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Local Magnetism of 3d and 4d Impurities in Ag and Pd Clusters

Q. Sun ^(1,2,*), Q. Wang ⁽²⁾, J.Z. Yu ⁽¹⁾, Z.Q. Li ⁽¹⁾, J.T. Wang ⁽¹⁾
and Y. Kawazoe ⁽¹⁾

⁽¹⁾ Institute for Materials Research, Tohoku University, Sendai 980-77, Japan

⁽²⁾ Physics Department of South-West Normal University, Chongqing, 630715, P.R.China

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Abstract. — The local magnetic properties of Ag₁₂TM and Pd₁₂TM clusters with I_h symmetry (TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Y, Zr, Nb, Mo, Tc, Ru, Rh, and Pd) have been systematically studied with the density functional formalism, and the Kohn-Sham equation is solved self-consistently with the discrete variational method (DVM). A special attention is paid to the comparison of local magnetism for impurities in Ag and Pd clusters with those in the bulk and on the (001) surface of Ag (Pd). It is found that the behavior of local moments in the Ag₁₂ cluster is more complex than the one of a single impurity in bulk Ag and on the Ag (001) surface, whereas the local moments in Pd₁₂ display very similar features as the ones of a single impurity in bulk Pd and on the Pd (001) surface. In order to better understand these results, the roles of interactions between impurity and host atoms on the local moment of impurities are explored: the interactions of impurity-d with Ag-d orbitals have important contributions to the local magnetic moments for impurities with less than half-filled d shell, such as Sc, Ti, V, Y, Zr and Nb, but have minor roles on the local magnetic moments for impurities Cr, Mn, Fe, Co, Ni, Tc, Ru and Rh. However, in the Pd₁₂ cluster, d-d interactions between impurity and host have major roles on all the 3d and 4d impurities. Based on the interaction point of view, explanations are presented for the similarities and differences of moment behavior in the cluster, in the bulk and on the surface. The comparison of the obtained results with those in the Cu₁₂ cluster is also made. This study would provide more comprehensive understandings on the local magnetism of 3d and 4d impurities in different environments.

1. Introduction

The local magnetism is one of the most interesting and challenging problem in physics as well as in materials science (*e.g.* in dilute alloys, spin-glasses, concentrated systems and ultrathin magnetic films), some of the basic physics for the mechanisms involved have been understood for some time [1–3]. But the complexity of the interactions between impurity and the host as well as the interplay of several mechanisms make it difficult to relate model predictions to real systems. In addition, because of solubility problems and low resolution, only a few of these very dilute impurity systems were experimentally accessible in the past. In the last decade,

(*) Author for correspondence (e-mail: sunq@pucc.princeton.edu)

with the advent of flexible and precise experimental techniques, fast computers, and more exact *ab initio* calculations, there has been a renewed interest in this field. Recently, a lot of effort have been devoted to the studies of the local magnetism of impurities in the bulk [4–9], the local magnetism in overlayers and interlayers [10–15] and the local magnetism of impurity as single adatom on surfaces [16,17].

By applying perturbed γ -ray distribution techniques following heavy-ion reactions and recoil implantation, Riegel and his co-workers [4–6] have experimentally studied the behavior of 3d and 4d ions in sp metal host (K, Na, Rb and Cs), in transition-metal host (Pd) and in noble-metal host (Cu, Ag and Au). They found different behavior of impurities in sp-band metals and in d-band metals. Using the KKR Green function method and jellium model, Papanikolaou *et al.* [7] have systematically calculated the local magnetism of 3d and 4d impurities in bulk Cu, Ag, Li, Na, K, Rb and Cs, being in a good agreement with the available experimental data. In order to explore the development of magnetic moments from single adatoms to monolayers, the local magnetism of 3d, 4d and 5d transition-metal impurities as single adatoms on the (001) surfaces of Cu, Ag, Pd and Pt has been extensively studied [16,17]. In all the cases, it has been found that the local magnetism is sensitive to the local structure and environment. It is well known that clusters offer a unique opportunity to study how the magnetic properties change as the local electrons of an isolated atom start to delocalize in the cluster, and how the itinerant magnetism of the solid state develops with increasing cluster size. Moreover, 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 [18,19]. Therefore, the studies for the local magnetism of impurities in clusters are rather desirable, which can highlight our understandings for the local magnetism in various environments besides in the bulk and on the surface.

For the local magnetism of impurities in sp-electron clusters, Gong and Kumar [20] have studied the electronic structure and stability of 3d, 4d and 5d impurities in Al_{12} cluster with I_h symmetry, and found that except for Ru (its moment is quenched to zero) all other impurities have rather large local moments. For the local magnetism of impurities in d-electron clusters, we have systematically studied the electronic structure and stability of 3d and 4d impurities in Cu_{12} cluster with I_h symmetry [21], and found that the behavior of local magnetism is quite different from that in the bulk. How about the situation is in Ag and Pd clusters? What are the general trends of moment changes for 3d and 4d impurities in Cu, Ag and Pd clusters when compared with the behavior in bulk Cu, Ag, Pd and on the (001) surfaces of Cu, Ag and Pd? No studies on these problems have been reported to our knowledge. In this paper, we shall deal with these subjects by using the spin density functional theory with the local density approximation, because density functional theory is most reliable in predicting trends rather than results for isolated cases. We believe that this study would provide more comprehensive understanding on the local magnetism of 3d and 4d impurities in different environments.

