Local magnetic properties and electronic structures of 3d and 4d impurities in Cu clusters

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The local magnetic properties and electronic structures of $Cu_{12}R$ clusters with I_h and O_h symmetries (R=Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, and Ag) have been systematically studied with the density-functional formalism, and the Kohn-Sham equation is solved self-consistently with the discrete variational method. By calculating the binding energies for $3d$ series, we find that the icosahedral structure is more stable than the octahedron structure. Pd and Ag doping can enhance the stability of a cluster, and the alloying effects in such doped clusters have an important effect on binding energy. The electronic structures calculated in equilibrium configurations show that the clusters with R=Cu, Cr, Mo, or Ag have closed electronic shells, while the others have open electronic shells. In particular, we have performed comprehensive calculations on the local magnetism of impurities in a cluster, and found that the behavior of local magnetism for $3d$ and $4d$ impurities in Cu_{12} clusters is different from that in bulk as well as from that in Al_{12} clusters. In contrast to the d-d interaction picture for local magnetism in the d-band bulk host, we have found that there are more complicated interactions acting in clusters to affect the local magnetism of impurities: the interactions of the Cu-p orbital with R-spd orbitals play a crucial role on the local magnetic moment for impurities with more than a half-filled d shell, such as Mn, Fe, Co, Ni, Tc, Ru, and Rh; the interactions of the Cu-d orbital with R-spd orbitals contribute to the local magnetic moment for impurites with a less than half-filled d shell, such as Sc, Ti, V, Y, Zr, and Nb. We have also tested and discussed the Stoner-like criterion for the occurrence of a local moment in a cluster. [S0163-1829(96)08039-3]

I. INTRODUCTION

Studies on the local magnetic moment have played a major part in the investigation of magnetism of magnetic impurities in dilute alloys, spin glasses, and concentrated systems.[1] It has been proposed that the magnetism of $3d$ ions in metals depends strongly on the type of conduction electrons in the host.[2–4] $3d$ ions in sp-band metals display an ionic-type magnetism; the tendency toward magnetic behavior is driven by intra-atomic correlations, and the tendency toward nonmagnetic behavior is essentially governed by spin fluctuations, which stems from the antiferromagnetic exchanges of impurity $3d$ electrons with the host sp-band electrons. This ionic-type picture can be even generalized to the magnetism of $4d$ ions in alkali-metal hosts.[2] On the other hand, for impurities in transition-metal hosts, the situation is changed, the hybridizations of impurity-d states with the d band of the host metal play an important role in the existence of the local moment.[3,4] However, in all cases, the local mag-

netism is very sensitive to its local structure and environment. We know that the cluster offers a unique opportunity to study how 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.[5,6] Therefore, the local magnetism of an impurity in a cluster is interesting, and would be different from the behaviors in bulk and film.

For the local magnetism of an impurity in sp-electron clusters, one of the authors systematically studied the electronic structure and stability of $3d$, $4d$, and $5d$ impurities in an Al_{12} cluster with I_h symmetry,[7] and found that except for Ru (its moment is quenched to zero) all other impurities have rather large local moments. How about the local magnetism of $3d$ and $4d$ impurities in transition-metal and noble-metal

clusters? What are the major factors that affect the local moments? What is the influence of interactions between impurity-d and host-d states on the local magnetism? Is the d-d interaction picture proposed in Refs. 3 and 4 valid for description of local magnetism in these clusters? In this paper, we use $Cu_{12}R$ clusters as prototype systems of $3d$ and $4d$ impurities in noble-metal cluster, and we present systematic theoretical studies of the local magnetism and electronic structures of $3d$ and $4d$ impurities in Cu clusters. In fact, Blaha and Callaway[8] and Bagayoko, Blaha, and Callaway[9] have used a cluster model ($Cu_{18}R$, R=Cr, Mn, Fe, Co, or Ni) to study the magnetic properties and electronic structures of the corresponding dilute alloys, where the impurity atom is placed in the center of a cluster and the bond length is taken to be the bulk value; they found that the magnetic moments for the impurity atoms Cr, Mn, Fe, Co, and Ni are 3.53, 4.04, 3.05, 2.05, and 0.69 (in μ_B), respectively. Braspenning *et al.*[10] studied the magnetic properties of $3d$ impurities in the bulk Cu with an embedded 55-atom cluster model. Their calculations were based on density-functional theory in the local-spin-density approximation and on the Korringa-Kohn-Rostoker Green-function method, and they found that only Sc, Ti, and Ni are nonmagnetic; the other $3d$ impurities (V, Cr, Mn, Fe and Co) are magnetic, and the corresponding magnetic moments (in μ_B) are 1.07, 3.01, 3.40, 2.51, and 0.88. Furthermore, they found that all $4d$ impurities in bulk Cu are nonmagnetic, and the Stoner-like criterion is far from being met. However, in these two studies, the cluster models are actually parts of the bulk. How about the situation in the Cu cluster? Is the Stoner-like criterion valid for the occurrence of a local magnetic moment for an impurity in a cluster? No systematic studies of these problems have been reported, to our knowledge. In this paper, we will explore these subjects by using the local-spin-density-functional formalism with the discrete variational method.

II. THEORETICAL METHOD

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

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

We used the Barth-Hedin type for the exchange-correlation potential $V_{xc}(r)$.[11] V_{ext} is an external potential including the Coulomb potential generated by ions. The numerical atomic wave functions are used as a basis set for the expansion of wave functions. 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 wave function, Φ_j is a symmetrized basis function, and D_{ij} is the so-called symmetry coefficient which is determined only by the symmetry of cluster. In this work we have used $3d$, $4s$, and $4p$ orbitals of the Cu atom, $3d$, $4s$, and $4p$ orbitals for the $3d$ impurity, and $4d$, $5s$, and $5p$ orbitals for the $4d$ impurity as the basis set ϕ_i. The wave

functions 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[12] was used to solve the matrix equation self-consistently. To obtain the electronic density of states (DOS) from the discrete energy level ε_i, the Lorentz expansion scheme is used, and 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 $\delta = 0.42$ eV is used. $A_{nl,i}^\sigma$ is the Mulliken population number, and n and l are orbital and angular quantum numbers, respectively. The total energy is evaluated by

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

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

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

The binding energy E_b is determined by

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

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

III. RESULTS AND DISCUSSIONS

In this paper, we concentrate on $Cu_{12}R$ clusters with I_h and O_h symmetries. For all the structures considered, the atomic distances are optimized by maximizing the binding energy within the symmetry constraints. Mulliken population analysis has been used to obtain the occupation number of atomic orbitals, and the magnetic moment is the difference between the occupation numbers in spin-up and spin-down states. In order to test our calculations, we first performed calculations for Cu_2, and obtained the bond length 2.21 Å and the binding energy 2.45 eV, which are very close

TABLE I. The symmetry, equilibrium bond length r (Å), binding energy E_b (eV), and magnetic moments μ_{Cu} and μ_R(R=3d), where $\Delta_b = E_b(Cu_{12}R) - E_b(Cu_{12}Cu)$.

