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Magnetic properties of icosahedral MRu_{12} clusters

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Abstract. The magnetic properties of icosahedral MRu_{12} clusters are studied using the discrete-variational local-spin-density-functional method, where M = V, Cr, Mn, Fe, Co, and Ni. The results show that all of the I_h MRu_{12} clusters, just like the case for the I_h Ru_{13} cluster, have double magnetic solutions. In contrast to the moment of 4 μ_B for the I_h Ru_{13} cluster, the total magnetic moments of the I_h MRu_{12} clusters, ranging from 1 μ_B to 20 μ_B, have been changed greatly by the substitution of the central Ru atom with M. Among them, the $NiRu_{12}$ cluster has a giant moment of 20 μ_B. Furthermore, the $NiRu_{12}$ cluster has nondegenerate ground state and could be expected to be remarkably stable. Therefore, for the purpose of enhancing the magnetic moment of the I_h Ru_{13} cluster, Ni is a promising candidate as a dopant. Finally, we predict that all the I_h MRu_{12} clusters except $NiRu_{12}$ might belong to the class in which the magnetization of the cluster increases with temperature.

1. Introduction

Magnetic properties of transition-metal (TM) clusters have become a fascinating subject of widespread investigations in recent years due to their perspective of practical applications in developing new magnetic materials with large moments [1]. Because of the reduced dimensionality and coordination number as well as enhanced symmetry in clusters, it is expected that magnetization might be found in small clusters of appropriate bulk nonmagnetic materials, probably in those of the nonmagnetic TMs [2, 3]. This expectation has come true since both the theoretical and experimental studies have shown that small rhodium [3–5] clusters are ferromagnetic though bulk rhodium is not. This surprising success is naturally stimulating further widespread research on the other small 4d clusters.

For ruthenium clusters, Reddy *et al* [4] first predicted theoretically that the I_h Ru_{13} cluster should be magnetic with a moment of 12 μ_B, or 0.92 μ_B per atom. This prediction is, unfortunately, not demonstrated experimentally by Cox *et al* [3]. They found that the Ru_{13} cluster might be nonmagnetic within their experimental uncertainty. In order to find out why such an obvious difference occurs between the theory and the experiment, we [6] studied the electronic structure of a 13-atom Ru cluster under three high symmetries (I_h, O_h, and D_{3h}) in an earlier paper. The results showed that there are two self-consistent

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magnetic solutions for the I_h Ru_{13} cluster, which we called a low-spin solution and a high-spin solution, and that Reddy's prediction is only a metastable state that corresponds to our high-spin solution. The ground state of the cluster we found is the low-spin solution possessing a magnetic moment of 4 μ_B, or 0.31 μ_B per atom, which is in good agreement with the upper limit of the experimental measurement, 0.29 μ_B per atom. The contradiction between previous theory and experiment is thus attributed to the existence of the multiple magnetic solutions in the I_h Ru_{13} cluster. Moreover, our calculation results [6] indicated that the icosahedron is not a stable geometry of the Ru_{13} cluster since it has a degenerate ground state. An interesting question is then asked: can we stabilize the icosahedral geometry of Ru_{13} via replacing the centre Ru atom with an appropriate impurity and meanwhile energetically upturn the sequence of the high- and low-spin states that exist in Ru_{13} so that the stabilized cluster has an enhanced magnetic moment?

To answer this question, in this paper, we performed a comprehensive first-principles study on I_h MRu_{12} clusters, where M = V, Cr, Mn, Fe, Co, and Ni. Considering that the alloying atoms M we considered all have smaller atomic radius than Ru, we placed M at the centre of the icosahedron. Such a choice has been made in the previous studies on the I_h MAl_{12} [7, 8], I_h MFe_{12} [9], and I_h MCo_{12} [10] clusters. In what follows, we shall first describe our computational method in section 2 and then present our results and discussion in section 3. Finally, a summary of our results is given in section 4.