2. Theoretical Method

In the density functional theory, the Hamiltonian for electrons has the following form in atomic units

$$\mathbf{H} = \sum_i -\frac{1}{2}\nabla_i^2 + \int \frac{\rho(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} + V_{xc}(\mathbf{r}) + V_{ext}. \quad (1)$$

We have used the Barth-Hedin type for the exchange-correlation potential $V_{xc}(r)$ [22]. V_{ext} is an external potential including the Coulomb potential generated by ions. The numerical atomic wave functions are used as the basis set for the expansion of wavefunctions. The group

theory is employed to symmetrize the basis functions

$$\Phi_j = \sum_i D_{ij} \phi_i \quad (2)$$

where ϕ_i is an atomic wavefunction, Φ_j a symmetrized basis function, D_{ij} the so-called symmetry coefficient which is determined only by the symmetry of cluster. In this work we use 3d, 4s and 4p orbitals of 3d impurity, 4d, 5s, 5p orbitals of 4d impurity and Ag (Pd) as the basis set ϕ_i . The wavefunctions of the electrons in the clusters are expanded in the symmetrized basis function Φ_j

$$\Psi_i = \sum_j C_{ij} \Phi_j. \quad (3)$$

Then a matrix equation can be obtained,

$$(H - \varepsilon S)C = 0 \quad (4)$$

where H is the Hamiltonian matrix and S is the overlap matrix. The discrete variational method (DVM) [23] has been used to self-consistently solve the matrix equation. To get the electronic density of states (DOS) from the discrete energy level ε_i , the Lorentz expansion scheme is used, where the total DOS is defined as

$$D(E) = \sum_{n,l,\sigma} D_{nl}^\sigma(E) \quad (5)$$

with

$$D_{nl}^\sigma(E) = \sum_i A_{nl,i}^\sigma \frac{\delta/\pi}{(E - \varepsilon_i)^2 + \delta^2} \quad (6)$$

where σ is the spin index, i labels the eigenfunction and a broadening factor $\delta = 0.24$ eV is used. $A_{nl,i}^\sigma$ is the Mulliken population number, n and l are orbital and angular quantum numbers respectively. The total energy is evaluated by

$$E_{\text{tot}} = \sum_i f_i \varepsilon_i - \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')d\mathbf{r}d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} + \int \rho(\mathbf{r})(\mu_{\text{xc}} - V_{\text{xc}})d\mathbf{r} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \quad (7)$$

where f_i is the occupation number, Z_I is the proton number of atom I , $\rho(r)$ is the charge density, μ_{xc} is an universal potential related to V_{xc} by

$$\frac{d}{d\rho}(\rho\mu_{\text{xc}}) = V_{\text{xc}}. \quad (8)$$

The binding energy E_b is determined by

$$E_b = E_{\text{ref}} - E_{\text{tot}} \quad (9)$$

where E_{tot} is the total energy of the cluster, and E_{ref} is the sum of total energy of all isolated free atoms in the cluster, the average binding energy is defined as the ratio of the total binding energy to the number of atoms.

3. Results and Discussions

For all the clusters considered, the bond length between the impurity atom and host atom is optimized by maximizing the binding energy within the symmetry constraints. Mulliken population analysis has been used to obtain the occupation number of atomic orbitals, the magnetic moment is the difference between the occupation numbers in spin-up and spin-down states.

Table I. — *Equilibrium bond length r (Å), average binding energy ε_b (eV), the induced host moments μ_{Ag} , the impurity moment μ_{TM} (TM = 3d, 4d) in Ag_{12} cluster.*

cluster	r	ε_b	μ_{TM}	μ_{Ag}
$Ag_{12}Sc$	2.70	2.619	0.754	0.085
$Ag_{12}Ti$	2.80	2.710	0.995	0.084
$Ag_{12}V$	2.70	2.736	0.904	0.001
$Ag_{12}Cr$	2.70	2.505	0.0	0.0
$Ag_{12}Mn$	2.70	2.460	2.298	-0.108
$Ag_{12}Fe$	2.70	2.480	2.419	-0.034
$Ag_{12}Co$	2.70	2.465	1.793	0.102
$Ag_{12}Ni$	2.70	2.654	1.066	0.104
$Ag_{12}Y$	2.90	2.400	0.872	0.107
$Ag_{12}Zr$	2.80	2.640	0.811	0.099
$Ag_{12}Nb$	2.80	2.636	0.619	0.029
$Ag_{12}Mo$	2.85	2.570	0.0	0.0
$Ag_{12}Tc$	2.75	2.580	0.510	0.040
$Ag_{12}Ru$	2.75	2.530	0.640	0.103
$Ag_{12}Rh$	2.75	2.420	0.490	0.100
$Ag_{12}Pd$	2.75	2.190	0.075	-0.090
$Ag_{12}Ag$	2.75	2.060	0.077	-0.030

3.1. THE LOCAL MAGNETISM OF IMPURITIES IN THE Ag CLUSTER. — Table I shows the results for 3d and 4d impurities in the center of Ag_{12} . From the binding energy per atom we can see that doping can enhance the stability of the cluster. The results for the moments indicate that the moments of Cr and Mo are quenched to zero, that the impurity Pd is nearly nonmagnetic, and that the other impurities get sizable local moments. Figures 1a and b present the comparison of the local moments in different environments. It is well recognized that the environment with fewer nearest neighbors and weaker interatomic hybridization are conducive to enhance magnetism, therefore, the local moment of an impurity on the surface is larger than that in the bulk. Moreover, the general trends in changes of moments in bulk and on surface are similar. But for the moment in Ag cluster, the situation changes a lot, and the behavior of the local moments is more complex. What makes the moment behavior in Ag cluster so special? It should stem from the different interactions between impurity and host. In the following, we will explore the roles of interactions on the local moment.

