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Shan-Ying Wang

Tohoku University, Tsinghua University

Jing-Zhi Yu

Tohoku University

Hiroshi Mizuseki

Tohoku University

See next page for additional authors

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Authors

Shan-Ying Wang, Jing-Zhi Yu, Hiroshi Mizuseki, Qiang Sun, Chong-Yu Wang, and Yoshiyuki Kawazoe

Energetics and local spin magnetic moment of single 3,4*d* impurities encapsulated in an icosahedral Au₁₂ cage

Shan-Ying Wang,^{1,2,*} Jing-Zhi Yu,¹ Hiroshi Mizuseki,¹ Qiang Sun,³ Chong-Yu Wang,² and Yoshiyuki Kawazoe¹

¹*Institute for Materials Research, Tohoku University, Aoba-ku, Sendai 980-8577, Japan*

²*Department of Physics, Tsinghua University, Beijing 100084, People's Republic of China*

³*Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284-2000, USA*

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The energetics and local spin magnetic moment of a single 3,4*d* impurity (Sc-Ni, Y-Pd) encapsulated in an icosahedral Au₁₂ cage have been studied theoretically by using a real-space first-principles cluster method with generalized gradient approximation for exchange-correlation functional. The relativistic effect is considered by scalar relativistic pseudopotentials. All doped clusters show unexpected large relative binding energies compared with icosahedral Au₁₃ cluster. The smallest and the largest values appear at Pd and Zr, 2.186 and 7.791 eV per cluster, respectively, indicating doping could stabilize the icosahedral Au₁₂ cage and promote the formation of a new binary alloy cluster. Comparatively large magnetic moments are observed for 3*d* elements Cr, Mn, Fe, Co, and Ni (2.265, 3.512, 3.064, 1.947, and 0.943 μ_B), and 4*d* elements Tc, Ru, and Rh (0.758, 1.137, and 0.893 μ_B). The density of states and the relativistic effects on electronic structure are discussed.

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I. INTRODUCTION

Single transition metal element isolated in an *sp* metal host is a classical ideal system for studying how the *d* electron interact with nearly free electron gas to form a local magnetic moment (LMM).¹⁻⁴ The recent advanced synthesis techniques are making scientists able to explore such a problem in many different types of system. For example, it has been shown experimentally that transition metal element can also display unusual large LMM when absorbed on or embedded into an *sp* metal surface.^{5,6} The LMM of transition metal element is rather sensitive to the environment, and adjusted dramatically by the shape and size of the environment formed by the host atoms. From this point of view, one can design many different types of system for studying the local magnetism problem. For example, a single 3,4*d* impurity encapsulated in an *sp* metal cage may be an interesting system. The idea of doping an impurity into a cluster cage initially appeared in the work^{7,8} of Callaway and Dunlap, and then extended explicitly by Gong, Kumar, Sun, and Kawazoe as studying the stability and local magnetic properties of 3,4*d* impurities encapsulated in icosahedral Al₁₂, Cu₁₂, and Ag₁₂ cages.⁹⁻¹¹ These theoretical works predicted that some 3,4*d* impurities could show relatively large local spin magnetic moments (LSMM's) when encapsulated in an *sp* metal cage.

On the other hand, the studies on pure noble metal element and its binary alloy clusters have attracted considerable interest in recent years. A more recent experiment¹² did prove the presence of small binary alloy Au_{*N*}X clusters (*X* = Sc, Ti, V, Cr, Mn, Fe, Co, and Ni). In contrast to pure Cu and Ag clusters, small pure Au cluster is believed^{13,14} to favor three-dimensional amorphous or planar configurations. While from technical viewpoint, high-symmetrical clusters sometimes are necessary as building blocks in nanostructures such as nanograin-film and nanocrystalline materials. For the unstable icosahedral Au₁₂ cage (Au₁₃), doping an 3,4*d* im-

purity (substituting the center Au atom with an 3,4*d* impurity) may be a good way to stabilize the structure. This has been proved feasible for Mo by a recent experiment.¹⁵

The above research background motivates the present study. As a continuation of previous theoretical research work, we have investigated the energetics and LSMM of a single 3,4*d* impurity encapsulated in an icosahedral Au₁₂ cage by employing a state-of-the-art first-principles method called density functional for molecules (DMol)^{16,17} based on density functional theory (DFT).^{18,19} The case of the impurity atom substituting a surface Au atom is not included in the present study. It will be seen that some 3,4*d* impurities do display very large LSMM in the icosahedral Au₁₂ cage. The calculated binding energy suggests that doping an 3,4*d* element will be a feasible way to stabilize icosahedral Au₁₂ cage to yield a binary alloy cluster. The LSMM and electronic structure are discussed in detail within the spin DFT scheme. As having been frequently found in many other kinds of low-dimensional systems such as surface, overlayer, sandwich, superlattice and adatom absorbed on a surface, we believe that large magnetic moment could also be found in a binary alloy cluster.

