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Structural evolutions and electronic properties of Au_nGd (n = 6–15) small clusters: A first principles study*

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Structural, electronic, and magnetic properties of Au_nGd (n = 6–15) small clusters are investigated by using first principles spin polarized calculations and combining with the ab-initio evolutionary structure simulations. The calculated binding energies indicate that after doping a Gd atom Au_nGd cluster is obviously more stable than a pure Au_{n+1} cluster. Au_6Gd with the quasiplanar structure has a largest magnetic moment of 7.421 μ_B. The Gd-4f electrons play an important role in determining the high magnetic moments of Au_nGd clusters, but in Au_6Gd and $Au_{12}Gd$ clusters the unignorable spin polarized effects from the Au-6s and Au-5d electrons further enhance their magnetism. The HOMO–LUMO (here, HOMO and LUMO stand for the highest occupied molecular orbital, and the lowest unoccupied molecular orbital, respectively) energy gaps of Au_nGd clusters are smaller than those of pure Au_{n+1} clusters, indicating that Au_nGd clusters have potential as new catalysts with enhanced reactivity.

Keywords: Au_nGd clusters, structural evolution, first-principles calculations, electronic structure, magnetic property

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1. Introduction

In contrast to the pervasive inertness of bulk Au, Au nanoparticles exhibit an astonishingly high chemical activity.[1,2] A great breakthrough for excellent catalytic activities of highly dispersed gold particles on a nanoscale in participating in low temperature CO oxidation[3] has stimulated the intensive search for new Au-based nanocatalysts. Especially, the tunable magnetism can be obtained in nonmagnetic gold nanoparticles by doping transition metal (TM) or rare earth (RE) atoms.[4,5] The distinguished quantum-size effect, element synergies, and plasmonic characteristics of Au_nM (M = TM, RE) bimetallic clusters can be tailored through changing the size of cluster and the composition of endohedral atom,[6–9] which has exerted a tremendous fascination on designing and synthesizing highly efficient catalysts, electronic devices, imaging equipment, and many other versatile aspects.[10,11] Ultrasmall Au_nM clusters consisting of a few to tens of atoms have been emphatically considered as ideal candidates of catalysts due to their high specific surface area, multitudinous active sites, and high utilization efficiency of precious metal. While in the process of sample preparation, high surface energy and Ostwald ripening are generally detrimental to maintain the isolated configurations and lead ultrasmall particles to easily agglomerate together,[12,13] which adds the difficulty in obtaining ideal Au_nM small clusters for further investigation. Moreover, the in-situ characterizations of nanocatalysts by applying experimental methods are still underdeveloping,[14] which brings stumbling blocks to figuring out the catalytic active sites.

Currently, the state-of-the-art first principles calculations have provided an effective way to investigate and understand the structural and physicochemical properties of nanoclusters.[15–19] Some researchers have devoted a great deal of effort to theoretically designing noble metal-based bimetallic clusters doped by a TM atom like Au_nCu,[20] Au_nTi,[21] and Ag_nCo,[22] but a systematic study on noble metal-based small clusters doped by a RE atom is still scarce. As is well known, the relativistic effect boundary lying in the fifth and sixth period of the periodic table of elements results in significant differences in electronic configurations and elemental natures between TM and RE elements. Recently, Yadav and Kumar[23] have theoretically found a $Au_{15}Gd$ cluster with a cage structure and large magnetic moment of 7 μ_B by performing ab-initio calculations, which is desirable for cancer therapy. To the best of our knowledge, however, the investigation on the structural evolution of the Au_n small cluster doped by a Gd atom (Au_nGd) has not been made until now. In this paper we present a systematic search for the global stable structures of Au_nGd (n = 6–15) clusters by employing the *ab-initio* evolutionary simulations, and further investigate the corresponding electronic and magnetic properties of Au_nGd

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clusters with the lowest energy based on first-principles spin polarized calculations. The ultimate goal of our study is to shed light on the explanation of correlation between electronic and geometric features when dealing with RE atom doped gold nanoclusters.

