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THE MAGNETIC PROPERTIES OF $4d$ IMPURITIES IN Ag_n CLUSTERS

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The magnetic properties of small Ag_nTM clusters ($n = 3$–7, 12; TM = Ru, Rh, Pd) have been studied using a linear combination of atomic orbitals approach with the density functional formalism, and the Kohn–Sham equation is solved self-consistently with the discrete variational method (DVM). The symmetry-quenching effect is found that the magnetic moments of Rh in D_{3h} structure and Ru in T_d structure are quenched to zero. Meanwhile, it is 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 moment of $4d$ impurities are discussed.

1. INTRODUCTION

MAGNETISM is one of the most interesting and challenging problems in cluster physics as well as in material science. Although $3d$, $4d$ and $5d$ transition metals all have unfilled localized d states, it is only certain $3d$ metals which form magnetic solids, none of $4d$ or $5d$ solid are magnetic, as discussed by Janak [1] and Gunnarsson [2], the stoner condition for ferromagnetism can not be met by these metals. If they could be made magnetic, they might provide a new class of magnetic materials with enhanced magneto-crystalline anisotropy. Since the work of Hattox et al. [3], showing that Vanadium undergoes a transition from paramagnetic (P) to a ferromagnetic (F) configuration as the lattice parameter is increased, considerable attention has been devoted to transition metals which are paramagnetic in bulk phase. From these, V, Ru, Rh and Pd have been singled out as possible candidates for the onset of magnetism at the surface or as overlayer on noble-metal [4–7] or as free cluster [8–10]. Various theoretical calculations and experimental results have been reported. Wu and Freemann [11] have indicated that for Rh/Ag(0 0 1) the moment

for Rh is $0.69\,\mu_b$, and for the sandwiched structure Ag/Rh/Ag(0 0 1) the moment for Rh is $0.49\,\mu_b$. All calculations show that Pd monolayer on Ag(0 0 1) is non-magnetic [12–14], and a large moment of $1.7\,\mu_b$ for Ru monolayer on Ag(0 0 1) was found [15]. Recently, Willenborg et al. [16] calculated systematically the electronic structures and magnetic properties of $4d$ impurities in Ag by using local-spin density functional theory and KKR–Green function method, the calculations indicated that Ru and Rh and Pd impurities in bulk Ag are nonmagnetic, which are quite different from the behaviors of monolayer or overlayers. What is the situation for $4d$ impurities (Ru, Rh, Pd) in Ag_n clusters? No systematic studies on this subject have been reported to our knowledge. In this paper, we will study this interesting question by using the discrete-variational local-spin-density functional method. Although electronic structure calculations using the nonlocal density approximation (NLDA) have obtained excellent results for the binding energies of molecules and solids [17, 18], no improvement on magnetism of iron [19, 20], as compared with experiment, has been made. In this paper, we have not considered the NLDA correction, and the emphasis is placed at the effects of symmetry, coordination number and atomic distance on the magnetic properties of $4d$ impurities.

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2. THEORETICAL METHOD

In the density functional theory, the one-electron equation has the following form in atomic units,

$$\left(-\frac{1}{2}\nabla_i^2 + V_c + V_{xc}^{\sigma} - \epsilon_{i\sigma}\right)\Psi_{i\sigma} = 0, \tag{1}$$

where the one-electron Hamiltonian h_{σ} includes the kinetic energy, the electron–nucleus and electron–electron Coulomb potential V_c and spin-dependent exchange-correlation potential V_{xc}^{σ}. The last one is a function of electron density $\rho_{\sigma}(\mathbf{r})$ for spin σ, given by

$$\rho(\mathbf{r}) = \sum_i f_{i\sigma}|\Psi_{i\sigma}|^2, \tag{2}$$

where $f_{i\sigma}$ is the occupation of the cluster spin orbital $\Psi_{i\sigma}$, chosen according to Fermi–Dirac statistics. In this paper, we adopt local-spin-density-functional approximation (LSDA), and take V_{xc}^{σ} to be the Barth–Hedin form [21], in which the parameters are chosen to agree with those of Moruzzi et al. [22]. The numerical atomic wave function ϕ_j are used as the basis set for the expansion of wavefunctions. The group theory is used to symmetrize the basis functions

$$\Phi_j = \sum_i D_{ij}\phi_i, \tag{3}$$

where Φ_j is a symmetrized basis function which transforms as one of the irreducible representations of the point group of the cluster, D_{ij} is the so-called symmetry coefficient which is determined only by the symmetry of clusters. In this work we have used $4d$, $5s$ and $5p$ orbitals of host atom and impurity atom as the basis set ϕ_j. The cluster spin orbitals are expanded in a linear combination of Φ_j,

$$\Psi_{i\sigma} = \sum_j C_{ij}^{\sigma}\Phi_j. \tag{4}$$

The one-electron equation (1) is solved by the Rayleigh–Ritz variational method, which is done by using equation (3) and minimizing error function Δ_{ij}^{σ} defined as

$$\Delta_{ij}^{\sigma} = \langle\Psi_{i\sigma}|h_{\sigma} - \epsilon|\Psi_{j\sigma}\rangle. \tag{5}$$

