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First-principles study of the magnetic properties of 4d impurities in Cu_n clusters

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Abstract

The magnetic properties of small Cu_nTM clusters ($n = 3$–7, 12, TM = Ru, Rh, Pd) have been studied using a linear combination of the atomic orbital approach with the density functional formalism, and the Kohn–Sham equation is solved self-consistently using the discrete variational method (DVM). It is found that the magnetic moments of Rh in the D_{3h} structure and Ru in the T_d structure are quenched to zero (we call this phenomenon the symmetry-quenching effect). It is also found that Ru and Rh are magnetic (except for symmetry-quenching), and Pd is nearly nonmagnetic. The effects of symmetry, coordination number and atomic distance on the magnetic moments of 4d impurities are discussed.

1. Introduction

Magnetism in very small transition metal clusters is an only recently explored area of metal cluster physics. Investigation of the magnetic properties of clusters is important not only in itself but also in the magnetic recording industry. In clusters, the reduced coordination number and higher symmetry are expected to narrow the electronic bands, to enhance magnetization in ferromagnetic materials, and to cause magnetization in nonmagnetic materials. Both theoretical and experimental studies of small Fe, Co and Ni clusters have indicated that cluster atoms have larger average magnetic moments per atom than those in the bulk phase [1–5]. Theoretical calculations [6,7] also predicted nonzero magnetic moments for other 3d TM clusters (V_n, Cr_n), though their corresponding bulk phases have no moments. For 4d clusters, using the local-spin-density functional (LSD) theory, Reddy et al. [8] found that 13-atom clusters of Pd, Rh and Ru are magnetic. Cox et al. [9] observed experimentally giant magnetic moments in small Rh_n clusters with $n = 9$–34.

We know that Cu can form many useful dilute alloys with 3d transition-metal impurities. Blaha and Callaway [10] and Bagayoko et al. [11] have used the local-spin-density approximation with the cluster model ($Cu_{18}TM$, TM = Cr, Mn, Fe, Co, Ni) to study the magnetic properties and electronic structures of the corresponding dilute alloys, where the impurity atom is placed in the center of the cluster, and found that the magnetic moments for the impurity atoms

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Cr, Mn, Fe, Co and Ni are 3.53, 4.04, 3.05, 2.05 and 0.69 (in μ_b) respectively. Although there is no theoretical calculation for 4d impurities in bulk Cu, Willenborg et al. [12] have pointed out that no local 4d-moments in a Cu-matrix are expected, since the hybridization with the host electrons is much stronger due to the smaller lattice constant of Cu. However, in clusters, as mentioned above, the reduced coordination number and higher symmetry are expected to favour the magnetization. How is the situation for 4d impurities (Ru, Rh, Pd) in Cu_n clusters? No systematic studies on this subject have been reported to our knowledge. In this paper, we will study this interesting problem, with special attention to the roles of symmetry, coordination number and atomic distance on the 4d moments.

In recent years, Cu_n clusters have received a great deal of attention due to their special atomic structure ($3d^{10}4s^1$) with a single s electron outside a closed-shell electronic configuration. The Cu 3d states lie closely below the 4s states in energy, these d states can thus be expected to play a role in determining the properties of Cu clusters. The isotopic effect in the formation of Cu clusters was observed by one of the authors [13], and detailed experimental studies of the electronic properties of small Cu clusters have been performed [14,15]. Cluster-size effects on the electronic structures in clusters have also been investigated [16]. As far as the structures of small Cu_n clusters are concerned, the triangular form (D_{3h}) for Cu_3 and the tetragonal form (T_d) for Cu_4 clusters are found to be the most stable [17,18], and ab initio calculations [19] predicted the trigonal-bipyramidal structure (D_{3h}) for Cu_5 clusters as most stable, the square-bipyramid (O_h) for the Cu_6 cluster [18,20], the pentagon-bipyramid (D_{5h}) for the Cu_7 [18] and the icosahedron (I_h) for the Cu_{13} [21] clusters.