Because the interplay of intra-atomic, interatomic and intrahost interactions is highly complex, it is usually difficult to give some quantitative theoretical analysis for the interactions. In order to get some insight into the qualitative effects of the interaction between impurity and host atoms on the local magnetism, we will single out the interaction related with a certain orbital by switching off this orbital, *i.e.* not to let this orbital participate in interaction. For example, if we want to see the role of the Ag-4d orbital on the local moment of the impurity, we will switch off the Ag-4d orbital by setting the valence orbitals as 5s5p(3d4s4p), where the symbols outside the bracket and inside the bracket are the valence orbitals of Ag and 3d

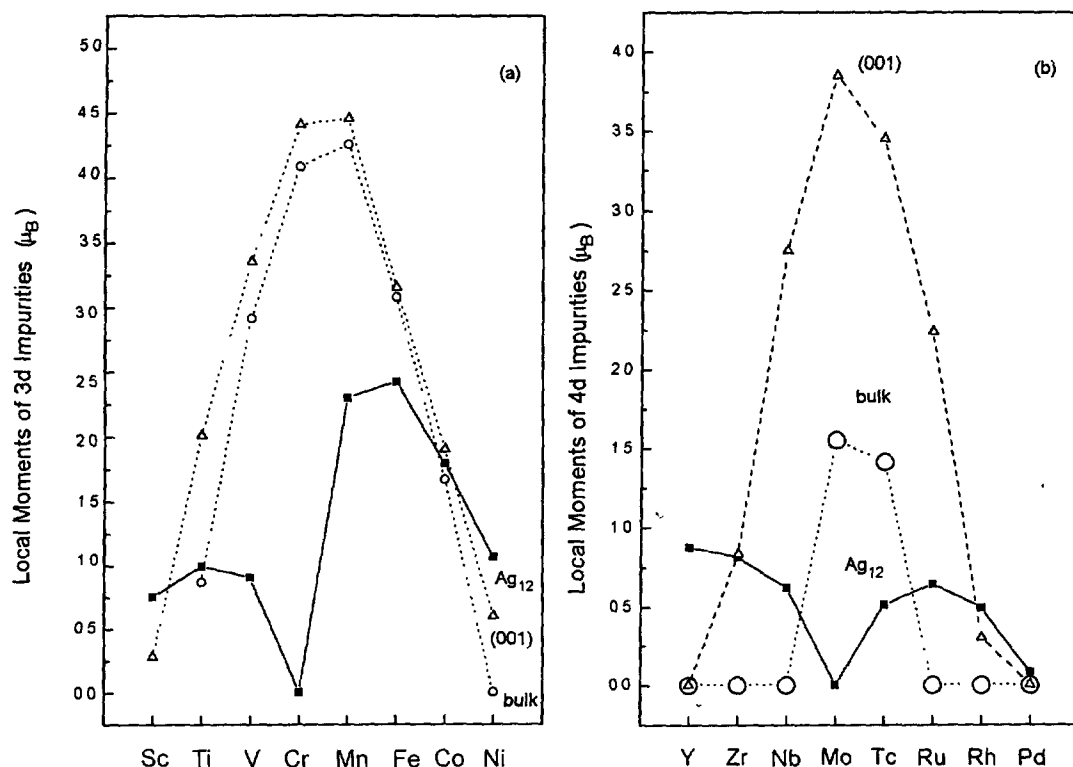


Fig. 1. — Local magnetic moments for 3d (a) and 4d (b) impurities in the Ag₁₂ cluster (solid square), in bulk Ag (open circle, from Ref. [7]) and on the Ag (001) surface (open triangle, from Ref. [17]).

impurity atom, respectively. Therefore, the interactions exist only among these valence orbitals. Calculations are performed with the bond length given in Table I. The obtained local moments of impurities are displayed in Table II for 3d and 4d series, respectively.