Cluster	Symmetry	r	$r_{Cu}+r_R$	E_b	Δ_b	μ_{Cu}	μ_R
$Cu_{12}Sc$	I_h	2.375	2.919	43.84	5.06	0.208	0.504
	O_h	2.400	2.919	41.85	5.00	0.006	0.240
$Cu_{12}Ti$	I_h	2.350	2.726	46.20	7.42	0.124	0.512
	O_h	2.375	2.726	44.55	7.70	0.100	0.760
$Cu_{12}V$	I_h	2.350	2.589	46.80	8.02	0.050	0.404
	O_h	2.375	2.589	44.74	7.89	0.035	0.578
$Cu_{12}Cr$	I_h	2.325	2.527	44.77	5.99	0.0	0.0
	O_h	2.350	2.527	42.06	5.21	0.0	0.0
$Cu_{12}Mn$	I_h	2.425	2.644	42.78	4.02	0.026	1.322
	O_h	2.375	2.644	40.29	3.44	0.061	1.727
$Cu_{12}Fe$	I_h	2.375	2.519	42.82	4.04	0.025	1.699
	O_h	2.400	2.519	40.99	4.14	0.032	2.10
$Cu_{12}Co$	I_h	2.350	2.531	42.17	3.39	0.127	1.471
	O_h	2.400	2.531	40.59	3.73	0.080	2.000
$Cu_{12}Ni$	I_h	2.350	2.524	40.94	2.16	0.252	0.978
	O_h	2.425	2.524	39.29	3.45	0.070	0.923
$Cu_{12}Cu$	I_h	2.346	2.556	38.78	0.0	0.040	-0.124
	O_h	2.400	2.556	36.85	0.0	0.080	0.010
Cu_{12}	I_h	2.200		35.40		0.240	
	O_h	2.250		33.24		0.120	

TABLE II. The equilibrium bond length r (Å), binding energy E_b (eV), and magnetic moments μ_{Cu} and μ_R(R=4d) in I_h structures, where $\Delta_b = E_b(Cu_{12}R) - E_b(Cu_{12}Cu)$.

Cluster	r	$r_{Cu}+r_R$	E_b	Δ_b	μ_{Cu}	μ_R
$Cu_{12}Y$	2.50	3.081	40.10	1.32	0.210	0.426
$Cu_{12}Zr$	2.50	2.868	45.64	6.86	0.128	0.455
$Cu_{12}Nb$	2.50	2.707	46.27	7.49	0.035	0.331
$Cu_{12}Mo$	2.40	2.641	45.85	7.07	0.000	0.000
$Cu_{12}Tc$	2.45	2.630	45.24	6.46	0.050	0.396
$Cu_{12}Ru$	2.45	2.603	43.83	5.05	0.124	0.512
$Cu_{12}Rh$	2.45	2.623	41.77	2.99	0.216	0.396
$Cu_{12}Pd$	2.40	2.654	38.64	-0.32	-0.350	0.213
$Cu_{12}Ag$	2.45	2.723	36.06	-2.72	-0.425	0.153

doping can have an energy gain up to 8 eV. For 4d impurities, except for Pd and Ag, all others can have an energy gain up to 7 eV. The relative instabilities of $Cu_{12}Pd$ and $Cu_{12}Ag$ are not due to the large atomic radius of the impurity as compared with that of the host atom, because other impurities (Y, Zr, or Nb) have even larger atomic radii as well as large binding energies. This fact arises from the more extended nature of the d orbitals at the beginning of the 4d series, resulting in a stronger hybridization with the host. Accordingly, the binding energies should be larger, but for Pd and Ag impurities the contractions of the d orbital cause weaker hybridizations with host; therefore, their binding energies are smaller.

Figure 1 shows average binding energies in all the icosahedral structures considered. The square and circle stand for 3d and 4d impurities, respectively, and the dotted horizontal line is for the Cu_{12} cluster. We can see that the average binding energies for 3d and 4d impurities have the same tendency. V and Nb have the largest binding energies, which are different from the behaviors of 3d and 4d impurities in Al_{12} clusters,[7] where the largest binding energes are for Cr and Tc, respectively. However, comparing the average binding energy of the R impurity in the cluster with the experimental value for R bulk,[17] we find that the general trends in variation are similar, but deviate from theoretical trends calculated by Moruzzi, Janak, Williams.[17] The computation methods we used are essentially the same as that of Ref. 17, so there are two possible reasons for this deviation: size effect and alloying effect. The former one could be excluded according to Painter's work,[18] in which the binding energy of all 3d six-atom clusters with octahedral symmetry were studied by using functional formalism with the local-density approximation, and it was found that the qualitative features in the variation of the binding energy through the series of 3d transition metals are rather well reproduced by six-atom clusters, and the size effect is not essential. In our cases, the alloying effect is important for the binding energy; in fact, comparing the energy spectra of the doped clusters with those of Cu_{12}, we find that doping with V and Nb maximizes the level shift downwards, resulting in the largest binding energies for $Cu_{12}V$ and $Cu_{12}Nb$.