On the other hand, experiments on the chemisorption and catalytic properties of materials containing Cu and Ru or Rh led to the discovery of Ru–Cu and Rh–Cu clusters [22,23], and EXAFS experiments have been performed on Ru–Cu clusters [24] and Rh–Cu clusters [25]. It was found that Cu atoms were present on the surface of Ru and Rh, analogous to an adsorption layer. Montejano-Carrizales and Moran-Lopez have studied the segregations in Cu–Pd clusters and found that in clusters of $Cu_{19}Pd_{36}$ and $Cu_{27}Pd_{28}$ and $Cu_{36}Pd_{19}$ the outmost shell is occupied by Cu atoms [26]. Although Dunlap found that smaller atoms prefer to go inside an I_h 12-atom Fe shell [27] (in our cases, the radius of the Cu atom is smaller than those of Ru, Rh and Pd, but the differences are small), as a first step, it is reasonable for us to place one 4d impurity atom (Ru, Rh, Pd) in the center of a Cu_n cluster.

2. Theoretical method

Here we adopt the local-spin-density-functional approximation (LSDA). We take the spin-dependent exchange-correlation in the Barth–Hedin form [28]. Numerical atomic wave functions are used as the basis set for the expansion of wavefunctions. Group theory is used to symmetrize the basis functions, which transform as one of the irreducible representations of the point group of the cluster. We have used the 3d, 4s, 4p orbitals of Cu and the 4d, 5s and 5p orbitals of the impurity atom as the basis set, the cluster spin orbitals are expanded in a linear combination of the symmetrized basis functions. The Kohn–Sham equation is solved self-consistently using the discrete variational method (DVM) [28–30]. To obtain the electronic density of states (DOS) from the discrete energy level $\varepsilon_{i\sigma}$, the Lorentz expansion scheme is used. The total DOS is defined as

$$D(E) = \sum_{n,l,\sigma} D^{\sigma}_{nl}(E), \tag{1}$$

with

$$D^{\sigma}_{nl}(E) = \sum_{i} A^{\sigma}_{nl,i} \frac{\delta/\pi}{(E-\varepsilon_{i\sigma})^2 + \delta^2}, \tag{2}$$

where i labels the eigenfunction and σ labels spin, the broadening factor $\delta = 0.42$ eV is used. $A^{\sigma}_{nl,i}$ are the Mulliken population numbers, n and l are the orbital and angular quantum numbers respectively. The binding energy is determined by the difference of the total energy of the cluster and that of a reference system (i.e. the ensemble of isolated atoms).

3. Results and discussion

For all clusters considered, the atomic distances are optimized by maximizing the binding energy

Table 1
Structure, equilibrium Cu–TM distance r (Å) and average binding energy ε_b (eV); μ_{Cu} and μ_{TM} are the moments for the Cu and 4d impurity atoms, respectively

Structure and symmetry	Cluster	r	ε_b	μ_{Cu}	μ_{TM}
triangle (D_{3h})	Cu_3Ru	2.37	1.75	0.1901	1.4605
	Cu_3Rh	2.37	1.80	0.0	0.0
	Cu_3Pd	2.37	1.15	0.1077	0.0254
tetrahedron (T_d)	Cu_4Ru	2.33	2.05	0.0	0.0
	Cu_4Rh	2.36	1.93	0.149	0.3893
	Cu_4Pd	2.39	1.20	0.1176	0.0495
triangle-bipyramid (D_{3h})	Cu_5Ru	2.54	1.74	0.1005	0.9263
	Cu_5Rh	2.56	1.73	0.0	0.0
	Cu_5Pd	2.56	1.14	0.1041	0.0242
square-bipyramid (O_h)	Cu_6Ru	2.47	2.00	0.1552	2.8914
	Cu_6Rh	2.40	1.98	0.2524	1.4844
	Cu_6Pd	2.33	1.75	0.1170	0.0262
pentagon-bipyramid (D_{5h})	Cu-Ru	2.59	2.45	0.1570	2.4641
	Cu-Rh	2.61	2.31	0.1429	0.9903
	Cu-Pd	2.63	1.96	0.1065	0.0170
icosahedron (I_h)	$Cu_{12}Ru$	2.45	3.40	0.1245	0.4913
	$Cu_{12}Rh$	2.45	3.26	0.2176	0.3832
	$Cu_{12}Pd$	2.40	2.83	0.1007	−0.0198
cuboctahedron (O_h)	$Cu_{12}Ru$	2.48	3.38	0.1021	0.7688
	$Cu_{12}Rh$	2.50	3.23	0.1796	0.7784
	$Cu_{12}Pd$	2.55	2.80	0.0250	0.0559

