

Magnetic properties of M_{13} clusters ($M=Y, Zr, Nb, Mo, \text{ and } Tc$)

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The magnetic properties of 13-atom M clusters ($M=Y, Zr, Nb, Mo, \text{ and } Tc$) with three possible high-symmetry geometries have been studied using the discrete-variational local-spin-density-functional method. While the ground states of most transition-metal 13-atom clusters correspond to the icosahedral structure, we found that the cuboctahedral structure is more energetically stable than the icosahedral one for Mo_{13} and Tc_{13} clusters. The ground states of all the clusters are shown to be magnetic, but their magnetic moments are not striking. [S0163-1829(96)04041-6]

In recent years, the $4d$ transition-metal (TM) clusters have been paid dramatic attention because of their promising applications in developing new magnetic materials.¹⁻⁸ Both theoretical and experimental studies²⁻⁶ have shown that small Rh clusters have giant magnetic moments though bulk rhodium has not. Theory² and experiment³ also agree in assigning very small magnetic moments to Pd clusters. For Ru clusters, while Reddy *et al.*² predicted that theoretically the icosahedral (I_h) Ru_{13} cluster has a magnetic moment of $12 \mu_B$ or $0.92 \mu_B$ per atom, the experiment measurement of Cox *et al.*³ gave nonmagnetic results in the limits of experimental resolution for Ru_{10-115} clusters. Such a discrepancy could arise because of the possibility of solutions with different multiplicities being close in energy which make the identification of ground state difficult.⁹

In contrast to Ru, Rh, and Pd clusters, there are few studies of the other $4d$ TM clusters. Goodwin and Salahub¹ studied the stable geometries and ground-state multiplicities of the small Nb_N ($N=2-7$) clusters. Zhao *et al.*,⁷ by means of a tight-binding Friedel model of d -band and Stoner criteria, investigated the magnetic-nonmagnetic transition in $4d$ TM clusters and predicted that the transition critical size is small for Zr, Nb, Mo, and Tc clusters, but is as large as 93 for Y clusters.

In this paper, we extend our previous work^{4,8} on 13-atom Ru and Rh clusters to study the other $4d$ M_{13} clusters, in the hope of exploring the magnetic properties of these clusters, where $M=Y, Zr, Nb, Mo, \text{ and } Tc$. Since the actual geometry cannot be fully optimized for such a large and heavy TM cluster at the present stage, we choose, as many researchers and we did before,^{2,4,9} three possible high-symmetry structures for each M_{13} cluster. Though the high symmetry as-

sumed in calculations, which usually results in a high magnetic moment, may be different from that of the real cluster, this fact does not rule out its value. Current cluster sources can produce more than one isomer at particular masses. When significant isomerization occurs, it is also not necessary that the isomers be nearly degenerate in total energy; high and thick barriers to interconversion could allow the energies of stable isomers of a given cluster to differ greatly. On the other hand, if other internal forces in the cluster make its geometry depart slightly from the symmetric configuration, then enhanced magnetism can persist.

The three possible high symmetries we chose for M_{13} clusters are I_h , O_h , and D_{3h} , respectively. The I_h point group, being that of an icosahedron, is too highly symmetric for any crystal. The O_h structure is a cuboctahedron, which is a compact portion of the fcc crystal lattice. The D_{3h} structure is obtained from the O_h cluster by rotating any triad of nearest-neighbor surface atoms by 60° about their center. This third cluster is a compact portion of the hcp lattice.

The method we used is the discrete-variational local-spin-density-functional (DV-LSD) method. Since it has been described in detail elsewhere,^{10,11} we will not give a further description here. Suffice it here to say that in the formulation of Kohn-Sham equations we used a spin-dependent exchange and correlation potential of the von Barth-Hedin¹² form with parameters taken from Moruzzi *et al.*¹³ The atomic basis functions to represent the valence electron orbitals were $4d-5p$ for M , and the rest of the core orbitals were treated as frozen. Using 600 sample points per atom in the numerical integrations we achieved sufficient convergence for both the electronic spectrum and the binding energy. A self-consistent charge (SCC) model density was used to fit the electron den-

TABLE I. The equilibrium bond lengths, binding energies, and magnetic moments for all M_{13} clusters (r is the distance between the center and surface atoms).