Table III lists some numerical results on the electronic structure of a $Cu_{12}R$ cluster with I_h symmetry. The gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) changes
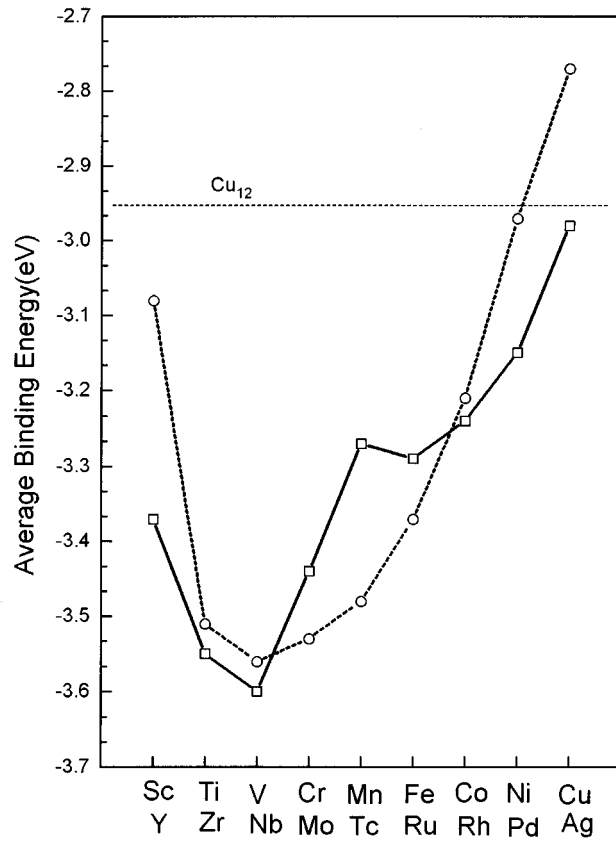
to the experimental values 2.22 Å and 2.05 eV.[13] Recently, the structural and electronic properties of small Cu_n clusters ($n=2$, 3, 4, 6, 8, and 10) were studied by Massobrio, Pasquarello, and Car[14] using the Car-Parrinello method; it was found that for Cu_2 the bond length and binding energy are 2.18 Å and 3.02 eV, respectively. We also calculated the moment of the $Cu_{12}Fe$ cluster with O_h symmetry, and an atomic distance equal to that in the bulk phase, and found that the local magnetic moment of Fe is 2.28μ_B, which is in good agreement with the calculated value of 2.25μ_B found by Blaha and Callaway;[8] all these results indicate that our calculations are reliable.

A. Binding energy and stability

Table I shows the results for 3d impurities in the center of Cu_{12}. It can be seen that the binding energy of an icosahedral structure is about 2 eV higher than that of an octahedral, one, which suggests that the icosahedral structure is more stable than octahedral structure. In fact, pure Cu clusters with icosahedral closed-shell structure are most stable up to 2500 atoms, and cuboctahedral clusters with closed-shell structure are unstable up to 2000 atoms.[15] For bimetallic Cu-Ni and Cu-Pd systems, embedded-atom-method studies also indicated that an icosahedral structure is favored over a cuboctahedral one.[16] All these results imply that doping with 3d does not change the symmetry of equilibrium structure. For 4d impurities, calculations were carried out on icosahedral structure; the results are given in Table II. By comparing the difference Δ_b, which is defined as the difference between the binding energy of $Cu_{12}R$ and $Cu_{12}Cu$ clusters, we can examine the relative stability between the genuine $Cu_{12}Cu$ and doped $Cu_{12}R$ clusters. For all 3d impurities,

FIG. 1. The average binding energy for $Cu_{12}R$ clusters with I_h symmetry. The square is for the $3d$ element, and the circle is for the $4d$ element.
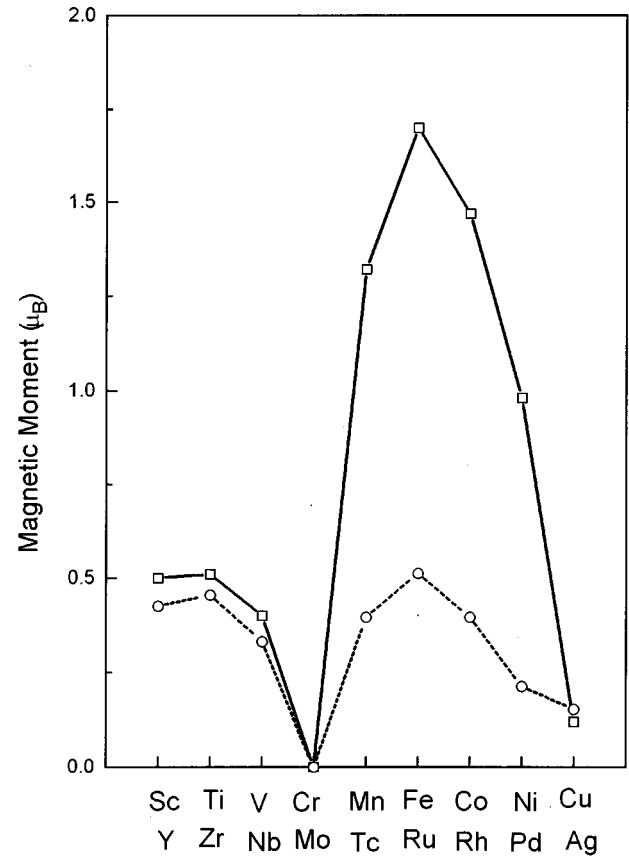
FIG. 2. The local magnetic moments for $3d$ and $4d$ impurities in I_h symmetry. The square is for the $3d$ element, and circle is for the $4d$ element.