with the symmetry constraints. Mulliken population analysis has been used to obtain the occupation number of atomic orbitals, the magnetic moments are the differences between the occupation numbers in the spin-up and spin-down states. The data for the average equilibrium TM–Cu distance r (Å), the binding energy per atom ε_b (eV), and the magnetic moments (μ_b) are listed in Table 1, from which we can obtain the following conclusions:

Regarding the TM–Cu distance, we know that the nearest-neighbor distances in elemental solids are 2.56, 2.65, 2.69 and 2.75 (Å) for crystalline Cu, Ru, Rh and Pd respectively [31]. In Cu_nTM clusters, the TM–Cu distance is shorter than the sum of the radius of the TM and Cu atoms, showing the contraction effect in the bond length.

The magnetic moments of Rh in Cu_3TM and in Cu_5TM are quenched to zero, in spite of the different

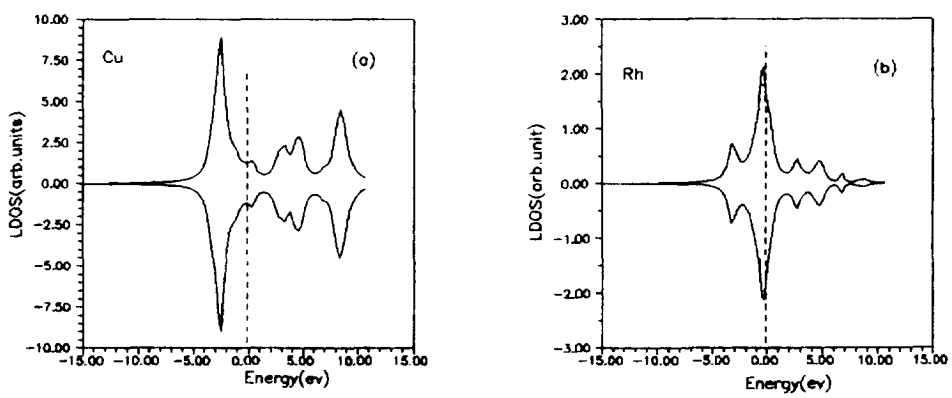

Fig. 1. Local densities of states (LDOS) for the host atom (a) and impurity atom (b) in the Cu_3Rh (D_{3h}) cluster.