2. Computational method

The discrete-variational local-spin-density-functional (DV-LSD) method is used in this study. For the details of this method, one is referred to [11, 12]. Recently, excellent results for the binding energies of molecules, clusters, and solids [13–15] have been obtained by using the nonlocal-density approximation (NLDA), but no improvement on the magnetic moment [15, 16] has been made. Therefore we do not consider the NLDA corrections here. To solve the Kohn–Sham equations, we used the self-consistent multipolar (SCM) scheme [17] and a spin-dependent exchange and correlation potential of the von Barth–Hedin form [18] with parameters taken from Moruzzi *et al* [19]. The atomic basis functions to represent the valence electron orbitals are 3d–4p for M and 4d–5p for Ru, and the rest of the orbitals are treated as a frozen core. With 600 sampling points per atom in the numerical integrations, sufficient convergence for both the electronic spectrum and the binding energy is achieved.

As is well known, in the density-functional formulation, the exchange–correlation potential in the Kohn–Sham equations is only a function of the charge density of the system. The solution to the Kohn–Sham equations is then obtained by optimizing the charge distribution of the system, which will lead to just one self-consistent solution to the system. In the LSD scheme, however, the exchange–correlation potential is spin dependent, and is determined not only by the charge distribution but also by the spin polarization of the system. Therefore, the Kohn–Sham equations should be solved by simultaneously optimizing the charge and spin distributions of the system, and this can yield more than one solution. These solutions correspond to the local minima of the total energy as a function of the magnetic moment of the system, among which the one that gives the lowest total energy is regarded as the ground state of the system and the rest with higher energies are only metastable states. In other words, different choices of the input potential in the LSD calculations may lead to different self-consistent solutions. In this paper, we have examined the possible multiple solutions for each cluster.

3. Results and discussion

We first calculated the total binding energy for each MRu_{12} cluster at several internuclear configurations and, by maximizing the total binding energy, determined the equilibrium bond length $r_{M\text{–}Ru}$. The multiple magnetic solutions were explored in all calculations. Table 1 lists the bond length and the multiple magnetic moments of each MRu_{12} cluster at its equilibrium configuration. Similar to what we obtained in Ru_{13}, all MRu_{12} clusters are found to have double self-consistent magnetic solutions. The binding energy of the low-spin solution is 0.75, 0.66, 0.37, 0.17, and 0.66 eV higher than that of the high-spin solution for VRu_{12}, $CrRu_{12}$, $MnRu_{12}$, $FeRu_{12}$, and $CoRu_{12}$ respectively, but 0.25 eV lower for $NiRu_{12}$. Therefore, the ground state of all the MRu_{12} clusters except $NiRu_{12}$ still corresponds to the low-spin solution as is the case for Ru_{13}, and the magnetic moments of these clusters are not changed much as compared to that of Ru_{13}. For the $NiRu_{12}$ cluster, however, the high-spin solution turns out to be the ground state, which leads to a dramatically enhanced moment of 20 μ_B, or 1.54 μ_B per atom. This moment is five times the moment of the I_h Ru_{13} cluster and even 1.5 times larger than the moment of the I_h Ni_{13} cluster (8 μ_B, or 0.61 μ_B per atom) whose bulk phase is well known to be ferromagnetic. The dramatic variation of the magnetic moment in I_h MRu_{12} clusters, up to 400%, is quite different from the cases for I_h MFe_{12} [9] and MCo_{12} [10] clusters, where, by substituting the central Fe atom with Ti, Mn, Ni, Zn and the central Co atom with Ti, V, Cr, Mn, Fe, Ni, the magnetic moment changes from 38 to 40 μ_B and from 22 to 31 μ_B as compared with that of 34 μ_B for I_h Fe_{13} and 31 μ_B for I_h Co_{13} clusters. The alterations are no more than 20% and 30%, respectively. For the comparision with other clusters based on other metals than Ru, we also explored the posibility of multiple magnetic solutions of I_h MCo_{12} clusters ($M = V$, Cr, Mn, Fe, Co, and Ni). Unfortunately, we found there is only one magnetic solution for each MCo_{12}. The existence of double magnetic solutions in MRu_{12} clusters may be due to the fact that the sequence of magnetic states is particularly rich for the 4d elememt clusters [20].