2. Computational methods

The global structure searches of Au_nGd ($n = 6$–15) clusters were performed using the evolutionary algorithm implemented in the USPEX code.[24,25] The population size was set to be 30 and the initial population was randomly produced by applying the possible point group symmetries. The succeeding generations were obtained by applying heredity, mutation operators with probabilities of 50% and 30%, respectively. Currently, the USPEX code has a great number of successful applications in the structure determination of various materials including bulk solids,[26,27] surfaces,[28] and isolated clusters.[29] The underlying total energy calculations were performed within the spin-polarized density functional theory by using the all-electron projector augmented wave (PAW) method[30] as implemented in the Vienna *Ab-initio* Simulation Package (VASP).[31] The exchange–correlation functional was dealt with the Perdew–Burke–Ernzerhof (PBE) form of generalized gradient approximation.[32] The energy cutoff for the plane-wave basis set was set to be 380 eV, which guarantees good convergence. All the obtained clusters were optimized in a 15 Å×15 Å×15 Å cubic cell, large enough to neglect the interaction between the cluster and its replicas in neighboring cells. The Brillouin zone was sampled using a single Γ point for the geometry optimization. The atomic coordinates of clusters were relaxed until the self-consistent total energy was less than 0.01 meV, and the ionic forces on each atom were less than 0.005 eV/Å.

3. Results and discussion

3.1. Geometries of stable Au_nGd clusters

For comparison, the lowest-energy structures of pure Au_{n+1} ($n = 6$–15) clusters are first predicated from our evolutionary simulations and presented in Fig. 1. Their geometries are consistent with previously reported results.[33] The most stable isomers of Au_nGd ($n = 6$–15) found in our predications are shown in Fig. 2. For Au_6Gd, the guest impurity atom Gd is capped on the center of the Au_6 ring, contriving a regular hexagonal pyramid with C_{6v} symmetry. Note that the equilibrium geometry of Au_6Gd is different from transition-metal-doped Au_6 clusters, Au_6TM (TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni), in which the TM atom is located in the center of the hexagonal Au_6 ring, forming a perfectly planar two-dimensional (2D) structure with a higher symmetry (D_{6h}).[4,34] In the case of Au_7Gd, a perfectly planar structure with D_{7h} symmetry is its ground state isomer, where Gd is just in the center of the Au_7 ring. Moreover, our predication for the Au_7Gd cluster is in good agreement with a previous report on the structure of the Ac_7Gd cluster.[35] It is noticeable that the most stable structure of Au_8Gd possesses C_s symmetry and can be explained as an evolution from Au_6Gd capped by two Au atoms symmetrically. Obviously, it can be found from Fig. 2 that for Au_nGd the transition from 2D planar structure to three-dimensional (3D) structure occurs at Au_9Gd. Meanwhile, our predicated results have clearly indicated that the 2D–3D crossover for Au_nGd occurs in advance in comparison with pure Au_{n+1} clusters presented in Fig. 1. On the one hand, the 5d–6s hybridization between Au atoms has a tendency to form σ-like directional bonds,[36] causing Au_n clusters to conserve planarity up to larger sizes. On the

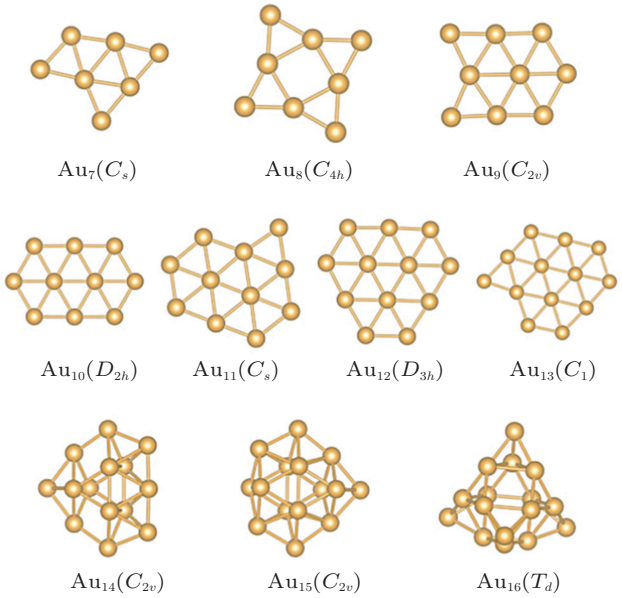


Fig. 1. (color online) Geometrical structures of the lowest-energy Au_{n+1} ($n = 6$–15) clusters determined from the structural evolutionary simulations.