coordination numbers of Rh and the different atomic distances in these two clusters, the same symmetry gives the same quenching for Rh. We called this phenomenon the symmetry-quenching effect. The moment of Ru in the tetrahedron (T_d) is also quenched to zero. For comparison, calculations have also been performed on a square structure (D_{4h}) with Ru in the center, and it is found that the moment for Ru is $2.813\mu_b$ in an equilibrium structure with bond length 2.3 Å. In these cases, symmetry dominates over the coordination number and atomic distance in determining the moment of 4d impurities. So we can see that the symmetry of the cluster has an important effect on the impurity moment. Figs. 1 and 2 show the local density of states (LDOS) of the host atoms and impurity atoms in the Cu_3Rh (D_{3h}) and Cu_4Ru (T_d) clusters respectively, in which the Fermi energy has been shifted to zero (as indicated by the vertical dashed lines). We see that there are no net magnetic moments for the host atom nor for the impurity atom, which is in agreement with the Mulliken population analyses. We also find that the orbital splittings of the central impurity Rh and Ru atoms in the crystal fields are different, similarly to the Cu_5Rh (D_{3h}) cluster. It was found by Reddy et al. [8] that in the $FePd_{12}$ cluster the introduction of Fe increases the moments at the outer Pd atoms due to the exchange enhancement. This kind of exchange enhancement in Pd can also be brought about by introducing a 4d atom (Ru, Rh). There for Cu_nTM clusters, Ru and Rh are magnetic (except for the symmetry-quenching), and the 4d impurities induce the host Cu atom to be polarized. However, Pd is nearly nonmagnetic. For the Cu_3TM and Cu_5TM clusters with the same symmetry (D_{3h}), except for Rh, the magnetic moment of the TM atom in Cu_5TM is smaller than that in Cu_3TM. This is caused by the increase in the overlap of the nearby atomic orbitals as the coordination number increases. Although the coordination number of the TM in Cu_6TM is larger than that in the Cu_5TM cluster, and the bond length in Cu_6TM is smaller than that in Cu_5TM, the moment of the TM is larger than that in Cu_5TM, which arises from the different symmetry. For comparison, we also calculated the moments for the cuboctahedron (O_h) of the $Cu_{12}TM$ cluster, for comparison with the Cu_6TM cluster. They have the same symmetry and the bond lengths are nearly the same, but due to the increase of coordination number in $Cu_{12}TM$, the moment of the TM is decreased.

The average degeneracy of an irreducible representation (IR) of the icosahedron (I_h) and cuboctahedron (O_h) point group is 3.2 and 2.0, the maximal degeneracy of the IR of these two groups is 5 and 3 respectively. Because of the higher symmetry of the I_h, it is found that the moments of Fe_{13} and Co_{13} with the I_h structure are larger than those of other 13-atom isomers [2,3]. However, in our cases, because the equilibrium bond length in the icosahedron is smaller than that in the cuboctahedron, the magnetic moment of the TM in the former structure is also smaller than that in the latter one. The decrease in the atomic distance causes an increase in the overlap of the atomic orbitals, resulting in a decrease

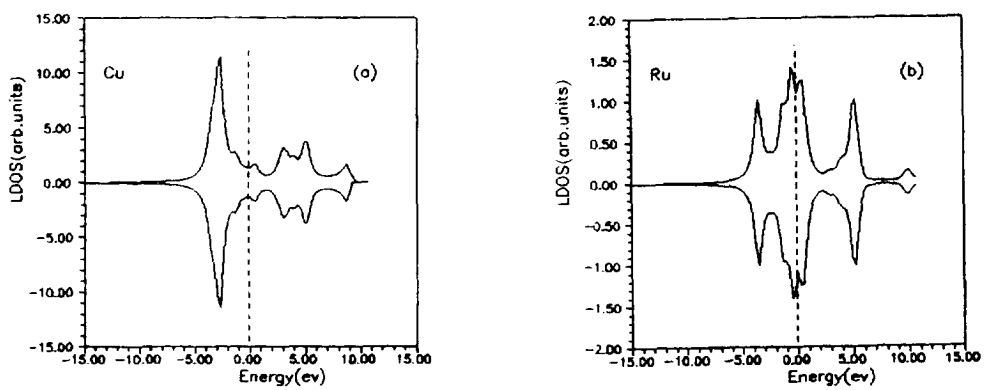

Fig. 2. Local densities of states (LDOS) for the host atom (a) and impurity atom (b) in the Cu_4Ru (T_d) cluster.

of the moment. Thus, the atomic distance dominates over the symmetry in determining the moment of 4d impurities.