In Table II for 3d series, comparing column 2 and column 3, we can see that switching off the Ag-5p orbital changes the moments of Sc, Ti and V slightly, but increases the moments of Cr, Mn, Fe, Co and Ni considerably, particularly for Cr, the moment of $2.78\mu_B$ is gained from zero, which indicates that the interactions of Ag-5p orbital with TM-spd orbitals have a crucial role on the local magnetic moment for Cr, Mn, Fe, Co and Ni. Comparing column 2 and column 4, switching off the Ag-4d orbital increases the moments of Sc, Ti and V considerably and decreases the moments of Mn, Fe, Co and Ni slightly, which suggests that the interactions of Ag-4d orbital with impurity orbitals strongly suppress the magnetism for impurities at the beginning of the series (Sc, Ti and V), and slightly enhance the moments for impurities at the end of the series. These results also imply that the d-d interactions between impurity and host atoms are very weak for Cr, Mn, Fe, Co and Ni, these conclusions can be confirmed from Figures 2a and b, which show the d-DOS of Ag atom and Cr atom in Ag₁₂Cr cluster respectively, we can see that the main part of d-DOS for Ag atom is well below the Fermi energy, therefore the d-d hybridizations between Cr and Ag are very weak. It can also be found that there are no exchange splitting for Cr resulting in zero local moment.

The situation for 4d impurities follows basically the same trends as discussed for 3d impurities. In Table II for the 4d series, comparing column 2 and column 3, we can find

Table II. — *Changes of the local magnetic moments for 3d and 4d impurities in the Ag_{12} cluster with the controlled host-impurity interactions, the first row is for the orbitals involved in interactions, the symbols in bracket are for impurities.*

	4d5s5p (3d4s4p)	4d5s (3d4s4p)	5s5p (3d4s4p)		4d5s5p (4d5s5p)	4d5s (4d5s5p)	5s5p (4d5s5p)
Sc	0.754	0.543	1.153	Y	0.872	0.711	1.168
Ti	0.995	0.950	1.323	Zr	0.811	0.710	1.173
V	0.904	1.023	1.147	Nb	0.619	0.679	0.910
Cr	0.0	2.78	0.0	Mo	0.0	0.0	0.0
Mn	2.298	4.070	2.096	Tc	0.510	0.974	0.434
Fe	2.419	3.539	2.161	Ru	0.640	1.203	0.544
Co	1.793	2.510	1.673	Rh	0.490	0.967	0.410
Ni	1.065	1.515	1.014	Pd	0.075	0.146	0.098

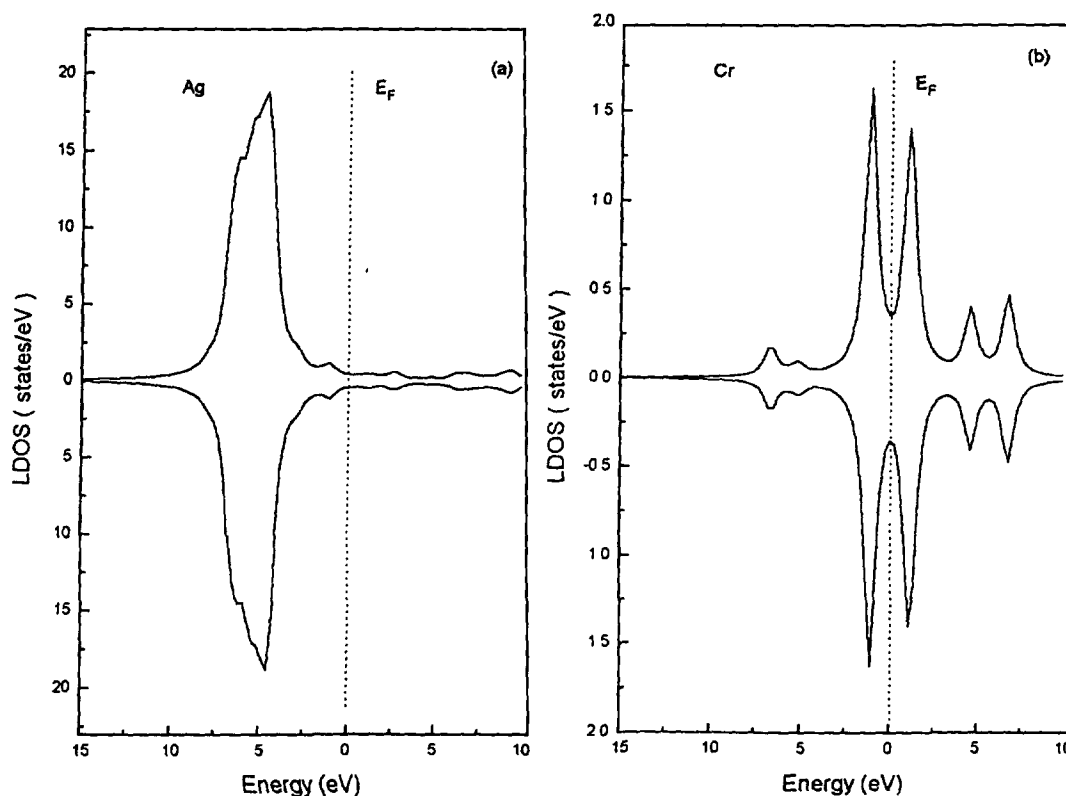


Fig. 2. — Local densities of states (LDOS) for d states of the Ag atom (a) and the Cr atom (b) in the Ag_{12}Cr cluster.