II. METHOD AND COMPUTATIONAL DETAIL

DMol is a widely used real-space first-principles cluster method, and has been successfully applied to many problems such as structural stability of molecular clusters, chemisorption and surface reconstruction. It can perform accurate and efficient self-consistent calculation and structural optimization. The equilibrium structure can be obtained by relaxing atom until the energy gradients are deemed to be zero.

To ensure the results accurate and reliable, we have chosen an exchange correlation functional proposed by Perdew (PW91),²⁰ a general gradient approximation (GGA) that has been successfully applied to the studies on transition metal systems, for instance, medium-size Mn clusters.²¹ The rela-

TABLE I. The binding energies (BE, in eV) and equilibrium distances (r , in Å) of 3,4*d* and Au dimers obtained by using a basis set composed of double numerical basis with polarized functions.

	Theory		Experiment ^a	
	BE	r	BE	r
Ti ₂	4.250	1.968	1.54±0.19	1.942
V ₂	5.355	1.799	2.75	1.783
Cr ₂	0.638	1.648	1.53±0.06	1.679
Mn ₂	0.802	2.580	0.3±0.3	3.4
Fe ₂	3.392	1.994	1.15±0.09	2.02
Ni ₂	5.535	2.107	2.04	2.155
Nb ₂	4.458	2.137	5.22±0.31	2.078
Mo ₂	2.617	1.990	4.474±0.010	1.94
Rh ₂	5.619	2.260	2.460±0.005	2.28
Au ₂	2.165	2.489	2.29	2.472

^aThe experimental data can be found in Refs. 32–44.

tivistic effect is significant for Au. Currently, DMol can consider scalar relativistic effects, such as Darwin and mass velocity, by either effective core potential calculation or all-electron calculation. The properties of those heavier atoms are reproduced using an essentially nonrelativistic Hamiltonian including pseudopotentials representing scalar relativistic effects.^{22–24} A basis set composed of double numerical basis (3*d*, 4*s* doubled for 3*d* impurity and 4*d*, 5*s* doubled for 4*d* impurity, and 5*d*, 6*s* doubled for Au) with polarized functions (4*p* for 3*d* impurity and 5*p* for 4*d* impurity, and 6*p* for Au) is adopted, and all-electron spin-unrestricted calculations are performed. These can ensure much better descriptions on binding energy and magnetism, and minimize the influence of basis on calculation results to the least. The quality of the basis set was discussed in detail in the previous literatures.^{16,17} We have further checked the basis set by calculations on some 3,4*d* and Au dimers. It can be seen from Table I that the present selected basis set can give reasonable results except for Mn dimer, comparable to the various different basis sets used in the recent *ab initio* studies.^{25,26} Note all these theoretical studies failed in Mn dimer and have some errors on binding energy.

Figure 1 shows the geometrical structure of a single 3,4*d* impurity encapsulated in an icosahedral Au₁₂ cage. In structural optimization, the 12 Au atoms are relaxed freely under I_h symmetry. The energy gradient and atomic displacement are converged to 3×10^{-3} eV Å⁻¹ and 1×10^{-4} Å respectively. For self-consistent field iteration, the charge density is converged to 1×10^{-5} , which corresponds to a total energy convergence of 1×10^{-6} eV. The order of the multipolar function used for fitting charge density and solving Coulomb potential is set to be one greater than the maximum angular momentum in the basis set. About 1500 fixed integration points around each atom are used. The binding energy (BE) is defined as

$$BE = E_a - E_t,$$

where E_a is the sum of the total energies of all single atoms and E_t is the total energy of the cluster.