According to the above discussions, we can see that the magnetic properties of a 4d impurity in Cu clusters are mainly affected by the symmetry, coordination number and atomic distance. Often these three factors combine to make the magnetic behaviour richer and more complicated.

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References

[1] X.G. Gong and Q.Q. Zheng, J. Phys. 7 (1995) 2421.
[2] B.I. Dunlap, Phys. Rev. A 41 (1990) 5691.
[3] Z.Q. Li and B.G. Gu, Phys. Rev. B. 47 (1993) 18611.
[4] G.M. Pastor, J. Dorantes-Davila and K.H. Benneman, Phys. Rev. B 40 (1989) 6742.
[5] W.A. de Heer, P. Milani and A. Chatelain, Phys. Rev. Lett. 65 (1990) 488.
[6] P. Alvarado, J. Dorantes-Davila and H. Dreysse, Phys. Rev. B 50 (1994) 1039.
[7] Keeyung Lee and J. Callaway, Phys. Rev. B 48 (1993) 15358.
[8] B.V. Reddy, S.N. Khanna and B.I. Dunlap, Phys. Rev. Lett. 70 (1993) 3323.
[9] A.J. Cox, J.G. Louderback and L.A. Bloomfield, Phys. Rev. Lett. 71 (1993) 923.
[10] P. Blaha and J. Callaway, Phys. Rev. B 33 (1986) 1706.
[11] D. Bagayoko, P. Blaha and J. Callaway, Phys. Rev. B 34 (1986) 3572.
[12] K. Willenborg, R. Zeller and P.H. Dederich, Europhys. Lett. 18 (1992) 263.
[13] G.H. Wang, Phys. Rev. B 37 (1988) 9093.
[14] D.G. Leopold, J. Ho and W.C. Lineberger, J. Chem. Phys. 86 (1987) 1715.
[15] C.L. Pettiette, S.H. Yang, M.J. Craycarft and J. Conceicav, J. Chem. Phys. 88 (1988) 3577.
[16] O. Cheshnovsky, K.J. Taylor, J. Conceica and R.E. Smalley, Phys. Rev. Lett. 64 (1990) 1785.
[17] J. Koutecky and P. Fantucci, Chem. Rev. 86 (1986) 539.
[18] S. Erkoc, Z. Phys. D 32 (1994) 257.
[19] C. Bachmann, J. Demuynck and J. Veihard, Faraday Symp. Chem. Soc. 14 (1980) 170.
[20] S.C. Richtsmeir, J.L. Gole and D.A. Dixon, Proc. Natl. Acad. Sci. USA. 77 (1980) 561.
[21] S. Vakelahti and M. Mannine, Phys. Rev. B 45 (1992) 4959.
[22] J.H. Sinfelt, Acc. Chem. Res. 20 (1987) 134.
[23] J.H. Sinfelt, J. Catal. 29 (1973) 308.
[24] J.H. Sinfelt, G.H. Via and F.W. Lytle, J. Chem. Phys. 72 (1980) 4832.
[25] W. Meitzner, G.H. Via, F.W. Lytle and J.H. Sinfelt, J. Chem. Phys. 78 (1983) 882.
[26] J.M. Montejano-Carrizales and J.L. Moran-Lopez, Surf. Sci. 239 (1990) 178.
[27] B.J. Dunlap, Z. Phys. D 19 (1992) 255.
[28] U.V. Barth and L. Hedin, J. Phys. C 5 (1972) 1629.
[29] D.E. Ellis and G.S. Paiter, Phys. Rev. B 2 (1970) 2887.
[30] E.J. Baerends, D.E. Ellis and P. Ros, Chem. Phys. 2 (1973) 41.
[31] A. Rosen, D.E. Ellis, H. Adachi and F.W. Averill, J. Chem. Phys. 65 (1976) 3629.
[32] C. Kittel, Introduction to solid state physics (Wiley, New York, 1976).