Table 1. The bond lengths and the multiple magnetic moments of all MRu_{12} clusters at their equilibrium configurations (the value in parentheses corresponds to the moment of the metastable state).

Cluster	$r_{M\text{–}Ru}$ (au)	$r_M + r_{Ru}$ (au)	Total moment (μ_B)
VRu_{12}	4.76	4.98	1
			(9)
$CrRu_{12}$	4.75	4.87	2
			(10)
$MnRu_{12}$	4.74	5.07	3
			(11)
$FeRu_{12}$	4.74	4.85	4
			(12)
$CoRu_{12}$	4.74	4.87	5
			(27)
$NiRu_{12}$	4.74	4.86	20
			(6)

Table 2 lists the local magnetic moments of the ground states of all MRu_{12} clusters. The ferromagnetic interactions are found in the $CoRu_{12}$ and $NiRu_{12}$ clusters since the moments of the central atoms align parallel to those of the surface atoms, while the interactions

Table 2. Spin populations for icosahedral MRu$_{12}$ clusters.

	Centre atom		Surface atom		
Cluster	Orbital	Net spin	Orbital	Net spin	Total moment
VRu$_{12}$	3d	−0.04	4d	0.09	1
	4s	0.00	5s	0.00	
	4p	0.01	5p	0.00	
	total	−0.03	total	0.09	
CrRu$_{12}$	3d	−0.11	4d	0.18	2
	4s	−0.01	5s	0.00	
	4p	0.02	5p	0.00	
	total	−0.10	total	0.18	
MnRu$_{12}$	3d	−0.15	4d	0.16	3
	4s	−0.01	5s	0.08	
	4p	0.11	5p	0.02	
	total	−0.05	total	0.26	
FeRu$_{12}$	3d	−0.27	4d	0.25	4
	4s	−0.01	5s	0.08	
	4p	0.11	5p	0.02	
	total	−0.17	total	0.35	
CoRu$_{12}$	3d	1.63	4d	0.28	5
	4s	0.04	5s	-0.01	
	4p	0.01	5p	0.01	
	total	1.68	total	0.28	
NiRu$_{12}$	3d	1.10	4d	1.44	20
	4s	−0.02	5s	0.06	
	4p	0.12	5p	0.06	
	total	1.20	total	1.56	

in the other clusters are antiferromagnetic. It is well known that for TM impurities in bulk Fe or Co the impurity polarization varies with its d-band occupation number [21, 22]. Impurities with the same or higher occupation number than that of the host generally polarize ferromagnetically with the host, while impurities with occupation number less than that of the host generally polarize antiferromagnetically with the host. This rule seems to hold also true for the MRu$_{12}$ clusters from our results.

Table 3. The ground-state electronic configurations for icosahedral MRu$_{12}$ clusters.

	HOMO		
Cluster	Symbol	Electrons	Electronic configuration
VRu$_{12}$	$\mathrm{h}_u \uparrow$	1	open
CrRu$_{12}$	$\mathrm{h}_u \uparrow$	2	open
MnRu$_{12}$	$\mathrm{t}_{1u} \uparrow$	3	closed
FeRu$_{12}$	$\mathrm{h}_u \uparrow$	1	open
CoRu$_{12}$	$\mathrm{h}_g \uparrow$	5	closed
NiRu$_{12}$	$\mathrm{g}_g \downarrow$	4	closed

Table 3 lists the ground-state electronic configurations for the MRu$_{12}$ clusters. From table 3, we can see that the MnRu$_{12}$, CoRu$_{12}$, and NiRu$_{12}$ clusters have nondegenerate ground states because their HOMOs (the highest occupied molecular orbitals) are fully occupied. So they are expected to be remarkably stable. This means that the substitution of the central Ru of the I_h Ru_{13} cluster with suitable M (here Mn, Co, and Ni) can indeed stabilize the icosahedral geometry of the I_h Ru_{13} cluster. On the other hand, the rest of the clusters have degenerate ground state and, according to the Jahn–Teller theorem, their ground-state geometric configuration should be not an ideal icosahedron but a distorted one.