TABLE III. The data for electronic structures for $Cu_{12}R$ clusters with I_h symmetry.

| Cluster	HOMO					LUMO			Δ
	spin	energy	symbol	electrons	configuration	energy	symbol	spin	
$Cu_{12}Sc$	−	-8.2807	h_g	2	open	-5.3308	a_g	+	2.952
$Cu_{12}Ti$	−	-8.2069	h_g	3	open	-5.4863	a_g	+	2.820
$Cu_{12}V$	−	-8.2983	h_g	4	open	-5.4926	a_g	+	2.806
$Cu_{12}Cr$	−	-7.8647	h_g	5	closed	-5.2926	a_g	−	2.572
$Cu_{12}Mn$	+	-5.7828	h_g	1	open	-5.4580	a_g	−	0.325
$Cu_{12}Fe$	+	-6.2188	h_g	2	open	-5.6662	h_g	−	0.553
$Cu_{12}Co$	+	-6.5017	h_g	3	open	-6.0172	h_g	−	0.485
$Cu_{12}Ni$	+	-6.7011	h_g	4	open	-6.3079	h_g	−	0.393
$Cu_{12}Cu$	+	-7.4089	h_g	5	closed	-7.0411	h_g	−	0.3678
$Cu_{12}Y$	−	-8.0357	h_g	2	open	-4.8302	a_g	+	3.206
$Cu_{12}Zr$	−	-8.1029	h_g	3	open	-5.1314	a_g	+	3.271
$Cu_{12}Nb$	−	-8.1173	h_g	4	open	-5.0365	a_g	+	3.081
$Cu_{12}Mo$	−	-8.0101	h_g	5	closed	-5.0112	a_g	+	3.000
$Cu_{12}Tc$	+	-5.2585	h_g	1	open	-5.1439	h_g	−	0.114
$Cu_{12}Ru$	+	-5.7133	h_g	2	open	-5.5406	h_g	−	0.173
$Cu_{12}Rh$	+	-6.0985	h_g	3	open	-5.8795	h_g	−	0.219
$Cu_{12}Pd$	+	-6.9203	h_g	4	open	-6.6272	h_g	−	0.293
$Cu_{12}Ag$	+	-7.0038	h_g	5	closed	-6.6366	h_g	−	0.367
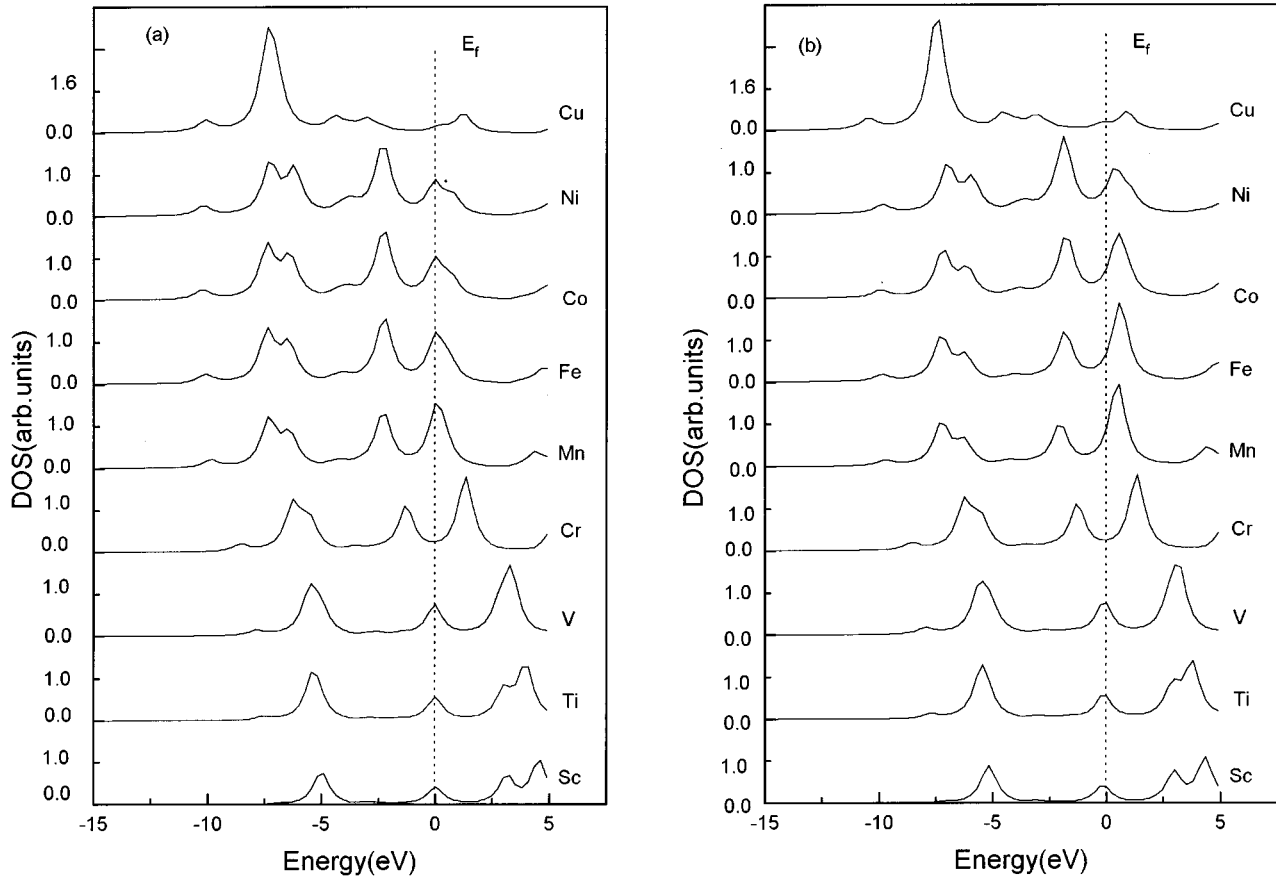
FIG. 3. The local densities of states (LDOS) for $3d$ impurities. (a) Spin-up. (b) Spin-down.

with the impurity species. A large gap exists for an impurity with a valence electron number less than or equal to 5; i.e., from Sc to Cr for $3d$ series and from Y to Mo for $4d$ series, a small gap exists. Table III also gives the ground-state elec-tronic configurations. The HOMO's for $Cu_{12}Cr$, $Cu_{12}Cu$, $Cu_{12}Mo$, and $Cu_{12}Ag$ are fully occupied; these clusters are thus stable. Moreover, for these clusters, $Cu_{12}Cr$ and $Cu_{12}Mo$ have large gaps and large binding energies, and $Cu_{12}Cu$ and $Cu_{12}Ag$ have small gaps and small binding en-ergies, which implies that for cluster with filled HOMO's the

magnitude of the gap reflects the binding strength to a certain degree; the smaller gap may be attributed to the weaker bind-ing. Accordingly, the binding energy per atom would be small.