Table III. — *Equilibrium bond length $r(\text{\AA})$, average binding energy ε_b (eV), the induced host moments μ_{Pd} , the impurity moment μ_{TM} ($TM = 3d, 4d$) in Pd_{12} cluster.*

cluster	r	ε_b	μ_{TM}	μ_{Pd}
$Pd_{12}Sc$	2.60	3.474	0.205	0.050
$Pd_{12}Ti$	2.55	3.580	0.468	0.080
$Pd_{12}V$	2.55	3.479	0.701	0.122
$Pd_{12}Cr$	2.55	2.939	3.583	0.030
$Pd_{12}Mn$	2.60	3.029	4.625	0.031
$Pd_{12}Fe$	2.60	3.082	3.965	0.200
$Pd_{12}Co$	2.60	3.016	2.791	0.109
$Pd_{12}Ni$	2.60	2.958	1.404	0.049
$Pd_{12}Y$	2.65	3.158	0.034	0.085
$Pd_{12}Zr$	2.65	3.423	0.302	0.141
$Pd_{12}Nb$	2.65	3.352	0.736	0.188
$Pd_{12}Mo$	2.65	3.100	1.532	0.205
$Pd_{12}Tc$	2.65	2.923	3.314	0.140
$Pd_{12}Ru$	2.65	2.930	3.057	0.203
$Pd_{12}Rh$	2.65	2.785	1.579	0.102
$Pd_{12}Pd$	2.65	2.553	0.092	0.052

that switching off the Ag-5p orbital changes the moments of Y, Zr, Nb slightly, and increases the moments of Tc, Ru, Rh and Pd considerably, which indicates that the interactions of Ag-5p orbital with TM-spd orbitals have large contribution to the moment for Tc, Ru, Rh and Pd. Comparing column 2 and column 4, switching off the Ag-4d orbital increases the moments of Y, Zr and Nb considerably and decreases the moments of Tc, Ru, Rh and Pd slightly, which indicates that the interactions of Ag-4d orbital with impurity orbitals have large contribution to the moment for Y, Zr and Nb, in particular, the d-d interaction between impurity and host has minor role on the local magnetic moments of Tc, Ru, and Rh.

In fact, we know that the wavefunctions of d orbitals at the beginning of 3d and 4d series are more extended than those of the late ones, the strength of d-d hybridization decreases with the increasing contraction of the d orbital, therefore the d-d hybridization effect is stronger for the early transition atom (Sc, Ti, V, Y, Zr, Nb) than that for the late ones (Cr, Mn, Fe, Co, Ni, Tc, Ru, Rh). It is obvious that the conclusions obtained above are physically reasonable. However, it should be pointed out that there are two competing factors to affect the stability and magnetic behavior: from Sc to Ni and from Y to Ag, the d orbital of the impurity is contracted, accordingly the d-d hybridization between the impurity and host is reduced. On the other hand, on going from Sc to Ni and from Y to Ag, the energy of d level is reduced to become close to the d level of Ag atom. So the d-d interaction is increased. The stability and magnetic behavior are results from the compromise of these two competing factors. Because the electronic states of d electrons of impurities in the cluster are different from those in the bulk and on the surface, the different magnetic behavior for impurity in the cluster and in the bulk and on the surface would be exhibited.

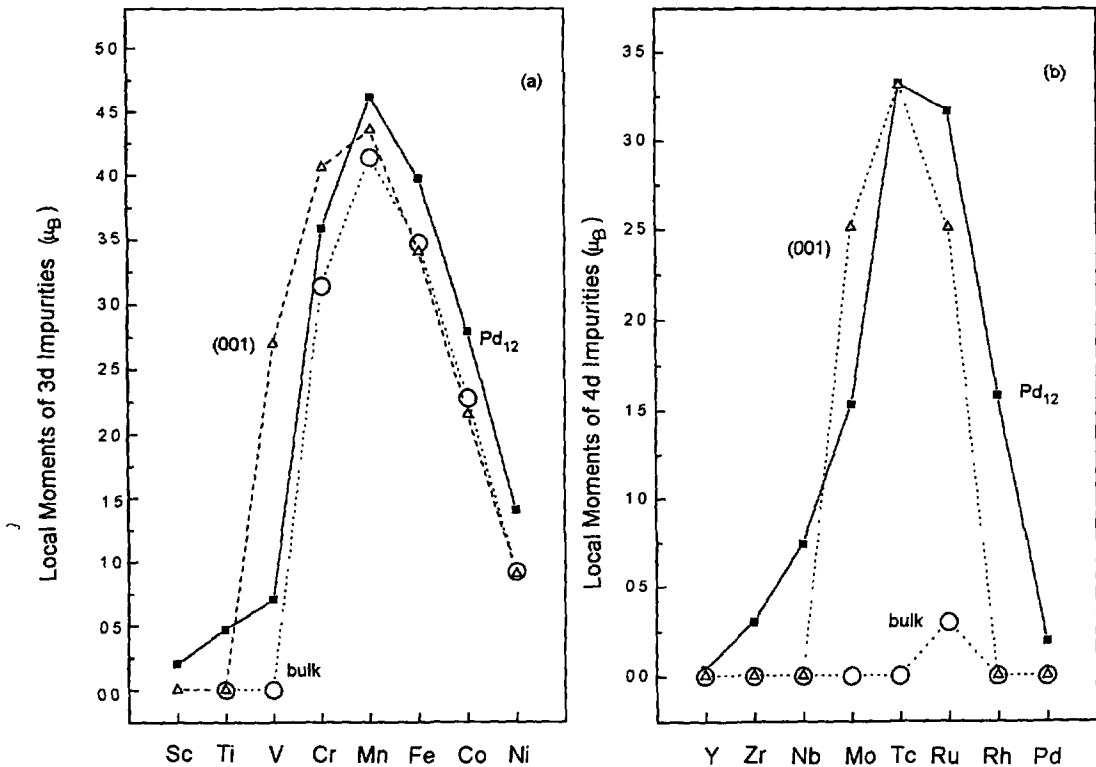


Fig. 3. — Local magnetic moments for 3d (a) and 4d (b) impurities in the Pd₁₂ cluster (solid square), in bulk Pd (open circle, from Refs. [6, 25]) and on the Pd (001) surface (open triangle, from Ref. [16]).