This procedure leads to the secular matrix equation

$$(H^{\sigma} - \epsilon S^{\sigma})C^{\sigma} = 0. \tag{6}$$

The discrete variational method (DVM) [23] has been used to self-consistently solve this matrix equation, in which the Hamiltonian matrix H^{σ} and the overlap matrix S^{σ} are obtained by a weighted summation over a set of sample points $\mathbf{r}_k$ (diophantine points), i.e.

$$H_{ij}^{\sigma} = \sum_k \omega(\mathbf{r}_k)\Phi_i^*(\mathbf{r}_k)h_{\sigma}\Phi_j(\mathbf{r}_k), \tag{7}$$

$$S_{ij}^{\sigma} = \sum_k \omega(\mathbf{r}_k)\Phi_i^*(\mathbf{r}_k)\Phi_j(\mathbf{r}_k), \tag{8}$$

where $\omega(\mathbf{r}_k)$ is appropriate integration weights.

To get the electronic density of states (DOS) from the discrete energy level $\epsilon_{i\sigma}$, the Lorentz expansion scheme is used, the total DOS is defined as

$$D(E) = \sum_{n,l,\sigma} D_{nl}^{\sigma}(E) \tag{9}$$

with

$$D_{nl}^{\sigma}(E) = \sum_i A_{nl,i}^{\sigma} \frac{\delta/\pi}{(E - \epsilon_{i\sigma})^2 + \delta^2}, \tag{10}$$

where i labels the eigenfunction and a broadening factor $\delta = 0.42\,\text{eV}$ is used. $A_{nl,i}^{\sigma}$ are the Mulliken population numbers, n and l are orbital and angular quantum numbers respectively. The total energy is evaluated by

$$E_{tot} = \sum_{i\sigma} f_{i\sigma}\epsilon_{i\sigma} - \sum_{\sigma}\frac{1}{2}\int\int\frac{\rho_{\sigma}(\mathbf{r})\rho_{\sigma}(\mathbf{r}')\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}$$
$$+ \sum_{\sigma}\int\rho_{\sigma}(\mathbf{r})(\mu_{xc} - V_{xc}^{\sigma})\mathrm{d}\mathbf{r} + \frac{1}{2}\sum_{IJ}\frac{Z_IZ_J}{|\mathbf{R}_I - \mathbf{R}_J|}, \tag{11}$$

where Z_I is the proton number of atom I, μ_{xc} is a universal potential related to V_{xc}^{σ} by

$$\frac{\mathrm{d}}{\mathrm{d}\rho_{\sigma}}(\rho_{\sigma}\mu_{xc}) = V_{xc}^{\sigma}. \tag{12}$$

The binding energy is determined by the difference between the total energy of the cluster and that of a reference system selected to minimize the numerical errors,

$$E_b = E_{tot} - E_{ref}. \tag{13}$$

In our calculations, the number of the Diophantus sample points per atom is 1000, and the convergence accuracy of the self-consistent charge process is 10^{-4}e.

3. RESULTS AND DISCUSSIONS

Due to many useful applications in chemistry and in optical materials, much attention has been devoted to the study of small Ag clusters. As far as the stable structures for Ag clusters are concerned, triangular form (D_{3h}) is for Ag$_3$ cluster [24, 25], tetragonal form (T_d) is for Ag$_4$ cluster [24, 26], triangle-bipyramidal

Table 1. The structure, equilibrium bond length r between silver and silver (Å) and average binding energy ϵ_b (eV), μ_{Ag} and μ_{TM} are the moments for Ag and 4d impurity atoms respectively