It should be emphasized that when the central Ru of the I_h Ru_{13} cluster is replaced by Ni, it can not only enhance the magnetic moment of the cluster enormously, but also stabilize the icosahedral geometry of the cluster. Therefore, Ni is a promising candidate as a dopant for the purpose of enhancing the magnetic moment of the I_h Ru_{13} cluster.

Finally, we would like to discuss the temperature dependence of the magnetization of the clusters. Stern–Gerlach experiments on small TM clusters have shown that in certain clusters the magnetization increases with temperature [23]. Recently, Reuse *et al* [24] explored this abnormal temperature dependence of magnetization for the Ni_{13} cluster theoretically. By performing the LSD calculations with various possible spin configurations, they found that there exist many states whose energies lie close to the ground state of $S = 4$. Among them, the states with higher spins ($S = 5$–8) are only 0.22–0.6 eV higher than the ground state, while the states with lower spins ($S = 0$–3) are 0.68–1.74 eV higher than the ground state in energy. Based on these results, they attributed the increase of the magnetization with temperature to the ordering of the various spin configurations they found in the Ni_{13} cluster. We think the multiple magnetic solutions of clusters could provide an alternative insight into this problem. As mentioned above, all MRu_{12} clusters are found to have double self-consistent magnetic solutions, and the low-spin solution is the ground state for all the clusters except $NiRu_{12}$. It is clear that if the clusters of the kind with their ground state of low spin were heated, some of them would occupy the state of high spin and undergo an increase in the total intrinsic moment. This would lead to an increase of the cluster magnetization, which is determined by the overall cluster moment, if the occupation of the high-spin state overrides the decrease in magnetization due to increase in temperature. Since the energy span between the high- and low-spin states of the VRu_{12}, $CrRu_{12}$, $MnRu_{12}$, $FeRu_{12}$, and $CoRu_{12}$ clusters is only 0.17–0.75 eV, the abnormal temperature dependence we predicted here would be observable for all of them, with $FeRu_{12}$ being the most promising candidate. In contrast, $NiRu_{12}$ would undergo a decrease of the cluster magnetization both due to the partial occupation of the low-spin state and due to the thermal disorder of the cluster intrinsic moment with increasing temperature. Hence we predict that all the MRu_{12} clusters except $NiRu_{12}$ might belong to the class in which cluster magnetization would increase with temperature.

4. Summary

In summary, we have reported a comprehensive study on the magnetic properties of the I_h MRu_{12} clusters. Our results show that all the I_h MRu_{12} clusters still have double magnetic solutions as the I_h Ru_{13} cluster has. The total magnetic moment of the cluster can be changed greatly by the substitution of the central Ru atom with M. Among them, the $NiRu_{12}$ cluster has the largest moment of 20 μ_B. The $MnRu_{12}$, $CoRu_{12}$, and $NiRu_{12}$ clusters have nondegenerate ground states and are expected to be remarkably stable. Therefore the substitution of the central Ru atom with an Mn, Co, or Ni atom could stabilize the icosahedral geometry of the I_h Ru_{13} cluster. On the other hand, the rest of the clusters have open electronic shells and are expected to undergo a Jahn–Teller distortion further. Since the ground state is the low-spin solution for all I_h MRu_{12} clusters but $NiRu_{12}$, and the energy span between the high- and the low-spin states of these clusters is only 0.17–

0.75 eV, we predict that they might belong to the class in which the magnetization of the cluster increases with temperature. We hope that our calculated results will stimulate further experiments to study the M–Ru alloy clusters.

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