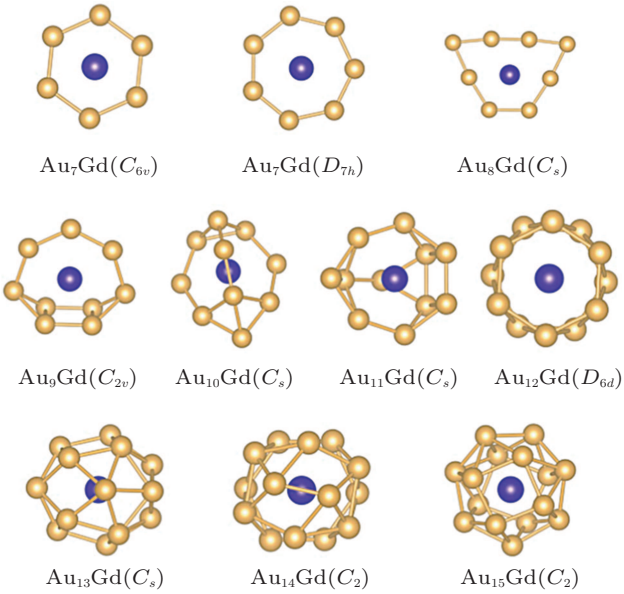


Fig. 2. (color online) Geometrical structures of the lowest-energy Au_nGd ($n = 6$–15) clusters determined from the structural evolutionary simulations.

other hand, a rare earth Gd atom tends to have a high coordination number (CN) by bonding with the nearest neighbor atom due to its various valence orbitals. As indicated in our predication, however, the maximum of CN of Gd atom in Au_nGd stable isomers with planar structure seems to be 7, reaching this limit in Au_7Gd. With further increasing the size of Au_nGd cluster, 2D planar isomers become unstable and 3D structures like Au_9Gd (C_{2v}), $Au_{10}Gd$ (C_s), and $Au_{11}Gd$ (C_s), respectively with the CN of 9, 10, and 9, are energetically favorable. For $Au_{12}Gd$, the lowest energy structure with D_{6d} symmetry is made up of two rotated Au_6 rings linked by the central Gd atom. The cage-like feature gradually appears in $Au_{13}Gd$ (C_s) and $Au_{14}Gd$ (C_2) clusters. It must be pointed out that the cage-like structure of $Au_{14}Gd$ is also analogous to that of $Au_{14}Th$ previously reported by Gao and Wang.[37] When $n = 15$, $Au_{15}Gd$, a nearly perfect Gd-encapsulated Au_{15} cage is formed, which agrees well with the previous prediction.[23] The optimized Gd–Au and Au–Au bond lengths in Au_nGd clusters are listed in Table 1. For comparison, the bond lengths of pure Au_{n+1} clusters are given in Table 1 and are in good agreement with previously calculated values.[33] In Au_nGd, the Au–Au bond lengths are obviously shorter than the Au–Gd bond lengths. The bond lengths gradually increase as the size of cluster increases, accompanied by an odd–even oscillation. Moreover, it can be found that the change trend in the Au–Gd bond length is almost contrary to that in the Au–Au bond length.

Table 1. Calculated values of interatomic distance ($d_{\text{Au-Au}}$, $d_{\text{Au-Gd}}$), substitution energy (E_s), binding energy (E_b), magnetic moment (M), and HOMO–LUMO energy gap (G) of Au_nGd clusters. The calculated values of pure Au_{n+1} clusters are listed for comparison.

Size	Au_nGd						Au_{n+1}		
(n)	$d_{\text{Au-Au}}$/Å	$d_{\text{Au-Gd}}$/Å	E_s/eV	E_b/eV	M/μ_B	G/eV	$d_{\text{Au–Au}}$/Å	E_b/eV	G/eV
6	2.738	2.845	−3.944	2.41	7.421	0.42	2.7	1.846	0.87
7	2.624	3.023	−4.187	2.487	6.971	0.60	2.676	1.964	1.41
8	2.739	2.875	−4.227	2.422	7.135	0.08	2.717	1.952	0.61
9	2.728	3.021	−4.441	2.480	6.999	0.94	2.722	2.036	1.29
10	2.743	2.965	−4.503	2.448	7.132	0.04	2.721	2.038	0.61
11	2.766	3.054	−4.398	2.472	6.997	0.82	2.724	2.106	0.98
12	2.817	3.017	−4.877	2.473	7.226	0.94	2.725	2.097	0.54
13	2.805	3.101	−5.184	2.51	6.994	0.76	2.849	2.14	1.56
14	2.822	3.07	−5.65	2.515	7.04	0.01	2.816	2.138	0.52
15	2.832	3.051	−6.151	2.562	7	1.47	2.761	2.177	1.35

