Magnetism of Free and Embedded Rhodium Clusters

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Magnetism of Free and Embedded Rhodium Clusters*

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The electronic structures of rhodium clusters with sizes of 6, 9, 13, 19, and 43 are studied by the first-principles spin-polarized calculations within the local density functional formalism. The bondlengths of all clusters are optimized by minimizing the binding energies. The magnetic moments of the clusters are presented and compared with the experiments. The electronic structure of Rh_{43} cluster has almost the similar features of rhodium bulk. Results for the Rh clusters embedded in the nickel matrix are also presented.
KEYWORDS: magnetism, rhodoum, cluster, LDA

1. Introduction

Rhodium has specially interesting magnetic properties. It is nonmagnetic in the bulk state. However, the rhodium monolayers on an iron substrate have a measured magnetic moment of 0.82 μ_B per atom[1]. The rhodium clusters are also found to have magnetic order with finite magnetic moments both theoretically and experimentally[2, 3].

Reddy, Khanna and Dunlap[2] recently calculated the magnetic moments for ruthernium, rhodium, and palladium 13-atom clusters with icosahedral and cubo-octahedral symmetry. They predicted moments of 1.62 μ_B per atom for icosahedral Rh_{13}, 1.02 μ_B per atom for icosahedral Ru_{13}, and 0.12μ_B for icosahedral Pd_{13}. Indeed, Cox *et al.*[3] observed experimentally giant magnetic moments in small Rh_n clusters with n=12–34. However, their observed value of the average magnetic moment per atom for Rh_{13} is 0.48μ_B, only about one-third of the theoretical prediction of Reddy *et al.*. They also found that the average moment per atom of the Rh clusters depends significantly on the cluster size. There are several sizes, Rh_{15}, Rh_{16}, and Rh_{19} which have magnetic moments per atom that are significantly larger than those of adjacent cluster sizes. The average moment of the rhodium cluster decreases to the bulk value of zero as the cluster size increases. Yang *et al.*[4] have also performed first principles studies on Rh_n (n=2-19) clusters, and they did not observe the magnetic transition from magnetic state to nonmagnetic state as the cluster size increases, due to small number of atoms in their studies.

The magnetism of the Rh overlayer on the transition metal is induced by the $d-d$ hybridization between the overlayer and the substrate. For most technological applications, the properties of embedded clusters (e.g. clusters in a matrix) are more relevant than the free clusters. Therefore, it is of considerable importance to extend our knowledge on free clusters to the cases where these clusters are embedded in a enviroment. Comparison between the behavior of the free and embedded clusters would also contribute significantly to the understanding of the specific properties of these materials.

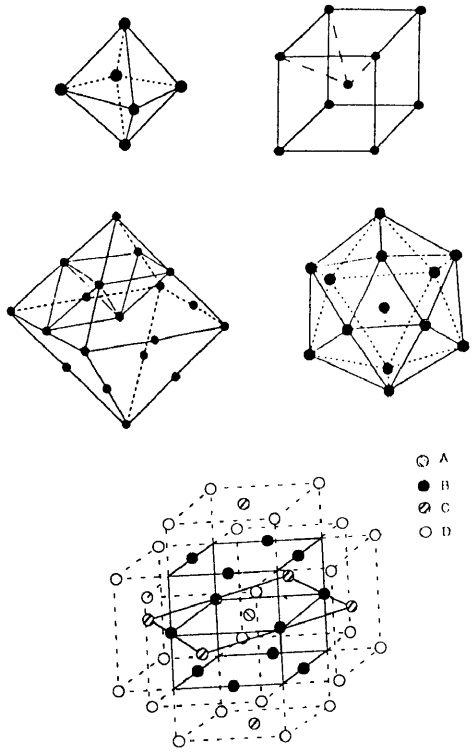

Figure 1: Structures of rhodium clusters

In this paper, we report an extensive first-principles study on Rh_n clusters with n=6, 9, 13, 19, 43 within the local spin density (LSD) approximation[5]. The bondlengths of all free clusters have been optimized by minimizing the binding energies, and the electronic structures are discussed. Studies on the Rh clusters in the nickel matrix are also presented. Prelinimary results has been published elsewhere[8]

2. Method

Since the exact structures of Rh_n clusters are not available experimentally, we assume the structure models for them in Fig.1. Rh_6 is octahedron, Rh_9 is cube, Rh_{13} is icosahedron, Rh_{19} is cubo-octahedron, Rh_{43}