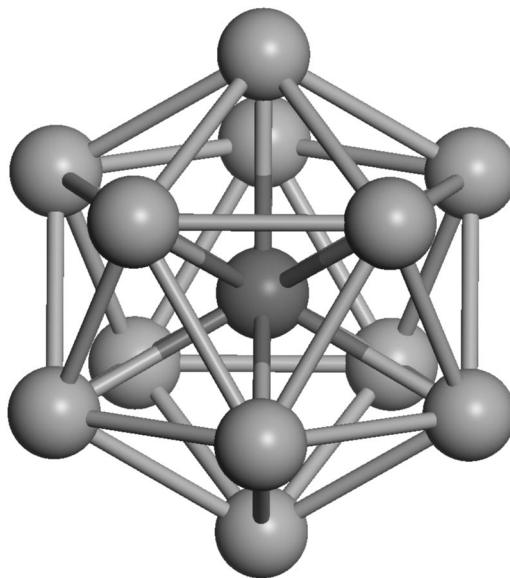


FIG. 1. The cluster model of a single 3,4*d* impurity encapsulated in an icosahedral Au₁₂ cage. The center dark ball represents the 3,4*d* impurity and the outside 12 gray balls represent Au atoms.

III. RESULTS AND DISCUSSIONS

The calculated results are summarized in Table II with that on icosahedral Au₁₃ for comparison. It is interesting to know if the doped icosahedral Au₁₂ could be stabilized at a three-dimensional shape. This can be simply concluded by comparing the BE of doped Au₁₂ with that of pure Au₁₃. As well known, energy difference between two isomers is rather significant if the value exceeds 1 eV per cluster. From Table II we can see that the BE's of the doped Au₁₂ clusters are surprisingly larger than that of pure icosahedral Au₁₃. The smallest and the largest relative BE's compared with pure icosahedral Au₁₃ appear at Pd and Zr, 2.186 and 7.791 eV per cluster, respectively. Clusters doped with Ti, V, and Ni also show very large relative BE's beyond 7.0 eV per cluster. The relative BE's of the rest doped clusters are beyond 3.2 eV per cluster. Even though it is not much strict to make conclusions only from BE, these unusual large relative BE's still convince us that doping a single 3,4*d* impurity could make the icosahedral Au₁₂ cage stable, and form a new binary alloy cluster of three-dimensional rather than planar structure.

Local magnetism is another interesting problem in these doped systems. For 3*d* impurities Sc, Ti, and V just show small LSMM's while relatively large LSMM's are observed from Cr to Ni. Mn has the largest one, about 3.51 μ_B and then Fe about 3.06 μ_B . These features basically extend to 4*d* impurities except that all their LSMM's decrease to a certain extent and an "abnormal" case occurs to Mo. The former part of elements Y, Zr, and Nb still show small LSMM's and the latter ones from Tc to Pd show relatively strong LSMM's. Ru has the largest LSMM about 1.14 μ_B and Rh is next to it, about 0.89 μ_B . It is meaningful to know why these 3,4*d* impurities display so different LSMM's as being encapsulated in an icosahedral Au₁₂ cage. We can give a simple qualitative explanation by considering the chemical bonding

TABLE II. The calculated data on a single $3,4d$ impurity encapsulated in an icosahedral Au_{12} cage: the cluster binding energy (BE, in eV), the cluster radius R (in Å), the HOMO and LUMO states (symmetry and spin), the HOMO-LUMO gap ΔE (in eV), the electron occupation number n in the HOMO, the total magnetic moment M_t of cluster (in μ_B), and the atomic magnetic moment M (in μ_B). Symbol + and - denote spin-up and spin-down states, respectively. Data on pure icosahedral Au_{13} and the relative binding energy (RBE, in eV) compared to Au_{13} are included. Some data obtained by nonrelativistic all-electron calculations are given in the parentheses for comparison.