Structure and symmetry	Cluster	r	ϵ_b	μ_{Ag}	μ_{TM}
Triangle (D_{3h})	Ag_3Ru	4.55	1.3250	−0.1688	2.4578
	Ag_3Rh	4.50	1.4400	0.0	0.0
	Ag_3Pd	4.55	0.9710	0.1303	0.0301
Tetrahedron (T_d)	Ag_4Ru	4.20	1.5975	0.0	0.0
	Ag_4Rh	4.20	1.5710	0.1402	0.4246
	Ag_4Pd	4.30	1.0125	0.1868	0.0427
Triangle–bipyramid (D_{3h})	Ag_5Ru	4.30	1.2515	−0.2095	1.292
	Ag_5Rh	4.20	1.4580	0.0	0.0
	Ag_5Pd	4.30	0.8670	0.1725	0.0241
Square–bipyramid (O_h)	Ag_6Ru	3.70	1.6348	0.1509	2.9215
	Ag_6Rh	3.70	1.6670	0.2599	1.3498
	Ag_6Pd	3.60	1.5100	0.1303	0.0575
Pentagon–bipyramid (D_{5h})	Ag_7Ru	4.25	0.8875	0.0526	2.8703
	Ag_7Rh	4.20	1.1080	0.0959	1.3161
	Ag_7Pd	4.40	0.7650	0.1375	0.0331
Cuboctahedron (O_h)	$Ag_{12}Ru$	3.90	2.7290	0.0923	0.8821
	$Ag_{12}Rh$	3.90	2.6356	0.1781	0.7864
	$Ag_{12}Pd$	3.90	2.3500	0.1007	0.0465

structure (D_3h) is for Ag_5 cluster [24, 25–27], square-bipyramidal form (O_h) is for Ag_6 cluster [24, 28], pentagon-bipyramid (D_{5h}) is for Ag_7 clusters [24]. The above structures are adopted in this paper, in which the 4d impurity atoms are placed in the centers, for comparison, calculations are also performed on cuboctahedron structure (O_h) for Ag_{13} cluster (the central Ag atom is replaced by an impurity atom). For all the clusters considered, the atomic distances are optimized by maximizing the binding energy with the symmetry constraints. Mulliken population analysis has been used to obtain the occupation number of atomic orbitals, the magnetic moments are the difference between the occupation numbers in spin-up and spin-down states. The data for bond length (Å), binding energy per atom (eV), and magnetic moments are listed in Table 1, from which we can obtain the following conclusions:
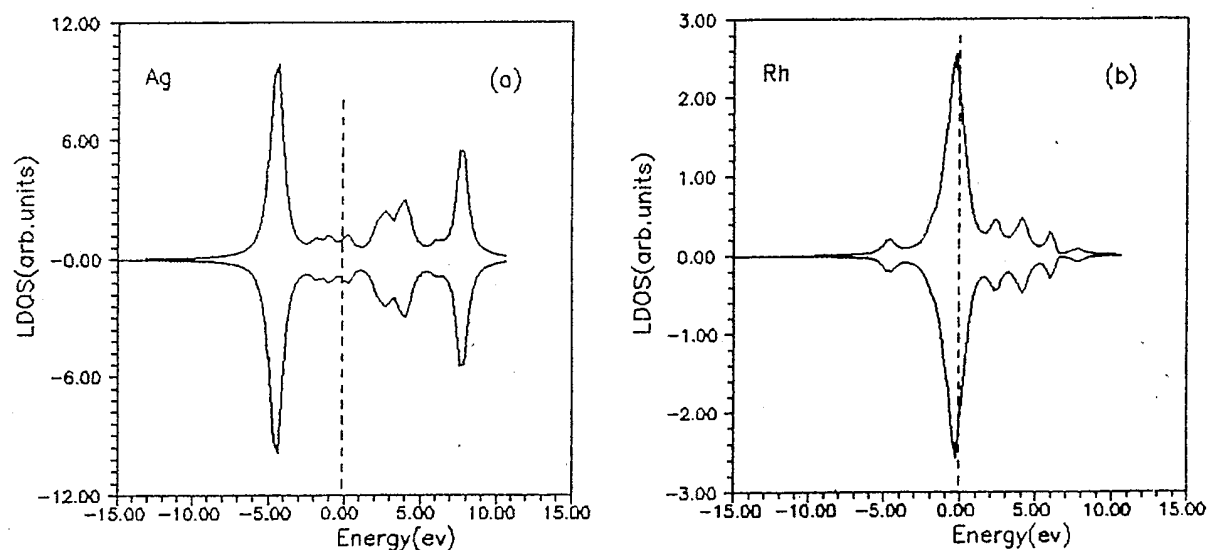