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Table 1: Binding energies E_b, interatomic bondlengths R and magnetic moments of Rh_n clusters

n	6	9	13	19	43	bulk	Expt. for bulk
Symmetry	O_h	O_h	I_h	O_h	O_h	fcc	
E_b(eV)	3.32	3.33	3.45	3.85	4.36	6.11	5.75
R (Å)	2.63	2.64	2.66	2.65	2.65	2.69	2.69
Moment (μ_B/atom)							
Present	0.0	0.556	0.692	0.427	0.016		
Expt.		0.8± 0.2	0.48± 0.13	0.61± 0.08	0.16 ±0.13		

consists of another shell of atoms surrounding Rh_{19} cluster. Different shells in the cluster are labelled by A–D. For the mixed clusters, we use the corresponding bulk interatomic distances for Rh-Rh and Ni-Ni, and the average value for the Rh-Ni.

The electronic structures of the clusters are calculated with the first principles discrete variational method (DVM)[7]. The same method has already been employed in several other studies on metal clusters[9, 10], and described in detail elsewhere[12]. In short, the numerical atomic orbitals are used in the construction of molecular orbitals. In the present work, atomic orbital configurations composed of $4d^8$, $5s^1$ for Rh atoms and $3d^7$, $4s^{1.99}$, $4p^{0.01}$ for Ni atoms are employed to generate the valence orbitals. The secular equation **(H-ES)C=0** is then solved self-consistently using the matrix elements obtained via three-dimensional numerical integrations on a grid of random points by the diophantine method. About 900 sampling points around each site are employed. These points were found to be sufficient for convergence of the electronic spectrum within 0.01eV[9]. Self-consistent-charge (SCC) scheme[11] and von Barth-Hedin[6] exchange-correlation function are used in the calculations.

3. Results and Discussion

We discuss our results in three different steps. First, we optimize the bondlengths for all clusters by minimizing the binding energies. Second, the electronic configurations and the magnetic moments of each cluster calculated at the optimized bondlength are presented. This is followed by the discussion on the density of states (DOS) and the results for the embedded clusters. We optimize the bondlength of Rh_n (n=6,9,13,19,43) clusters while maintaining the specific symmetry of these clusters. The results are tabulated in Table 1. Comparing to the bulk interatomic spacing of 2.69Å, it is clear that the bondlengths for all rhodium clusters are a little shorter. The optimized interatomic spacing for fcc Rh_{43} is 2.65 Å which is still smaller than that of the bulk, see Table 1. The binding energy increases gradually as the cluster size increases (except for Rh_9 cluster; cubic structure may not be good for this cluster since its binding energy is lower than that of Rh_6 cluster). However, the binding energy of Rh_{43} is also smaller than the bulk cohesive energy of 5.75 eV, because there are 24 surface atoms which are more weakly bonded than the atoms in the bulk. It should be pointed out that the binding energy calculated by the DVM depends on the variational basis set. Yang *et al.*[4] got higher binding energy for the Rh_{13} cluster since they included $5p$ atomic orbitals in the basis set. The binding energy for Rh_{13} cluster, in the present study, agrees well with that of Reddy *et al.*[2]. We have also calculated the Rh_{13} cluster in fcc structure, and found that it is energetically unfavorable to the icosahedral structure. The cohesive energy and lattice spacing of fcc rhodium bulk have been calculated by Moruzzi *et al.*[13] by using the LDA method, and they obtained the cohesive energy of 6.11 eV, larger than the experimental value, which is ascribed to the overestimate of cohesive energy in LDA schemes. The lattice constant, however, is calculated accurately.

Next we discuss the magnetic moments of the clusters, which are obtained by taking the difference between the spin-up and spin-down Mulliken populations and by counting the unpaired spins below the Fermi level. Table 2 presents the magnetic moments of Rh_n clusters at each inequivalent site calculated at the optimized interatomic distances. The calculated magnetic moments per atom are compared with the experimental results in Table 1. It is noted from the table that Rh_6 cluster is nonmagnetic while Rh_9, Rh_{13} and Rh_{19} clusters exhibit finite magnetic moments $5\mu_B$, $9\mu_B$ and $8\mu_B$ per cluster, respectively, and Rh_{43} converges to the nonmagnetic state of the bulk. Reddy *et al.*[2] have reported the calculated magnetic moment for Rh_{13} of 1.62 μ_B which is almost three times larger than the experimental value of $0.48\mu_B$. The reason for this is that their solution for the Rh_{13} cluster is not the realistic ground state.