Clusters	Symmetry	r (a.u.)	E_b (eV)	Moment (μ_B)
Y ₁₃	I_h	6.27	50.05	13
	I_h	6.27	49.77	9
	O_h	6.23	50.39	3
	D_{3h}	6.27	50.26	3
Zr ₁₃	I_h	5.52	76.58	4
	O_h	5.64	70.88	0
	D_{3h}	5.60	71.64	0
Nb ₁₃	I_h	5.16	75.48	7
	O_h	5.25	73.28	1
	D_{3h}	5.22	72.36	7
	D_{3h}	5.22	72.42	3
Mo ₁₃	I_h	4.92	59.60	0
	O_h	4.98	62.05	2
	D_{3h}	4.96	60.86	2
Tc ₁₃	I_h	4.82	69.27	13
	O_h	4.87	72.05	1
	D_{3h}	4.87	70.72	5

sity. To accelerate the iteration convergence, a fractional occupation-number technique was adopted in present calculations. That means we allowed the electrons to occupy the cluster orbitals according to the nonzero-temperature Fermi distribution. The Fermi distribution parameter was chosen to be 1000/hartree corresponding to tens of kelvin degrees and therefore has little influence on the results. In addition, we explored the possible multiple magnetic solutions by performing spin-unrestricted calculations on the electronic structure for each cluster geometry, in which we repeated electronic-structure calculations by using different initial spin polarizations as the starting potential and allowing the system to develop its own magnetic moment as the iterative calculation converges to a self-consistent solution. For the cases that there are more than one self-consistent solution, we chose the one which gives the largest cluster binding energy as our final solution.

We first calculated the total binding energy for each M_{13} cluster at several internuclear configurations, and determine the equilibrium configuration by maximizing the total binding energy. The equilibrium bond length and binding energy of each M_{13} cluster are presented in Table I. As usual, all clusters have small bond length contractions as compared with their bulk interatomic spacings and the binding energy per atom for each kind of cluster is smaller than its bulk cohesive energy. These phenomena are attributed to the surface effect of cluster. The ground states of Zr₁₃ and Nb₁₃ clusters are found to correspond to the I_h cluster, which is more stable than the D_{3h} and O_h clusters. For Mo₁₃ and Tc₁₃ clusters, however, the O_h structure is the most stable among the three structures we considered. It is at odds with a general argument that 13-atom TM clusters tend to have I_h symmetry (or with slight distortion) in their ground state because the directional bonding is not too important in the clusters and only in this geometry do all surface atoms have the maximum number of nearest-neighbor atoms possible. In

fact, the ground states of all Co₁₃, Ni₁₃, Ru₁₃, Rh₁₃, and Pd₁₃ clusters have been shown to correspond to an icosahedron rather than a cuboctahedron. Since the energy differences between the O_h structure and I_h (or D_{3h}) structure for those clusters are large enough, we can expect that the above results will not be changed qualitatively by using the gradient correction to the LSD, which is known for its importance in determining the phase diagram of some bulk materials.^{14–16}

The binding energies for the three structures of Y₁₃ clusters are almost the same. The differences among them are less than 0.03 eV/atom, which is close to the accuracy of our method; therefore, it is difficult to make a definite conclusion that which structure is the most stable one. Below, we simply follow the numerical values we obtained, and regard the O_h structure as its ground state.

With the equilibrium bond lengths obtained above, the magnetic properties of M_{13} clusters have been calculated. First, we discuss the possible multiple magnetic solutions in M_{13} clusters.

As is well known, in the local-density-functional (LDF) formulation, the exchange-correlation potential in the Kohn-Sham equations is a function of the charge density of the system only. The solution to the Kohn-Sham equations is then obtained by optimizing the charge distribution of the system only, which will lead to just one self-consistent solution to the system. In the LSD scheme, however, the exchange-correlation potential is spin dependent, which is determined by not only the charge distribution but also 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. As a matter of fact, there are indeed multiple magnetic solutions existing in TM clusters. Furthermore, many researches^{4,8,17,18} have demonstrated that it is helpful to explore the possibility of multiple magnetic solutions of a cluster especially when an apparent contradiction appears between theoretical predictions and experimental measurements for the magnetism of the cluster. It also seems to be necessary that a theoretical study of the magnetic properties of TM clusters should include a check on whether the multiple magnetic solutions exist in the considered clusters when the LSD scheme is employed. We have checked the possible magnetic solutions for all the M_{13} clusters, and the results are given in Table I. This result is quite different from the situations in Rh₁₃, Ru₁₃, and Co₁₃ clusters,^{4,8,18} where the icosahedron is the geometry of the ground states and all clusters have more than one self-consistent magnetic solution at their equilibrium configurations.

Table II lists the total magnetic moments of the ground states of all M_{13} clusters, which are obtained by counting the unpaired spins below the Fermi level. From the table, one may see that all the clusters are magnetic. Among them, the O_h Tc₁₃ cluster has the smallest magnetic moment, which is

TABLE II. Mulliken orbital and spin populations of the ground states for M_{13} clusters.

