package based on density functional theory (DFT) [14]. To reduce the computational cost, local density approximation (LDA) is adopted in the Dmol3 electronic structure calculations. DFT Semi-core Pseudopots (DSPP) type core electrons treatment and double numerical basis including d-polarization function (DND) are chosen. The local function is PWC (Perdew and Wang, 1992) [15]. Self-consistent field calculations are done with a convergence criterion of 2×10^{-3} a.u. on the total energy and electron density. We use convergence criterion of 0.004 Hartree/Å on the force and 0.005 Å on the displacement, and 2×10^{-5} Hartree on the total energy in the geometry optimization. All calculations are spin unrestricted. We perform calculations for all allowable spin multiplicities, starting with a spin-singlet configuration for the even-electron system and spin-doublet configuration for the odd-electron system. The ground state structures are obtained from the minimum in the total energy and preferred spin multiplicity. The atomic charge and the magnetic properties of the clusters are obtained via a Mulliken-type population analysis [16].

3. Results and discussions

To verify our calculation, we compare our results of Co_{13} and Pt_{13} with other works. The calculated structures of Co_{13} and Pt_{13} are all icosahedral pattern. The configuration of Co_{13} is the same as that of Refs. [17–19]. The binding energies per atom E_b (4.89 eV) and the bond length L_b (2.42 Å) are slightly larger than that of Ref. [17] (4.08 eV and 2.33 Å). The L_b is fine in agreement with that of Refs. [18,19] (2.44 Å) and the first-principles calculations [20] (2.44 Å). The structure of Pt_{13} is the same as that of Refs. [21,22]. The calculated L_b (2.79 Å) of Pt_{13} is very similar with that of Refs. [21,23] (2.6 Å and 2.65 Å). The E_b (4.38 eV) is also agreement with that of [21] (4.43 eV). For Co_{13}, the average magnetic moment (2.38 μ_B/atom) of it is fine in agreement with that of Refs. [18,19] (2.36 μ_B/atom) and the related references therein; all are much larger than the bulk values (1.72 μ_B/atom). To further assess the validity of our choice, we calculate the bulk properties. The results are shown in Table 1 and compared with the measurement. The calculation is in agreement with experiment except it overestimates the cohesive energy. From the above comparisons, the overall agreement of our results with other calculations is reasonable in a rather wide cluster size range.

The calculated structures of Co_mPt_n are shown in Fig. 1. An obvious structural transition can be seen. The structure of pure atomic clusters Co_{38} and Pt_{38} is truncated octahedral, and have symmetry of O_h configuration. These results are in agreement with that of Ref. [19] (Co_{38}) and Refs. [22,26] (Pt_{38}), respectively. Six atoms are in the inner of the two clusters, and the other 32 ones are on the surfaces. For the clusters with $n = 1, 2$ and 34–37, their structures are slightly distorted configuration of Co_{38} and Pt_{38}, respectively. The structures of all the other bimetallic clusters are defective pattern based on icosahedrons witch consist of 39 atoms. There are seven atoms in the inner shell. For clusters with $n = 3, 4, 25, 31$, they are cap-cutted icosahedral, while the rest are icosahedron minus an atom in the layer. It is also necessary to note that the Pt atoms prefer to locate on the surfaces for bimetallic clusters. This segregation effect can be seen in the ground structures of many bimetallic clusters [9,22,27–32]. This segregation effects may due to the difference of the surface energy and the cohesive energy between Co and Pt. To minimize the total energy, the atom with the smaller surface energy and cohesive energy favors to occupy the surface. Another possible reason is the atomic size effect: smaller atoms prefer to occupy inner sites to enhance the stability of the cluster. The average cohesive energy, surface energy of the bulk Pt is 5.84 eV/atom and 2.48 J/m^2 and the bond length of Pt is 2.77 Å, while corresponding parameters of the Co are 4.39 eV/atom, 2.55 J/m^2 and 2.50 Å, respectively. The competition of these factors determines the favorable structure of the clusters. So the structural transition is related to these factors. When the concentrations of one element are small, the effect of it can be neglected; the other element will dominate the structural properties of the cluster. Hence, we can alter the composition ratios to attain some new structures. The second differences in binding energies can be calculated as

$$\Delta_2 E = E(Co_{m-1}Pt_{n+1}) + E(Co_{m+1}Pt_{n-1}) - 2E(Co_mPt_n),$$

where $E(Co_mPt_n)$ represents the total binding energy for cluster with n Pt atom. In Fig. 2 we plot the relative stability, $\Delta_2 E$, of each cluster of n Pt atoms with respect to its adjacent cluster with $n-1$ and $n+1$ Pt atoms. Notice that clusters with $n = 3, 5, 23, 29, 33$, they are relatively high stability. In general, clusters with odd n are relatively more stable than the even ones. For all clusters, the HOMO-LUMO gaps (E_g) are not more than 0.12 eV, indicating these clusters are chemical active.

The calculated magnetic properties of Co_mPt_n are shown in Fig. 3. The average magnetic moment (1.89 μ_B/atom) of Co_{38} is in agreement with measurement [2] and [19] (2.0 μ_B/atom).

Table 1
The calculated results of the bulk properties and compared with the measurement. Here a and b are Ref. [24] and Ref. [25], respectively

	Cohesive energy (eV/atom)	Surface energy (J/m^2)	Bond length (Å)	Magnetic moment (μ_B/atom)	
Co	6.07	3.11	2.51	1.66	calculation
	4.39^a	2.55^b	2.50^a	1.72	experiment
Pt	6.78	2.07	2.77	0	calculation
	5.84^a	2.48^b	2.77^a	0	experiment