3.2. Structural stability of Au_nGd clusters

To verify whether it is favorable to dope/substitute a Gd atom in Au_n clusters, we calculate the substitution energy (E_s) which is defined as

$$E_s = E(Au_nGd) + E(Au) - E(Au_{n+1}) - E(Gd),$$

where $E(Au_{n+1})$ and $E(Au_nGd)$ refer to the total energies of pure Au_{n+1} and Au_nGd clusters, respectively; the $E(Au)$ and $E(Gd)$ are the energies of single Au and Gd atoms. Thus, according to the above definition, a negative value of E_s indicates that it is possible to introduce a Gd atom into the Au_n cluster. As presented in Fig. 3(a), the values of E_s of all studied cluster sizes are negative and gradually decrease with cluster size increasing. Our calculated results clearly indicate that doping a Gd atom into a small Au_n cluster is energetically favorable to its stability and this doping effect on the structural stability of the Au_n cluster becomes more obvious with the increase of cluster size.

In order to further investigate the size-dependent thermodynamic stability of Au_nGd clusters, the average binding energy (E_b) changing with cluster size is calculated. The values of E_b of Au_nGd and pure Au_{n+1} clusters are defined as follows:

$$E_b(Au_nGd) = -[E(Au_nGd) - nE(Au) - E(Gd)]/n,$$

$$E_b(Au_{n+1}) = -[E(Au_{n+1}) - (n+1)E(Au)]/(n+1),$$

where $E(Au_nGd)$, $E(Au)$, $E(Au_{n+1})$, and $E(Gd)$ are the energies of Au_nGd cluster, Au atom, Au_{n+1} cluster, and Gd atom, respectively. The results presented in Fig. 3(b) and Table 1 show that with increasing the sizes of both Au_nGd and Au_{n+1} clusters, the calculated E_b gradually increases accompanied by a slight odd–even oscillation. Especially, the E_b of Au_nGd cluster is about 0.5 eV larger than that of pure Au_{n+1} cluster, which indicates that the substitution of a Gd atom for an Au atom can evidently enhance the stability of the gold cluster. This should be directly related to the generation of stronger Gd-Au bonds in Au_nGd clusters. Moreover, Au_nGd clusters become more stable with the increase of cluster size due to the formation of more Gd-Au bonds.

3.3. Magnetic properties of Au_nGd clusters

The total magnetic moment of a cluster is a combination of the spin and orbital magnetic moments. However, the magnetic moment of a cluster is mainly dominated by the spin magnetic moment since the contribution from the orbital magnetic moment of an electron can be neglected. The total magnetic moments of Au_nGd clusters obtained from the spin-polarized calculations are presented in Table 1 and displayed in Fig. 4.

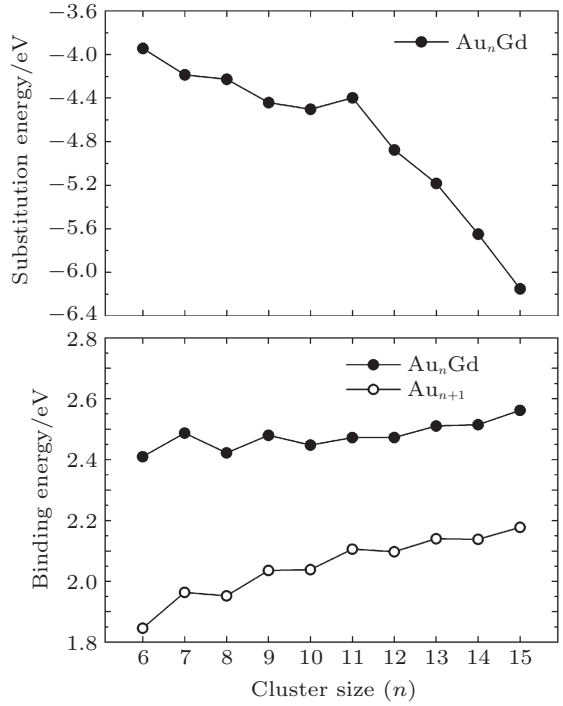


Fig. 3. Calculated values of substitution energy (E_s) and binding energy (E_b) of the ground state Au$_n$Gd (n = 6–15) clusters. For comparison, the calculated E_b of pure Au$_{n+1}$ clusters is presented.