Based on the above discussions, we can give an explanation for the shapes of moment curves in the Ag cluster. From Figure 1a, we can see that the curve can be divided into two parts: the first part is from Sc to V, where the d-d interactions between impurity and Ag atoms dominate the behavior of the moments, the second part is from Cr to Ni, in which the d-d interactions are much weaker. It is well known that for a single 3d impurity in the bulk Ag and on the Ag (001) surface, the changes of impurity moments are mainly governed by the hybridizations between impurity-d states and Ag-sp states [15, 16]. Therefore, we find that in the first part of the curve, the interactions are different from those in the bulk Ag and on the Ag (001) surface, resulting in quite different behavior in moment changes, in the second part of the curve, the interactions are similar to those in the bulk Ag and on the Ag (001) surface, consequently, producing similar behavior in moment changes. This explanation is also valid for 4d impurities in the Ag cluster (see Fig. 1b). Why the moments of Cr and Mo become to be zero? From the analysis of orbital components, we find that the d states of impurities and the s state of host atoms nearly have the same weight, the d-s hybridizations between impurities and host atoms are the strongest, which are much stronger than the ones in the bulk and on the surface and quench the moments of Cr and Mo to zero.

3.2. THE LOCAL MAGNETISM OF IMPURITIES IN THE PD CLUSTER. — Table III shows the results for 3d and 4d impurities in the center of Pd₁₂. From the binding energy per atom we can see that doping can enhance the stability of the cluster. The results for moment show

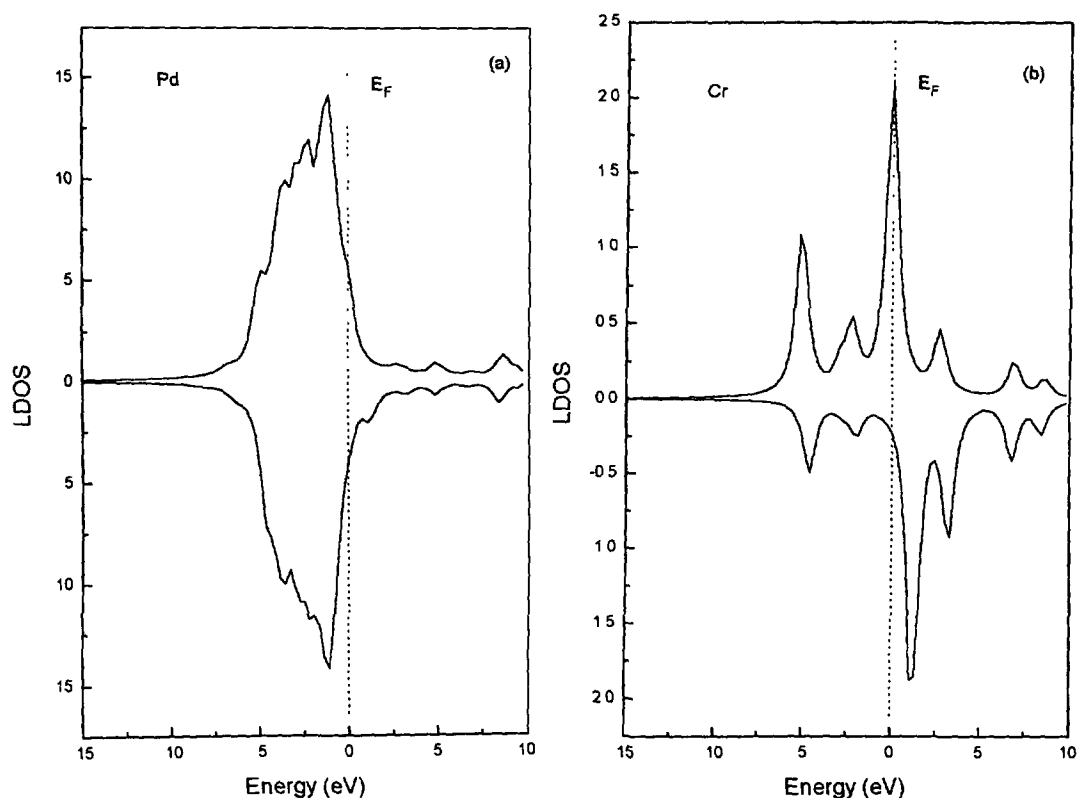


Fig. 4. — Local densities of states (LDOS) for d states of the Pd atom (a) and the Cr atom (b) in the Pd_{12}Cr cluster.