In a cluster, the contraction of the bond length is believed to be a reflection of the surface effect. In order to see this effect, we compared the bond length with the sum of the radii of Cu and impurity atoms ($r_{Cu} + r_R$); as listed in Tables I and II, the bond-length contraction effects in all clusters

TABLE IV. The changes of the local magnetic moments for $3d$ impurities with controlled host-impurity interactions. The first row is for the orbitals involved in interactions, and the symbols in brackets are for impurities.

	$3d4s4p$ ($3d4s4p$)	$3d4s$ ($3d4s4p$)	$4s4p$ ($3d4s4p$)	$3d4s4p$ ($3d4s$)	$3d4s$ ($3d4s$)
Sc	0.504	0.29	1.170	0.458	0.287
Ti	0.512	0.368	1.223	0.498	0.374
V	0.404	0.362	0.899	0.386	0.357
Cr	0.0	0.0	0.0	0.0	0.0
Mn	1.322	2.432	1.173	1.080	1.869
Fe	1.699	3.033	1.545	1.338	2.379
Co	1.471	2.399	1.380	1.198	1.903
Ni	0.978	1.583	0.938	0.800	1.244

TABLE V. The changes of the local magnetic moments for $4d$ impurities with controlled host-impurity interactions. The first row is for the orbitals involved in interactions, and the symbols in brackets are for impurities.

	$3d4s4p$ ($4d5s5p$)	$3d4s$ ($4d5s5p$)	$4s4p$ ($4d5s5p$)	$3d4s$ ($4d5s$)
Y	0.426	0.361	1.176	0.351
Zr	0.455	0.332	1.102	0.321
Nb	0.331	0.264	0.799	0.251
Mo	0.0	0.0	0.0	0.0
Tc	0.396	0.709	0.330	0.622
Ru	0.512	1.008	0.416	0.876
Rh	0.396	0.934	0.306	0.802
Pd	0.213	0.179	0.303	0.171
Ag	0.153	0.114	0.237	0.074

can clearly be seen. Taking $Cu_{12}Cu$ as an example, the bond length between the central and surface Cu atoms are 2.346 Å, which is 8.9% shorter than the nearest-neighbor distance of 2.556 Å in the fcc crystal; the magnitude of bond length contraction is reasonable. But for some other impurities (e.g., Sc and Y), the contraction is much larger. However, there are no data about the atomic distance available for Cu-Sc and Cu-Y crystal alloys, so the sum of the radii of Cu and impurity atoms is only an approximate reference.

B. Local magnetism of the impurity

Tables I and II give the calculated local moments for $3d$ and $4d$ impurities. We can see that Cr and Mo in Cu clusters are nonmagnetic, similar to the situation of Mo in bulk Pd.[4] All others are magnetic, which induces the host Cu atom to be weakly polarized. According to the coupling rules in the bulk,[19] a spin of a more than half-filled $3d$ shell impurity, such as Fe, Co, and Ni, induces a ferromagnetic d-spin polarization in hosts with a nearly filled or a nearly empty d shell. Our results indicate that in the cluster all impurities with less than a filled d shell can also induce a d-spin polarization parallel to that of impurity in the host. Figure 2 shows changes of local moments for $3d$ and $4d$ series. It is well known that in case of $4d$ element the magnetic moment and the exchange splitting are small, but the general features of changes in moments are similar to that of the $3d$ series. Figures 3 and 4 show the local density of state (LDOS) of

$3d$ and $4d$ impurities, from which we can see that there are no exchange splittings for Cr and Mo, resulting in a zero local moment. Comparing with situations of 3d and 4d impurities in Al_{12} clusters,[7] we find that the local moments of 3d and 4d in Cu clusters are considerably reduced. What interactions between impurity and host are responsible for these changes?

We know that the magnetism of Fe in noble- and transition-metal bulk hosts exhibits remarkable differences from the behavior of Fe in sp metals.[2–4] In transition-metal bulk hosts and in noble-metal bulk hosts (such as Cu, Ag, and Au), the local moment formation of Fe, Co, and Ni ions is governed by the interactions between impurity-d and host-d electrons. For example, Co and Ni were found to be nonmagnetic in sp metals investigated hitherto; moments have been found for Co in Cu, Au, Mo, W, Rh, Pd, and Pt,[1,20] and for Ni in Pd,[21–23] where Fe can also exhibit very stable moments. This interpretation also holds even for $4d$ systems; it has been found that impurity Mo is nonmagnetic in bulk Pd, whereas impurities Ru and Rh exhibit magnetic behavior in bulk Pd.[3] Of course, this d-d interaction picture is consistent with explanations of local magnetism in bulk materials. Now we wonder whether this picture holds for local magnetism in clusters, and what is the role of d-d interactions on the local magnetism in clusters.