	BE	RBE	R	HOMO	LUMO	ΔE	n	M_t	$M_{3,4d}$	M_{Au}
Sc	33.796(14.342)	5.965(4.682)	2.690(2.975)	HG(-)	AG(+)	1.973(1.315)	2	3	0.190(0.765)	0.234
Ti	35.320(15.374)	7.489(5.714)	2.659(2.943)	HG(-)	HG(+)	1.814(1.320)	3	2	0.265(1.286)	0.145
V	34.901(15.409)	7.070(5.749)	2.643(2.928)	HG(-)	HG(+)	1.241(0.982)	4	1	0.480(2.547)	0.043
Cr	31.507(12.631)	3.676(2.971)	2.642(2.925)	HG(-)	HG(+)	0.790(0.818)	5	0	2.265(3.646)	-0.189
Mn	31.061(12.526)	3.230(2.866)	2.648(2.920)	HG(+)	HG(-)	1.300(0.508)	1	1	3.512(3.785)	-0.209
Fe	32.035(13.585)	4.204(3.925)	2.643(2.908)	HG(+)	HG(-)	0.758(0.540)	2	2	3.064(2.826)	-0.089
Co	32.239(14.163)	4.408(4.503)	2.637(2.900)	HG(+)	HG(-)	0.469(0.414)	3	3	1.947(1.608)	0.088
Ni	32.009(14.321)	4.178(4.661)	2.638(2.900)	HG(+)	HG(-)	0.362(0.365)	4	4	0.943(0.665)	0.255
Y	32.934(14.366)	5.103(4.706)	2.760(3.039)	HG(-)	T2U(+)	2.116(1.579)	2	3	0.144(0.815)	0.238
Zr	35.622(16.334)	7.791(6.674)	2.722(2.996)	HG(-)	AG(+)	2.077(1.625)	3	2	0.163(0.887)	0.153
Nb	35.125(15.511)	7.294(5.851)	2.693(2.967)	HG(-)	HG(+)	2.016(1.715)	4	1	0.135(0.818)	0.072
Mo	32.675(14.442)	4.844(4.782)	2.677(2.945)	HG(\pm)	HG(\pm)	1.578(1.705)	10	0	0.000(0.000)	0.000
Tc	32.892(15.423)	5.061(5.763)	2.676(2.939)	HG(+)	HG(-)	0.242(0.233)	1	1	0.758(1.000)	0.020
Ru	31.184(14.720)	3.353(5.060)	2.678(2.938)	HG(+)	HG(-)	0.347(0.262)	2	2	1.137(0.961)	0.072
Rh	31.314(14.463)	3.483(4.803)	2.681(2.938)	HG(+)	HG(-)	0.323(0.274)	3	3	0.893(0.581)	0.176
Pd	30.017(11.790)	2.186(2.130)	2.688(2.950)	HG(+)	HG(-)	0.309(0.329)	4	4	0.460(0.233)	0.295
Au	27.831(9.660)		2.700(2.996)	HG(+)	HG(-)	0.358(0.408)	5	5	0.223(0.034)	0.398

and the magnetic interaction, two important opposite and competitive factors for BE of transition metal cluster or cluster including transition metal elements. A cluster usually tends to enhance its BE and to make the structure stable and compact by forming chemical bonds as more as possible. This, however, is not the most efficient way even the chemical bonding making the most contributions to BE. The magnetic interaction sometimes also plays an important role. To increase the exchange-splittings of d orbitals by reducing the strength of some chemical bonds can further enhance the BE. As a result of the competition between the two factors, a cluster finally reaches its stable structural and magnetic states. The former part of $3d$ elements such as Sc, Ti, and V show weak LSMM's because of the activities of their s, p electrons, which result in strong hybridizations that can suppress the occurrence of large exchange splittings of $3d$ orbitals, reducing the magnetic interaction. For the latter part of $3d$ elements from Cr to Ni, the magnetic interaction becomes strong enough to yield comparatively large LSMM. We can see that Cr, Mn, and Fe even make the polarization of Au_{12} cage antiparallel with their LSMM's. The relative weakness of LSMM's of $4d$ impurities is mainly related to their large atomic radii. Large overlaps between the atomic orbitals could not promote the formation of LSMM. The case of Mo seems "abnormal." The magnetic interaction is completely suppressed by the chemical bonding and all electrons are paired to give a closed-shell system. Our results on Mo are consistent with the experiment.¹⁵ It is worthwhile to mention another similar theoretical study on an $5d$ element of same column W,²⁷ where a highly stable closed-shell structure of W encapsulated in an icosahedral Au_{12} cage is predicted.

Compared with the doped clusters, Au_{13} has the highest total magnetic moment. The individual Au atom in it, however, just shows small magnetic moment. The most number of unpaired electrons rather than the largest exchange-splittings result in the highest total magnetic moment of Au_{13} . Certainly a small exchange-splitting of molecular orbital is necessary in this regard. This is physically reasonable since Au is not a magnetic element. The number of paired electrons in the HOMO and its neighboring occupied molecular orbitals increases from Sc to Cr and Y to Mo, and decreases from Mn to Ni and Tc to Pd. Consequently, the total magnetic moment of cluster decreases from Sc to Cr and Y to Mo, but increases from Mn to Ni and Tc to Pd. This looks similar to the occupation feature of the "rigid band" in an alloy with different impurities. Nevertheless, we should notice that the LSMM for each individual atom in these doped clusters is not proportional to the total magnetic moment of cluster. Such case is easily seen in the spin antiparallel systems such as Cr, Mn, and Fe doped clusters. For case of Cr, the total magnetic moment of cluster is zero. The Cr impurity, however, has a rather large LSMM ($2.265 \mu_B$).