It is well known that the Kohn-Sham equations in the local density functional(LDF) scheme have a unique solution for a given system [4]. In the LSD scheme, however, solving the equations can yield more than one solutions. Those solutions correspond to local minima of the cluster energy as a function of the cluster spin. One should be cautious about the solutions of the LSD calculations and make sure that the solution is the true ground state of the system concerned. In the present study, we used different input potential for one system and determine the ground state which has the lowest

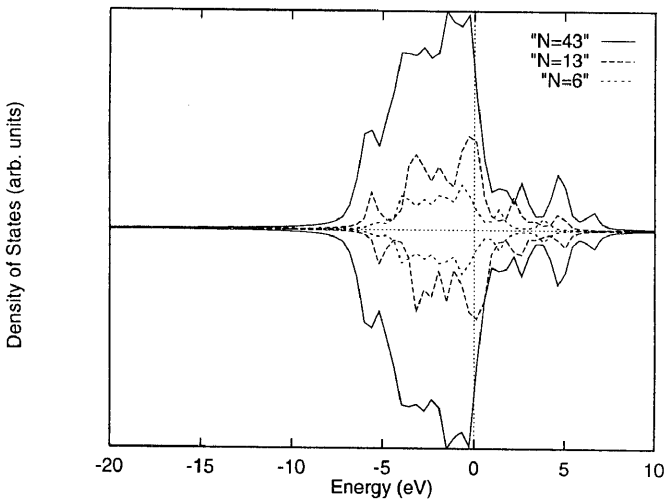

Figure 2: Total density of states of Rh_6, Rh_{13} and Rh_{43} clusters

binding energy of the system. Cox *et al.*[3] have measured the deflections of Rh_n clusters with n=12–100 in a gradient field, and deduced the cluster's internal magnetic moment per atom from their experimental moments per atom by assuming a superparamagnetic cluster model. They found that the moments vary substantially with the cluster size, which is different from that of other transition metal clusters[14]. From Table 1, we can see that the theoretical results are in good agreement with the experiments.

It is interesting to compare the magnetic properties of 4*d* rhodium clusters to the 3*d* element clusters. For iron and nickel clusters[12, 9], the calculated average moment is larger than the bulk value and the central atom in the cluster has smaller magnetic moment while the surface atoms have larger ones due to the reduced coordination numbers. However, for rhodium clusters, the situation is not so uniform. For example, in Rh_{19} cluster, see Table 2, the magnetic moments of the central atom, the nearest neighbors, and the next nearest neighbors are $0.059\mu_B$, $0.588\mu_B$ and $0.165\mu_B$, respectively. The central atom in the cluster has more bulk-like smaller moment.

Table 2: Magnetic moments of Rh_n and Rh_nNi_{43-n} clusters at different site A–D.

cluster	A	B	C	D
Rh_6	0.000			
Rh_9	-0.073	0.634		
Rh_{13}	1.595	0.634		
Rh_{19}	0.059	0.588	0.165	
Rh_{43}	0.001	0.130	0.037	0.006
Ni_{43}	0.668	0.743	0.898	1.114
$RhNi_{42}$	0.352	0.741	0.890	1.099
$Rh_{13}Ni_{30}$	0.495	0.523	0.987	1.111
$Rh_{19}Ni_{24}$	0.248	0.368	0.208	1.236

Figure 2 shows the total density of states (DOS) for

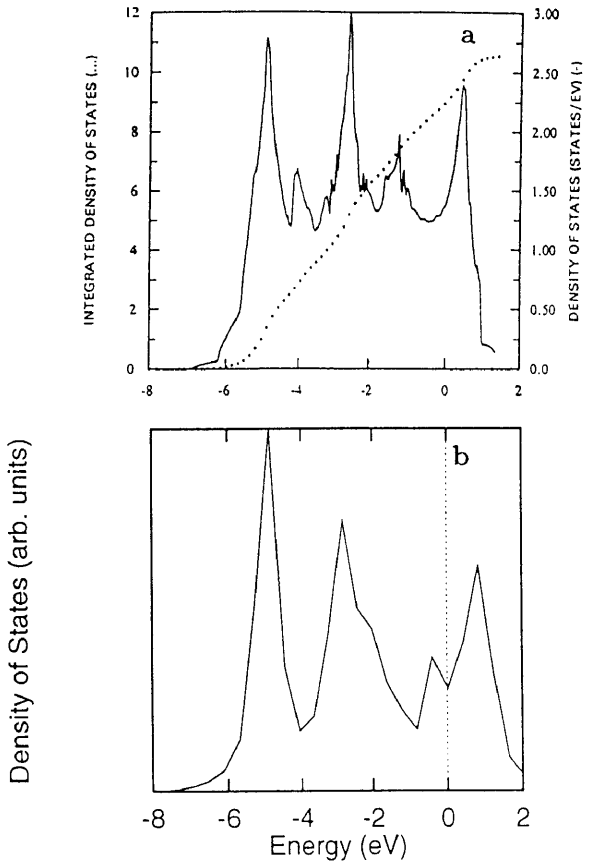

Figure 3: (a) Local density of states of the central atom in Rh_{43} cluster; (b) Density of states of rhodium bulk. From Ref.[13]