Because the interplay of intra-atomic, interatomic, and intrahost interactions is highly complex, it is usually difficult
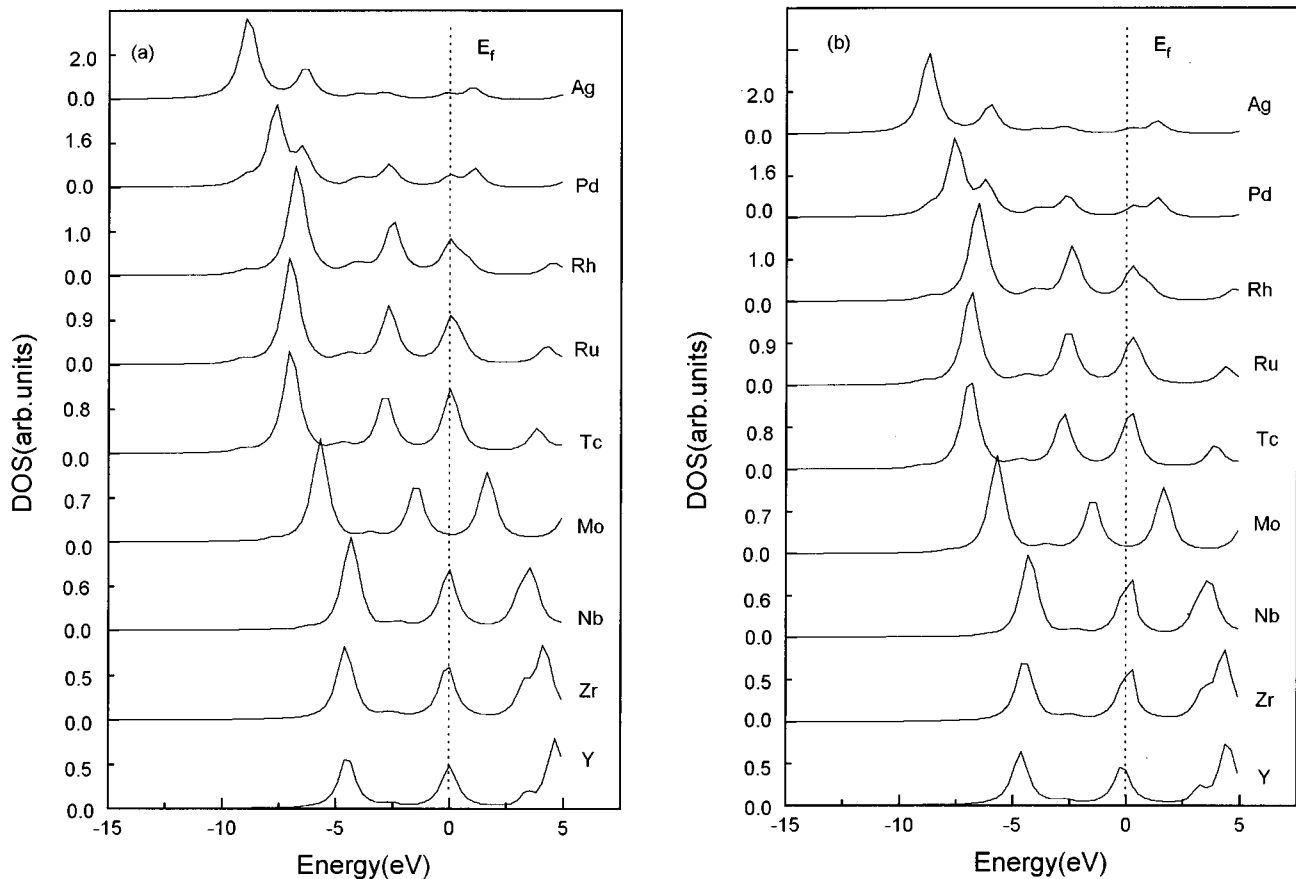

FIG. 4. The local densities of states (LDOS) for $4d$ impurities. (a) Spin-up. (b) Spin-down.

to give some quantitative theoretical analyses for interaction. In order to gain some insight into the qualitative effects of interaction between impurity and host atoms on the local magnetism, we will single out the interaction related to certain orbitals by switching off this orbital, i.e., not let this orbital participate in the interaction. For example, if we want to see the role of the Cu-$3d$ orbital on the local moment of the impurity, we can switch off the Cu-$3d$ orbital by setting the valence orbitals to $4s4p(3d4s4p)$, where the symbols outside and inside the brackets are the valence orbitals of Cu and $3d$-impurity atoms, respectively; therefore, the interactions take place only among these valence orbitals. Calculations are performed with the bond length given in Tables I and II. The obtained local moments of impurities are shown in Tables IV and V for $3d$ and $4d$ series, respectively. In the following, we will concentrate on more detailed analyses of the roles of interactions between impurity and host on the local magnetic moment of impurity.

In Table IV, comparing columns 2 and 3, we can see that switching off the Cu-$4p$ orbital makes the moments of Sc, Ti, and V slightly decreased and makes the moments of Mn, Fe, Co, and Ni considerably increased, which indicates that the interactions of Cu $4p$ orbital with R-spd orbitals have a crucial role on the local magnetic moments for Mn, Fe, Co, and Ni. Comparing columns 2 and 4, switching off the Cu $3d$ 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 Cu $3d$ orbital with R-spd orbitals make large contribution to the moments for Sc, Ti, and V; in particular, the d-d interaction between the impurity and host plays a minor role in the local magnetic moments of Mn, Fe, Co, and Ni, as opposed to the case in the bulk.[4] Comparing columns 2 and 5 and 3 and 6, switching off the R-$4p$ orbital does not much change the local moments of the impurities, implying that the interactions related to the R-$4p$ orbital make little contribution to the local moments.

TABLE VI. Orbital components (%) of HOMO for $Cu_{12}R$ clusters with I_h symmetry.

| Cluster | HOMO | R | | Cu | |
		$3d(4d)$	$3d$	$4s$	$4p$
$Cu_{12}Sc$	h_g	10.3	27.4	47.5	16.0
$Cu_{12}Ti$	h_g	14.1	29.0	42.2	15.9
$Cu_{12}V$	h_g	18.5	30.3	39.2	13.2
$Cu_{12}Cr$	h_g	27.9	35.1	27.1	10.3
$Cu_{12}Mn$	h_g	30.5	6.3	41.5	21.8
$Cu_{12}Fe$	h_g	27.1	15.3	41.5	23.7
$Cu_{12}Co$	h_g	22.5	9.3	43.4	24.8
$Cu_{12}Ni$	h_g	18.5	10.9	45.2	25.4
$Cu_{12}Y$	h_g	12.2	28.5	43.6	19.3
$Cu_{12}Zr$	h_g	15.4	32.7	38.7	16.3
$Cu_{12}Nb$	h_g	20.5	33.2	34.6	13.9
$Cu_{12}Mo$	h_g	23.3	41.1	25.3	11.7
$Cu_{12}Tc$	h_g	23.3	7.1	46.2	19.2
$Cu_{12}Ru$	h_g	21.6	7.4	47.1	23.6
$Cu_{12}Rh$	h_g	19.0	7.9	48.1	24.9
$Cu_{12}Pd$	h_g	9.9	11.3	50.6	27.6
$Cu_{12}Ag$	h_g	5.8	18.7	52.2	29.1

The situation for $4d$ impurities follows basically the same trends as discussed for $3d$ impurities. In Table V, comparing columns 2 and 3, we can see that switching off the Cu-$4p$ orbital decreases the moments of Y, Zr, Nb, Pd, and Ag slightly, and increases the moments of Tc, Ru, and Rh considerably, which indicates that the interactions of the Cu-$4p$ orbital with R-spd orbitals make large contributions to the moments for Tc, Ru, and Rh. Comparing columns 2 and 4, switching off the Cu-$3d$ orbital increases the moments of Y, Zr, and Nb considerably, decreases the moments of Tc, Ru, and Rh slightly, and increases the moments of Pd and Ag slightly, which indicates that the interactions of Cu-$3d$ orbital with R-spd orbitals make large contributions to the moments for Y, Zr, and Nb, in particular, the d-d interaction between the impurity and host plays a minor role in the local magnetic moments of Tc, Ru, and Rh. Comparing columns 3 and 5, switching off the R-$4p$ orbital does not much change the local moments of the impurities, implying that interactions related to R-$4p$ orbital make only slight contributions to the local moments.