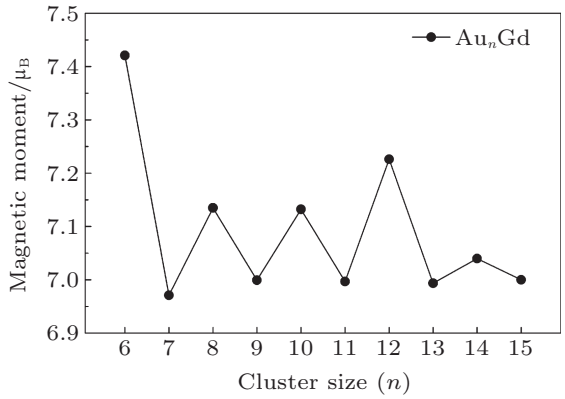


Fig. 4. Calculated magnetic moment (M) versus cluster size of the ground state Au$_n$Gd (n = 6–15) clusters.

It can be seen that the calculated magnetic moment shows an odd–even oscillation with the increase of cluster size. The calculated magnetic moment of Au$_{15}$Gd is 7 μ_B, and consistent with a previously reported value.[23] When n = 7, 9, 11, 13, the total magnetic moments of Au$_n$Gd clusters are also almost close to 7 μ_B. However, the calculated magnetic moments of Au$_n$Gd clusters with even n are larger than 7 μ_B. Especially, Au$_6$Gd atomic cluster possesses the largest magnetic moment of 7.421 μ_B. It is not surprising if one considers the fact that atomic clusters with the reduced coordination number and higher symmetry would exhibit enhanced magnetization.[34] In all of Au$_n$Gd atomic clusters considered here, as discussed above, Au$_6$Gd with C_{6v} symmetry has the lowest coordination number of 6. Although Au$_{12}$Gd has a relatively high coordination number, its symmetry with D_{6d} is the highest in Au$_n$Gd clusters. Hence, the calculated magnetic moment of Au$_{12}$Gd with 7.226 μ_B is also significantly larger than those of other Au$_n$Gd clusters except Au$_6$Gd. Additionally, our calculations indicate that the additional magnetic moments beyond 7 μ_B for Au$_n$Gd clusters with even n are fully from Au atoms. For Au$_6$Gd, the local magnetic moment on each Au atom is about 0.07 μ_B. In fact, Au bulk solid is known to be weakly diamagnetic, but a great variety of magnetic phenomena have been found in polymer-capped Au nanoparticles due to the strong chemical affinity of Au atoms to the capping molecules.[38] Moreover, recent experiments have confirmed the existence of spontaneous magnetic moments in bare Au nanoparticles.[39]

3.4. Electronic properties of Au$_n$Gd clusters

To gain an insight into the origin of magnetism in Au$_n$Gd clusters, the electronic density of states (DOS) is further investigated. For comparison, the calculated total DOS and partial DOS (PDOS) on Au and Gd atoms of Au$_6$Gd, Au$_{12}$Gd, and Au$_{15}$Gd clusters are presented in Fig. 5. It can be found that the high magnetic moments of Au$_n$Gd clusters are mainly ascribed to the PDOS of Gd-4f electrons centered in the two energy regions between −4.8 eV and −3.4 eV, and between 0.2 eV and 1.2 eV. For Au$_{15}$Gd, the spin-up and spin-down PDOSs of Au-6s and Au-5d electrons are almost identical, indicating that the spin polarized effects from the Au-6s and Au-5d electrons can be ignored. In the cases of Au$_6$Gd and Au$_{12}$Gd, however, the two spin channels of Au-6s and Au-5d electrons are not strictly symmetrical and have a slight shift toward higher or lower energy levels, which generates the exchange splitting and makes a few contributions to the magnetism of Au$_6$Gd and Au$_{12}$Gd clusters, respectively.