that impurity Y is nearly nonmagnetic, all the other impurities in the Pd_{12} cluster get rather large local moments especially the 3d ones. The comparison of the local moments in different environments is plotted in Figures 3a and b. We can find surprising similarities as far as the general trend is concerned, despite the very different environments. The explanations for these results also should be based on the interactions between the impurity and the host atoms. Note that for bulk Pd the d bands are crossing the Fermi level and are not completely filled, the d bands of Pd are near the threshold of becoming ferromagnetic and bulk Pd has the largest Stoner enhanced susceptibility among 4d metals, and impurities in bulk Pd and on the Pd (001) surface have stronger hybridizations of impurity-d and Pd-d states [15, 16, 24], differing from the d-sp hybridizations in bulk Ag and on the Ag (001) surface. The stronger d-d hybridizations are also found for impurities in the Pd cluster, which can be verified from the d-DOS of Pd atom and Cr atom in Pd_{12}Cr cluster, as shown in Figures 4a and b respectively (we show the d-DOS only for Pd_{12}Cr here, the similar features also exist for other clusters). We can see that the main part of d-DOS for Pd atom is near to the Fermi energy, and the d-d hybridizations between Cr and Pd are much stronger, by which the Cr-d states are pushed to E_F so that the Stoner-like criterion for a local moment is well satisfied and large moment appears (in contrast to the zero moment in Ag_{12}Cr cluster). Due to the similar interactions for impurities in the Pd cluster with those in bulk Pd and on the Pd (001) surface, the general trends in changes of moments are also similar.

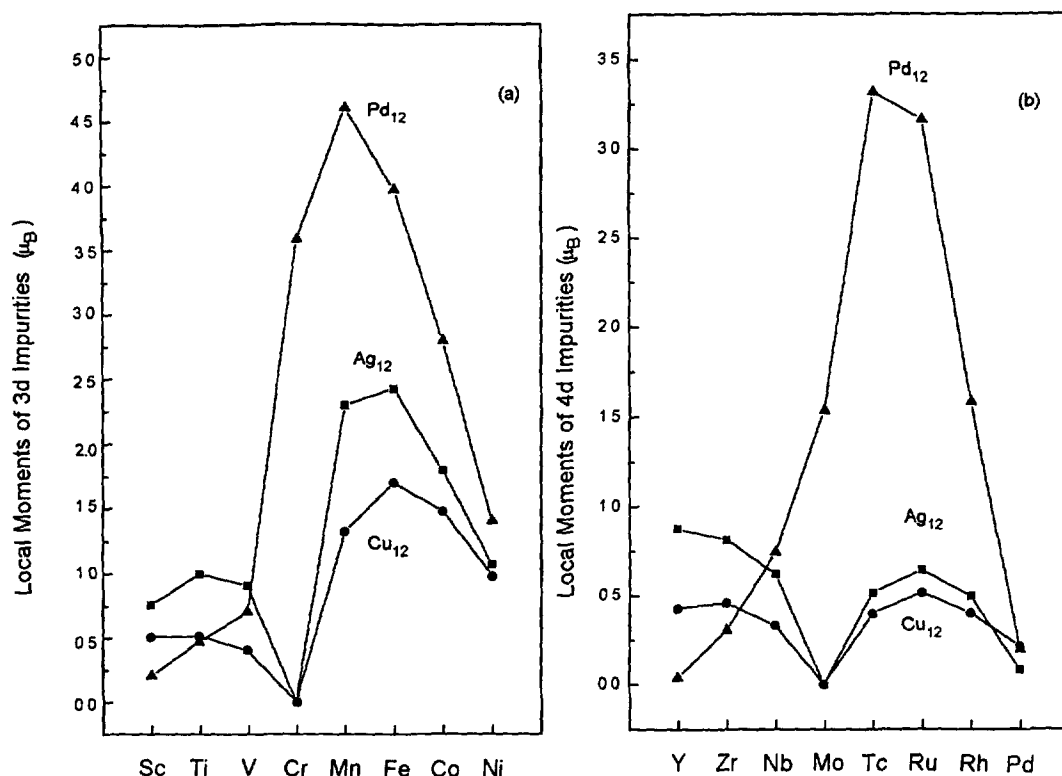


Fig. 5. — Comparisons of local moments for 3d (a) and 4d (b) impurities in the Cu₁₂ clusters (circle), in the Ag₁₂ cluster (square) and in the Pd₁₂ cluster (triangle).

In Figure 3b, because the 4d functions extend into a larger spatial region, the strong hybridizations in bulk Pd quench the impurity moment to zero (except for Mo with about $0.3\mu_B$). However, the reduced coordination for impurities in the Pd cluster and on the Pd (001) surface enhances the impurity moments. Furthermore, the high symmetry in Pd₁₂ cluster also favors the impurity moment. Comparing Figures 3a and b, it can be clearly seen that because the 3d functions are more localized spatially than those of 4d's, the magnetic properties are not as sensitive to the changes of the environment as those of 4d's.