We know that the main contribution to the magnetic moment comes from d states. For the impurity, the behavior of d levels are fivefold degenerate in icosahedral symmetry, and therefore hybridize only with H_g levels of the empty center icosahedral Cu_{12} cluster. The above changes of local magnetism are understandable in view of the hybridizations between d states of the impurity and the levels of Cu. For simplicity, Table VI gives the orbital percentage components only for HOMO's of all clusters considered, from which we can see that the clusters considered can be classified into three groups according to the orbital components. The first group includes the clusters where the impurities are Sc, Ti, V, Y, Zr, Nb, Pd, or Ag; the second group clusters where the impurities are Mn, Fe, Co, Ni, Tc, Ru, or Rh; and the third group clusters where the impurities are Cr or Mo. Comparing groups 1 and 2, we can see that the Cu-$4p$ orbitals more strongly hybridize with R-d orbitals in group 2 than those in group 1; accordingly the Cu-$4p$ orbitals have larger effects on the local magnetic moments of impurities in group 2 than those in group 1. However, the Cu-d orbitals more strongly hybridize with R-d orbitals in group 1 than those in group 2, and therefore the Cu-d orbitals play larger roles in the local magnetic moments of impurities in group 1 than those in group 2. In the third group, the d states of the impurity and the s state of Cu nearly have the same weight, indicating that there are much stronger d-s hybridizations between the impurity and Cu.

From the above discussions, we can see that d-d interactions between the impurity and host strongly suppress the impurity moment at the beginning of $3d$ and $4d$ series, and slightly enhance the impurity moment at the end of $3d$ and $4d$ series. In this sense, the d-d interactions are much stronger for impurities at the beginning of series than those at the end of series. In fact, we know that the wave functions 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 an increases of contraction of a d orbital, and therefore the d-d hybridization effect is stronger for the early transition atoms (Sc, Ti, V, Y, Zr, or Nb) than for the late ones (Mn, Fe, Co, Ni, Tc, Ru, or Rh). We can see that the conclusions obtained above are reasonable

TABLE VII. The local density of states (n_{loc}) at E_F for $3d$ impurities in $Cu_{12}R$ clusters with I_h structure (R:$3d$). The exchange integral I is taken from Ref. 28.

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
n_{loc}	0.79	1.12	1.49	0.43	2.08	1.71	1.57	1.40
I	0.68	0.68	0.70	0.76	0.82	0.92	0.98	1.00

physically. It should be pointed out that there are two competing factors that affect the stability and magnetic behaviors: from Sc to Ni and from Y to Ag, the d orbital of the impurity contracts; 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 the d level is reduced to close to the d level of the Cu atom, so the d-d interaction is increased. The stability and magnetic behaviors result from the compromise of these two competing factors. Because the electronic states of d electrons of an impurity in a cluster are different from those in the bulk, the different magnetic behaviors for impurities in cluster and in bulk can be displayed.

C. The test for Stoner-like criterion

A simple criterion has been proposed for the existence of the local magnetic moment[24]

$$I \times n_{loc}(E_F) \geq 1. \qquad (10)$$

Here I is the exchange integral for an impurity atom, which can be calculated as described by Refs. 25 and 28. $n_{loc}(E_F)$ is the LDOS at the impurity site. This criterion formally resembles the well-known Stoner criterion for the formation of a ferromagnetic phase, but in Stoner's criterion, $n_{loc}(E_F)$ in Eq. (10) should be replaced by the total DOS of the solid.

Willenborg, Zeller, and Dederich[26] studied the local magnetism of $4d$ impurities in an Ag matrix, and discussed the magnetism with the Stoner-like criterion for the occurrence of a local moment. They found that only Mo and Tc are magnetic and satisfy the Stoner-like criterion. Blügel also used this criterion to discuss qualitatively the existence of ferromagnetism for a $4d$-metal monolayer on Ag, Au, and Pd(001)surfaces.[27] Is this criterion valid for the local moment in a cluster? In Tables VII and VIII, we list $n_{loc}(E_F)$ for $3d$ and $4d$ impurities in Cu clusters, respectively. It has been found that for $3d$ elements in bulk I is about 0.68–1.0 eV, and for $4d$ elements in bulk I is about 0.6–0.82 eV.[28] If we adopt these values to judge the existence of the local magnetic moment for $3d$ and $4d$ impurities in Cu_{12} clusters, we can find that this criterion seems to be valid only for V, Mn, Fe, Co, Ni, Nb, Tc, Ru, and Rh, and not valid for the

TABLE VIII. The local density of states (n_{loc}) at E_F for $4d$ impurities in $Cu_{12}R$ clusters with I_h structure (R:$4d$), the exchange integral I is taken from Ref. 28.