the majority- and minority-spin electrons in the Rh_n (n=6, 13, 43) clusters. The DOS are obtained by a Lorentzian expansion of the discrete energy levels and a summation over them. The broadening width parameter is chosen to be 0.4eV. It is noted that the Fermi energy lies near the top of valence band. The majority- and minority-spin DOS's for Rh_6 and Rh_{43} clusters are identical, indicating that these clusters are nonmagnetic. However, the DOS of Rh_{13} cluster shows a little exchange splitting which gives rise nine unpaired spins. The valence band width(VBW) increases as the cluster size increases, and the VBW of Rh_{43} cluster is close to that of the bulk which was obtained by band-structure calculations. The total DOS of Rh_{43} has less structures compared with that of the bulk[13] because the DOS of Rh_{43} cluster has much contributions of the surface atoms which have less neighboring atoms, and then the overlaps of the molecular wavefunctions are not sufficient. In order to know if the electronic properties of Rh_{43} cluster converges to the bulk, we present the local DOS of the central atom of Rh_{43} and the DOS of bulk in Figs.3(a) and 3(b), respectively. It is obvious that the local DOS has almost the same features as that of the bulk. This is due to the fact that the central atom in the Rh_{43} cluster has the complete coordinations as that of the bulk atom. This is similar to the calculations on iron and nickel clusters[9] as well as slab calculations[15] where the central layer of a five-layer film has bulklike properties. The VBW of the

local DOS of Rh_{43} is wider than that of the bulk, since the optimized lattice spacing of Rh_{43} cluster is a little smaller than that used in the calculation of the bulk, see Table 1.

To characterize the effect of matrix on the magnetic moments of Rh clusters, we study the electronic properties of Rh_nNi_{43-n}clusters. We select nickel as the matrix because it has the same fcc crystal structure and it is a $3d$ ferromagnetic element. The results are shown in Table 2. For the cluster model Ni_{43}, we find the moment of the central atom is 0.668 which is the same as that of the nickel bulk, and the moment at the B shell is $0.743\mu_B$ which is also close to the bulk value. Therefore, the local enviroment of A and B sites of Ni_{43} cluster can represent the nickel bulk. Cluster $RhNi_{42}$ could be considered as a model of dilute Rh atom in the Ni crystal. It has been reported that dilute Rh atoms in the Fe matrix have magnetic moment of $0.60\mu_B$[16]. For the dilute Rh in Ni, we find it also has $0.352\mu_B$. From Table 2, it is noted that the magnetic moment of Rh atom in the $Rh_{13}Ni_{30}$ and $Rh_{19}Ni_{24}$ clusters are smaller than that of free Rh clusters, respectively. We have mentioned above, however, that the Rh_{43} cluster is nonmagnetic. This means that if we replace the C or D shells in this cluster with Ni atoms, the Rh atoms in the A and B sites are ferromagnetic.

Cluster Rh_9Ni_{34}, which has 9 Rh atoms in the horizonal plane, is used as a model of sandwich structure with one layer of Rh between Ni. In this case, the magnetic moment of the central atom in the cluster is $0.423\mu_B$.

4. Conclusions

The electronic structures of Rh_n (n=6, 9, 13, 19, 43) clusters have been studied by the first-principles spin-polarized calculations. In summary, we find:

(a) The ground state of Rh_6 is nonferromagnetic, while Rh_9, Rh_{13}, and Rh_{43} clusters have nonzero magnetic moments. The Rh_{43} cluster is nonmagnetic as the rhodium bulk.

(b) We obtain better magnetic moments for Rh_{13} cluster than the previous calculations compared with experiments.

(c) The calculated binding energies increase as the cluster size increases. However, the binding energy of Rh_{43} cluster is still smaller than the cohesive energy of the rhodium bulk. The local density of states of the central atom in the Rh_{43} cluster has similar features as the DOS of bulk.

(d) Single Rh atom and small Rh clusters embedded in the Ni matrix still maintain magnetic moments with reduced values compared with the free clusters. Sandwich structure of one Rh layer between Ni are also ferromagnetic.

Acknowledgments

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