Cluster	Symmetry	Orbital	Charge		Local moment		Total moment
			Center atom	Surface atom	Center atom	Surface atom	
Y ₁₃	O_h	4d	2.43	1.90	-0.05	0.18	3
		5s	0.48	0.76	-0.01	0.03	
		5p	0.64	0.29	0.16	0.03	
		total	3.55	2.95	0.10	0.24	
Zr ₁₃	I_h	4d	3.71	3.14	-0.08	0.27	4
		5s	0.24	0.53	-0.01	0.06	
		5p	1.05	0.25	-0.01	0.02	
		total	5.00	3.92	-0.10	0.35	
Nb ₁₃	I_h	4d	4.61	4.18	0.30	0.55	7
		5s	0.32	0.56	-0.01	0.01	
		5p	0.96	0.18	0.03	0.00	
		total	5.89	4.92	0.32	0.56	
Mo ₁₃	O_h	4d	5.58	5.26	0.01	0.15	2
		5s	0.35	0.47	0.00	0.00	
		5p	0.63	0.22	0.00	0.02	
		total	6.56	5.95	0.01	0.17	
Tc ₁₃	O_h	4d	6.45	6.22	-0.01	0.04	1
		5s	0.42	0.49	0.00	0.03	
		5p	0.61	0.25	0.00	0.01	
		total	7.48	6.96	-0.01	0.08	

$1\mu_B$. The $1\mu_B$ moment is just required by the fact that the cluster possesses an odd number of total electrons. This result is in good agreement with the prediction of Zhao *et al.* that the critical size of a magnetic-nonmagnetic transition for Tc clusters is small (about 7).

On the other hand, the magnetic moment of the I_h Nb₁₃ cluster is $7\mu_B$, which is almost as large as that of the I_h Ni₁₃ cluster¹⁹ and the experimental value of Rh₁₃ cluster.³ To see whether this is a general conclusion for small Nb clusters, we also have calculated the electronic structure of Nb₉ and Nb₁₅ clusters with body-centered-cubic symmetry. The magnetic moments of these clusters, together with those¹ of Nb_N ($N=2-7$), are listed in Table III. From this table, one can see that the magnetic properties of small Nb clusters are not striking as expected from the result of Nb₁₃ clusters. Although the small moments are for the Nb clusters, our results contradict the prediction of Zhao *et al.* that the magnetic-nonmagnetic transition of small Nb clusters should take place at size ≤ 5 .

For the Y₁₃ cluster, since we cannot determine its ground state, it is hard to get an unambiguous result for its magnetic moment. If the O_h or D_{3h} corresponds to the ground state, the cluster will have a $3\mu_B$ moment. If the I_h corresponds to the ground state, the cluster will possess a giant moment $13\mu_B$ (see Table I). If it is true, it may support the prediction of Zhao *et al.* that the critical size of magnetic-nonmagnetic

transition of an Y cluster is 93. To better understand the magnetic properties of small Y clusters, further theoretical and experimental studies would be useful.

The local magnetic moments of the ground states of all M_{13} clusters are shown in Table II. They are obtained by taking the difference between the spin-up and spin-down Mulliken populations. From Table II, it can be seen that the local moment of the central atom is smaller than that of surface atoms for all M_{13} clusters. This observation agrees well with the results for clusters of iron-group atoms. The magnetic interactions between the central and surface atoms are ferromagnetic for the Y₁₃, Nb₁₃, and Mo₁₃ clusters and antiferromagnetic for the Zr₁₃ and Tc₁₃ clusters.

Table II also lists the Mulliken populations for the ground states of all M_{13} clusters. It shows that the central M atoms have negative effective charges and the surface M atoms have positive charges in all clusters, which means that the central M atom obtains electrons from surface M atoms. This is a typical case for most of the clusters. In fact the lack of coordinative saturation for the exterior atoms of the cluster implies that some electrons, which in the bulk metal would be involved in bonding interactions with atoms that are absent in the cluster, are free to migrate to the central atom.

In conclusion, we have presented the magnetic properties of 13-atom M clusters with three possible high-symmetry geometries. The results show that (1) the Mo₁₃ and Tc₁₃ clusters with O_h symmetry are unusually more energetically stable than their counterpart with I_h symmetry, (2) the I_h Y₁₃ and D_{3h} Nb₁₃ clusters have two self-consistent magnetic solutions at their equilibrium configurations, (3) the ground states of all clusters are magnetic, while their magnetic moments are not striking, and (4) the binding energies for the

TABLE III. The total magnetic moments (μ_B) of the small niobium clusters.

Cluster	Nb ₂	Nb ₃	Nb ₄	Nb ₅	Nb ₆	Nb ₇	Nb ₉	Nb ₁₃	Nb ₁₅
Moment	2	1	0	1	2	1	3	7	1

three structures of Y_{13} clusters are almost the same, while their magnetic moments are quite different. To understand the magnetic properties of small Y clusters, further state-of-the-art theories and experiments are needed.

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