Figures 5a and b show comparisons of the local moments of 3d and 4d impurities in Ag₁₂ and Pd₁₂ with those in Cu₁₂ of our previous studies [21]. The bond length in Cu₁₂ is smaller than that in Ag₁₂, which increases the hybridizations with the host atoms. As a result, the local moments for impurities in Cu₁₂ are smaller than those in Ag₁₂, however, due to the similar electronic structures of Cu and Ag, the general trends in changes of moments are similar. Compared with the situations in Cu₁₂ and Ag₁₂, the moments of Sc, Ti, V, Cr, Y, Zr and Mo in Pd₁₂ are reduced, whereas the moments of the other impurities are increased, similar to the situations of adatoms on the (001) surfaces of Cu, Ag and Pd [15,16].

4. Summary

Cluster constitute an intermediate phase between atom and bulk, which is also one of the typical environments for impurities besides in the bulk and on the surface, and the studies

on the local magnetism of impurity in cluster will deepen our understandings for the local magnetism in different environments. On the other hand, in order to increase the number of variables for the purpose of material design and control, doped clusters are of special interest. In this paper we have presented a systematic study on local magnetic properties for 3d and 4d impurities in Ag₁₂ and Pd₁₂ clusters. We have found that the behavior of local moments in the Ag₁₂ cluster are more complex than those of single impurities in bulk Ag and on Ag the (001) surface, whereas the local moments in Pd₁₂ display very similar features as the ones of single impurities in bulk Pd and on Pd (001) surface. To understand these results, we have studied the roles of interactions between impurity and host atoms on the local moment of the impurity, and found that differing from the interaction picture for impurities in bulk Ag and on the Ag (001) surface, stronger interactions between impurity-d with Ag-d orbitals exist only for Sc, Ti, V, Y, Zr and Nb in Ag₁₂TM clusters, which suppress the magnetism for these impurities. However, in the Pd₁₂ cluster, strong d-d interactions exist for all the 3d and 4d impurities similar to the situation for impurities in bulk Pd and on the Pd (001) surface. Based on the analysis for the interactions, we give explanations for similarities and differences of moment behaviors compared to the ones in the bulk and the on (001) surface of Ag (Pd). We also compare the results with those in the Cu₁₂ cluster. Our studies clearly suggest that the local magnetism of impurity is determined by the interactions between impurities and host atoms, and that similar interactions result in the similar behavior of the local magnetism.

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References

- [1] Anderson P.W., *Phys. Rev.* **124** (1961) 41.
- [2] Wolff A., *Phys. Rev.* **124** (1961) 1030.
- [3] Kondo J., *Prog. Theor. Phys.* **32** (1964) 37.
- [4] Riegel D., Büermann L., Gross K.D., Luszik-Bhadra M. and Mishra S.N., *Phys. Rev. Lett.* **62** (1989) 316.
- [5] Gross K.D., Riegel D. and Zeller R., *Phys. Rev. Lett.* **63** (1989) 1176.
- [6] Gross K.D., Riegel D. and Zeller R., *Phys. Rev. Lett.* **65** (1990) 3044.
- [7] Papanikolaou N., Stefanou N., Zeller R. and Dederichs P.H., *Phys. Rev. B* **46** (1992) 10858.
- [8] Beuerle T., Hummler K., Elsässer C. and Fähnle M., *Phys. Rev. B* **49** (1994) 8802.
- [9] Hashi Y., Li Z.Q. and Kawazoe Y., *Mater. Trans., JIM* **37** (1996) 279.
- [10] Blügel S., *Phys. Rev.* **51** (1995) 2025.
- [11] Wildberger K., Stepanyuk V.S., Lang P., Zeller R. and Dederichs P.H., *Phys. Rev. Lett.* **75** (1995) 509.
- [12] Újfalussy B., Szunyogh L., Weinberger P., *Phys. Rev. B* **51** (1995) 12836.
- [13] Papanikolaou N., Stefanou N., Zeller R. and Dederichs P.H., *Phys. Rev. Lett.* **71** (1993) 629.
- [14] Wu R., Freeman A.J., *Phys. Rev. B* **45** (1992) 7222.
- [15] Blügel S., Drittler B., Zeller R. and Dederichs P.H., *Appl. Phys. A* **49** (1989) 547.

- [16] Stepanyuk V.S., Hergert W., Wildberger K., Zeller R. and Dederichs P.H., *Phys. Rev. B* **53** (1996) 2121.
- [17] Lang P., Stepanyuk V.S., Wildberger K., Zeller R. and Dederichs P.H., *Solid State Commun.* **92** (1994) 755.
- [18] Dunlap B.I., *Phys. Rev. A* **41** (1990) 5691.
- [19] Li Z.Q. and Gu B.L., *Phys. Rev. B* **47** (1993) 13611.
- [20] Gong X.G. and Kumar V., *Phys. Rev. B* **50** (1994) 17701.
- [21] Sun Q., Gong X.G., Zhen Q.Z., Sun D.Y. and Wang G.H., *Phys. Rev. B* **54** (1996) 10896.
- [22] Barth U.V. and Hedin L., *J. Phys. C* **5** (1972) 1629.
- [23] Ellis D.E. and Painter G.S., *Phys. Rev. B* **2** (1970) 2887.
- [24] Press M.R., Mishra S.N., Devare S.H. and Devare H.G., *Phys. Rev. B* **47** (1993) 14988
- [25] Oswald A., Zeller R. and Dederichs P.H., *Phys. Rev. Lett.* **56** (1986) 1419.