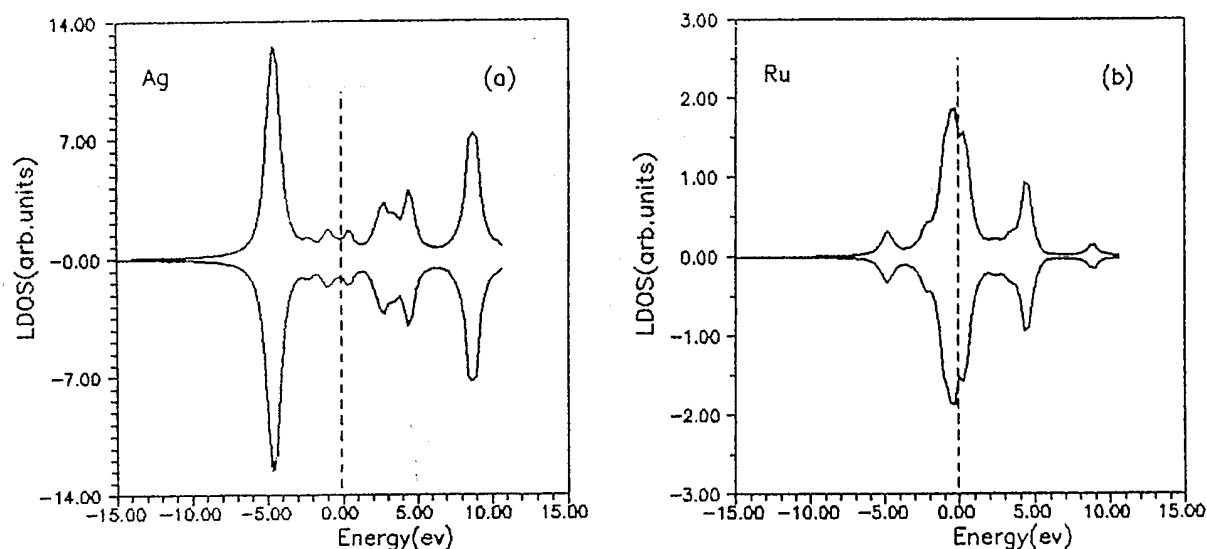Fig. 1. The local densities of states (LDOS) for the host atom and impurity atom in Ag_3Rh (D_{3h}) cluster.

Fig. 2. The local densities of states (LDOS) for the host atom and impurity atom in Ag$_4$Ru (T_d) cluster.

(1) The magnetic moments of Rh in Ag$_3$TM and in Ag$_5$TM are quenched to zero, in spite of the different coordination numbers of Rh and different atomic distance in these two clusters, the same symmetry makes the same quenching for Rh, and we called this phenomenon symmetry-quenching effect. The moment of Ru in tetrahedron (T_d) is also quenched to zero. For comparison, calculations are also performed on square structure (D_{4h}) with Ru in the center: it is found that the moment for Ru is 2.841 μ_b in equilibrium structure with bond length 3.8 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 important effect on the impurity-moment. Figures 1 and 2 show the local density of states (LDOS) of host atoms and impurity atoms in Ag$_3$Rh (D_{3h}) and Ag$_4$Ru(T_d) clusters respectively, we can see that there are no net magnetic moments for host atom as well as for impurity atom, which are in agreement with the Mulliken population analyses. We can also find that the orbital splittings of the central impurity Rh and Ru atoms in crystal fields are different, and the similar case is for Ag$_5$Rh(D_{3h}) cluster as well.

(2) It was found by Reddy et al. [9] that in FePd$_{12}$ cluster the introduction of Fe increases the moments at the outer Pd atoms due to exchange enhancement, and this kind of exchange enhancement in Pd can also be brought about by introducing atoms of 4d elements (Ru, Rh). In our case of Ag$_n$TM clusters, Ru and Rh are magnetic (except for symmetry-quenching), and the 4d impurities induce the host Cu atom to be polarized. The moment for Ru is larger than that for Rh, similar to the cases in monolayer Ru/Ag(0 0 1) [15] and Rh/Ag(0 0 1) [11]. However, Pd is nearly

nonmagnetic, similar to the cases in Pd/Ag(0 0 1) [12–14] and in bulk Ag [16].

(3) For Ag$_3$TM and Ag$_5$TM clusters with the same symmetry (D_{3h}), except for Rh, the magnetic moment of TM atom in Ag$_5$TM is smaller than that in Ag$_3$TM. This is caused by the increase in the overlap of the nearby atomic orbitals as the coordination number increases.

(4) Although the coordination number of TM in Ag$_6$TM is larger than that in Ag$_n$TM cluster ($n = 3, 4, 5$), and the bond length in Ag$_6$TM is smaller than that in Ag$_n$TM ($n = 3, 4, 5$), the moment of TM is larger than that in Ag$_n$TM ($n = 3, 4, 5$). This fact arises from different symmetry.

(5) Comparing Ag$_{12}$TM cluster with Ag$_6$TM cluster, both of them have the same symmetry (O_h) and the bond lengths are nearly the same, but due to the increase of coordination number in Ag$_{12}$TM, the moment of TM is decreased.

According to above discussions, we can see that the magnetic properties of 4d impurity in Ag clusters are mainly affected by symmetry, by coordination number and by atomic distance, and these three factors are often combined together to make the magnetic behaviours more rich and complicated.

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