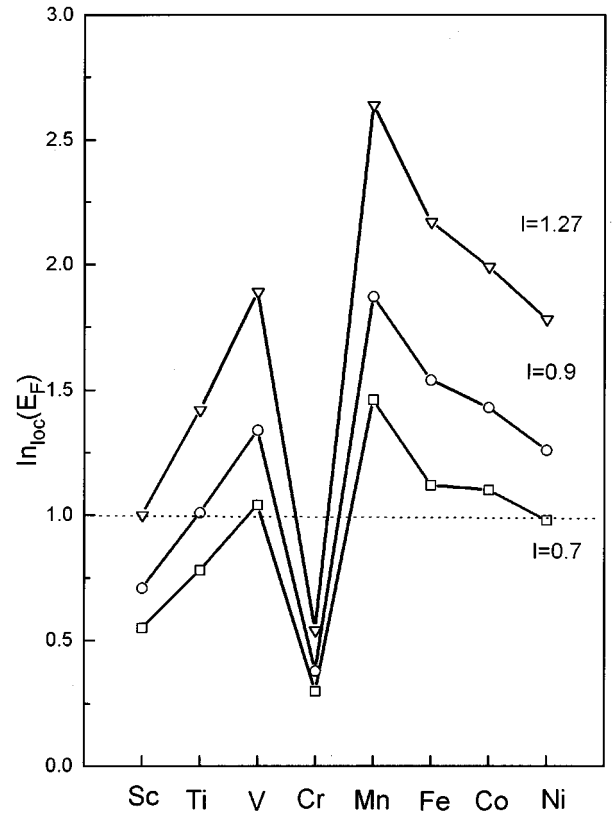|	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
n_{loc}	0.91	1.20	1.65	0.25	2.26	1.85	1.52	0.82	0.52
I	0.65	0.62	0.60	0.63	0.60	0.60	0.65	0.68	0.82

FIG. 5. Stoner-like criterion for $3d$ impurities in $Cu_{12}R$ clusters with I_h symmetry.
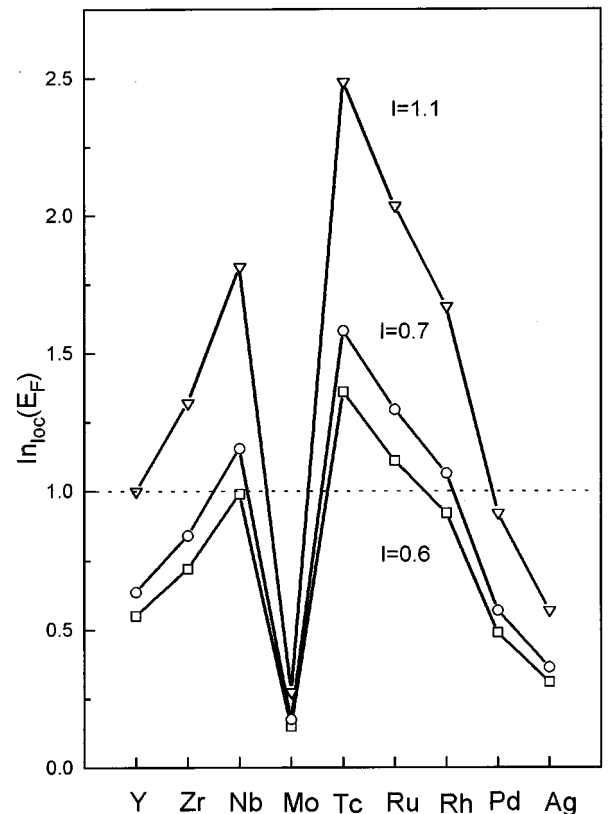

FIG. 6. Stoner-like criterion for $4d$ impurities in $Cu_{12}R$ clusters with I_h symmetry.

others. The most probable reason for this may be that the exchange integral I in a cluster would be different from that in bulk, because the local environment for an impurity in a cluster is quite different from that in bulk; e.g., there are bond-length contraction effects, reduced coordination number, and higher symmetry in a cluster, and all of these will affect the electronic structures of an impurity. However, there are no experimental and theoretical studies available for the exchange integral I of impurity in cluster, to our knowledge. Figures 5 and 6 show the product $n_{loc}(E_F)I$ for three different exchange integrals (I=0.7, 0.9, and 1.27 eV for the $3d$ impurity; I=0.6, 0.7, and 1.1 eV for the $4d$ impurity). For the $3d$ impurity, if I=0.7 eV, only V, Mn, Fe, and Co are magnetic; Ni is nearly magnetic, and the others are nonmagnetic. If I=0.9 eV, only Sc and Cr are nonmagnetic; whereas, for I=1.27 eV, except for Cr all other $3d$ impurities are magnetic. For a $4d$ impurity, if I=0.6 eV, only Tc and Ru are magnetic, and Nb is nearly magnetic; for I=0.7 eV, only Nb, Tc, Ru, and Rh are magnetic; and for I=1.1 eV, Y, Zr, Nb, Tc, Ru, and Rh are magnetic. In order to make Pd and Ag magnetic, the value of I must be equal to at least 1.92 eV, which is much larger than that in the bulk. We can see that the large density of states at E_F would suggest that the impurity has a tendency to develop a local magnetic moment; however, the quantitative relation is not clear yet.

IV. SUMMARY

In this paper we presented systematic studies on the stability and electronic and magnetic properties for $3d$ and $4d$ elements in Cu_{12} clusters. The icosahedral structure was found to be more stable than the octahedral structure. The alloying effects in doped clusters were seen to have an important effect on binding energy. Cr and Tc have the lowest energy in an Al_{12} cluster, and we predicted that V and Nb have the lowest binding energy in a Cu_{12} cluster. Special attention was paid to the roles of interactions between impurity and host on the local moment of impurity, which reveals a close resemblance of interactions between $3d$ and $4d$ impurities. It was observed that the behaviors of local magnetism for $3d$ ($4d$) impurities in Cu clusters are different from those in bulk as well as in Al clusters. Except for Cr and Mo, all other $3d$ and $4d$ elements exist in Cu_{12} clusters as impurities, displaying a definite local magnetic moment. Contrary to previous studies[3,4] in which d-d interaction was found to be responsible for the existence of the local magnetic moment, we found that interactions of Cu-p orbitals with R-spd orbitals play a crucial role in the local magnetic moments of impurities with more than a half-filled d shell, such as Mn, Fe, Co, Ni, Tc, Ru, and Rh. The interactions of Cu-d orbitals with R-spd orbitals make important contributions to the local magnetic moments for impurities with less than a half-filled d shell, such as Sc, Ti, V, Y, Zr, and Nb. We also tested the Stoner-like criterion for the occurrence of a local moment in $Cu_{12}R$ clusters, and found that the Stoner-like criterion is valid for many cases. However, this subject needs to be more extensively studied.

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