The size effect on LSMM is always dramatic. To see this, here we draw a comparison between the LSMM in the cluster and that in the solid for all $3d$ impurities except for Sc. Compared with the nearest neighboring interatomic distances in the solid (about 2.89, 2.62, 2.50, 2.48, 2.50, and 2.49 Å for hcp Ti, bcc V, bcc Cr, bcc Fe, hcp Co, and fcc Ni, respectively), the interatomic distance between the $3d$ impurity and Au (the cluster radius shown in Table II) decreases by about 8% for Ti, but increases by about 5% for Cr, Fe, Co, and Ni, and changes slightly for V. The bulk hcp Ti and bcc V are

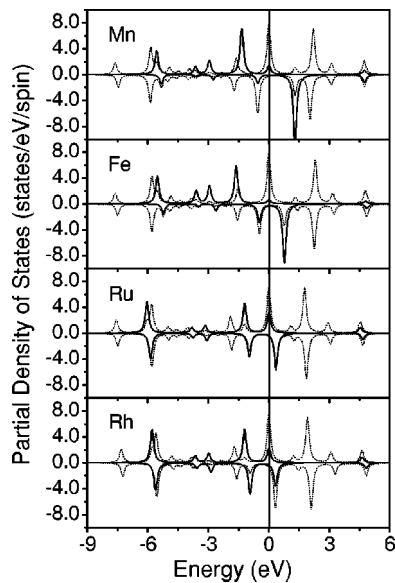


FIG. 2. The spin-dependent partial density of states for Mn, Fe, Ru, and Rh encapsulated in an icosahedral Au_{12} cage. The spin-up and the spin-down states are displayed in the up panel (plus value) and down panel (minus value), respectively. The solid line represents the d states of transition metal element, and the dashed line represents the s states of Au. Fermi level is shifted to zero.

Pauli paramagnets and hardly show any LSMM.²⁸ While in cluster they can have small LSMMs, about 0.27 and $0.48 \mu_B$, respectively. The bcc Cr is thought to be a spin density wave system with just a small amplitude of LSMM (the maximum is about $0.60 \mu_B$).²⁸ Mn, Fe, Co, and Ni are strong magnetic elements. They can show net LSMM's at complex cubic (the maximum is about $1.90 \mu_B$), bcc ($2.13 \mu_B$), hcp ($1.52 \mu_B$), and fcc ($0.57 \mu_B$) structures, respectively.^{28,29} From Cr to Ni, obviously all their LSMM's are enhanced greatly when they are encapsulated in an icosahedral Au_{12} cage, where the increased interatomic distance plays an important role.

For system made up of transition and noble metal elements, orbital usually makes little contributions to the magnetic moment. A spin exchange-splitting picture based on spin DFT is enough to give a good description on such problem. As an illustration, we present in Fig. 2 the spin-dependent partial density of states (PDOS) for four typical transition metal elements Mn, Fe, Ru, and Rh. The PDOS is calculated by broadening the energy levels ε_i^σ of molecular orbitals (σ denote spin state) by using a line-shape function Lorentzian with width $\delta=0.1$ eV as follows:

$$\text{DOS}_{\text{ant}}^\sigma(E) = \sum_i P_{i,\text{ant}}^\sigma \frac{\delta/\pi}{(E - \varepsilon_i^\sigma)^2 + \delta^2},$$

where $P_{i,\text{ant}}^\sigma$ (α denotes atom, n and l are, respectively, main and angular quantum numbers) is the state component of atomic orbital in molecular orbital (ε_i^σ) obtained by Mulliken analysis.³⁰ Obviously, strong hybridizations between the d orbitals of $3,4d$ impurity and the $6s$ orbital of Au occur in a wide energy range, from about -5.5 to 5.0 eV. A strong resonant peak appearing at a rather low energy site -5.5 eV

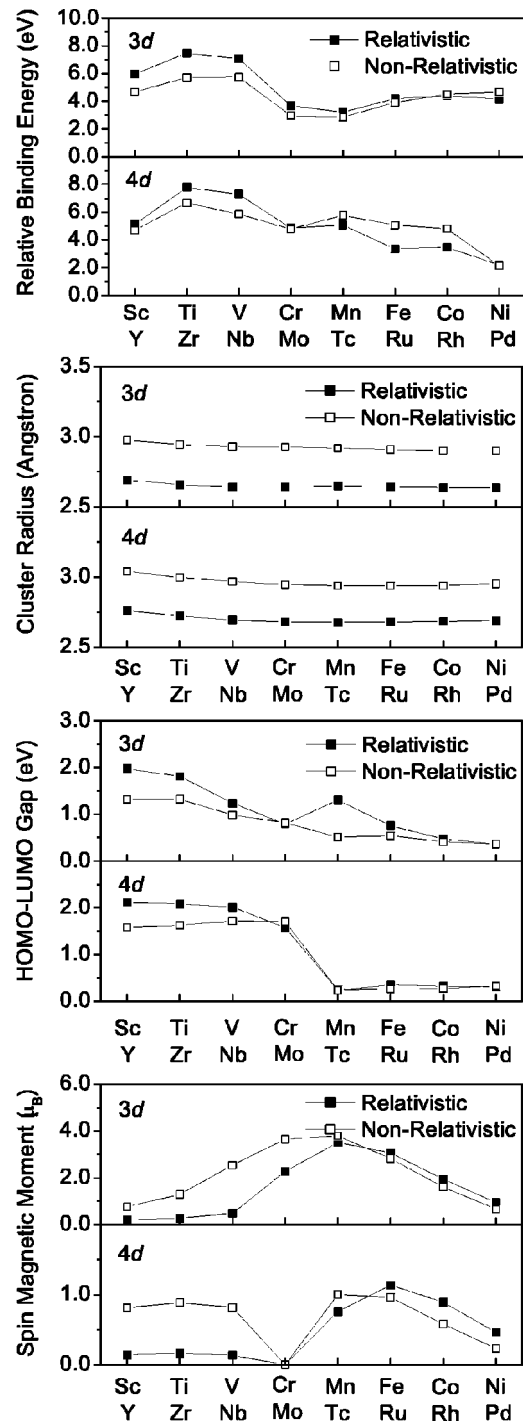


FIG. 3. The relativistic effects on the relative binding energy (compared with icosahedral Au_{13}), the cluster radius, the HOMO-LUMO gap, and the spin magnetic moment.

seems unusual since the d states are usually localized around the Fermi level. The d orbitals of Mn and Fe show larger exchange splittings than those of Ru and Rh near the Fermi level, resulting in larger magnetic moments. The s - d hybridizations and exchange-splittings of d orbitals are the main features of interaction in these doped clusters.

Relativistic effects (RE's) are particularly important for Au_{13} .³¹ Table II and Fig. 3 present, respectively, the results

obtained by relativistic and non-relativistic all-electron calculations and their comparisons. The RE's corrections on the results are not so systematic but obvious. They are more significant for the former part than for the latter part of 3,4*d* impurities. The RE's correction on relative BE (compared with icosahedral Au₁₃) is remarkable for all 3,4*d* impurities except for Co, Mo, and Pd. It yields the enhanced relative BE's for the former part of 3,4*d* impurities from Sc to Cr and Y to Nb, but the weakened relative BE's for the latter part of 4*d* impurities from Tc to Rh. The bond length is rather sensitive to the RE's correction for all the doped clusters, whose structures become more compact if the RE's correction is considered. The RE's corrections on these cluster radii are close to a stable value, about 0.27 Å. The change of HOMO-LUMO gap is significant for impurities from Sc to V and Y to Nb, and also for Mn and Fe. The RE's correction gives enhanced HOMO-LUMO gaps of these impurities. The LSMM is also sensitive to RE's correction for the former part of 3,4*d* impurities from Sc to Cr and Y to Nb, whose LSMM's are weakened greatly. The LSMM's of impurities from Fe to Ni and Ru to Pd, however, are enhanced to some extent. The results for Mo seem insensitive to the RE's correction except for cluster radius.

IV. SUMMARY

Cluster method based on DFT is used to explore the energetics and local spin magnetic moment of a single 3,4*d* impurity encapsulated in an icosahedral Au₁₂ cage. All doped clusters show unexpected large relative binding energies compared with icosahedral Au₁₃ cluster, indicating a high possibility of forming a new binary alloy cluster. Large spin magnetic moments are observed for 3*d* impurities Cr, Mn, Fe, Co, and Ni, and 4*d* impurities Tc, Ru, and Rh due to large exchange splittings of *d* orbitals. Strong hybridizations between the *d* orbitals of 3,4*d* impurity and the 6*s* orbital of Au occur. The correction of relativistic effect is very important for electronic structure.

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*Electronic address: sywang@imr.edu

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