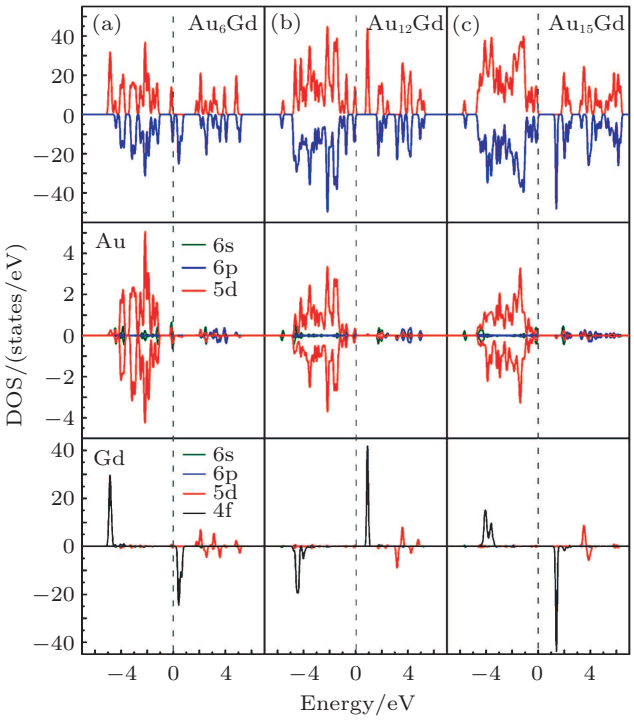


Fig. 5. (color online) Calculated curves of total and partial density of states versus energy of ground state Au$_6$Gd, Au$_{12}$Gd, and Au$_{15}$Gd clusters.

The calculated charge density difference between Au_6Gd and Au_7Gd is displayed in Fig. 6. It can be clearly found that most electrons withdraw to the intermediate zone between the circumambient Au atoms and the central Gd atom and transfer to Au atoms. The delimitation of delocalized electrons occurs in a finite margin around Au atoms and is cancelled out in a certain small scope. Whereas the quantity of overall electron transfer is still small, showing the covalent metallic bonding features in Au_6Gd and Au_7Gd clusters. The Coulomb repulsion between bonding basins inevitably interfere with the structure models, triggering the deformation of the electron cloud.

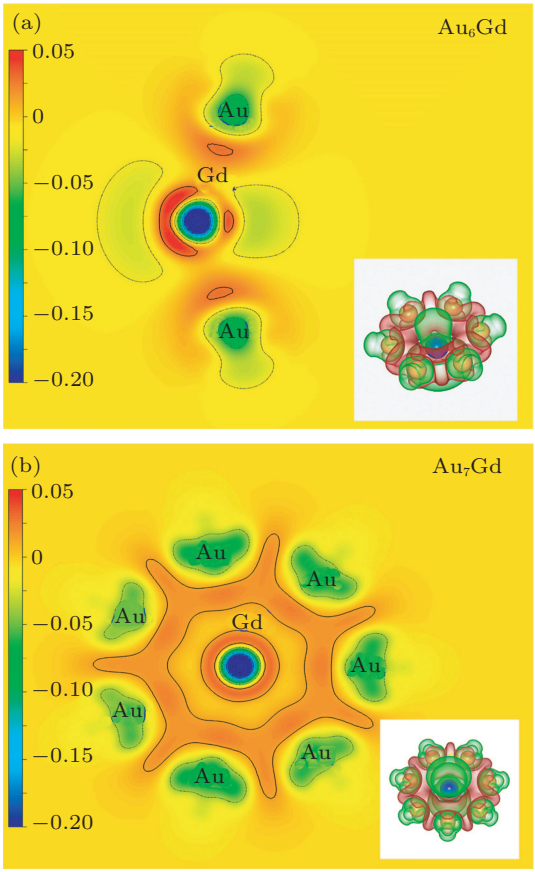


Fig. 6. (color online) Contours of charge density difference of Au_6Gd and Au_7Gd clusters across Au and Gd atoms. Insets show corresponding isosurfaces of charge density difference.

The calculated energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of Au_nGd and Au_{n+1} ($n = 6$–15) clusters are presented in Fig. 7 and listed in Table 1. Generally, the HOMO–LUMO energy gap can be used to measure the chemical stability of small clusters. A big energy gap is usually related to a high chemical stability. It can be found that pure Au_{n+1} small clusters show an obvious odd–even oscillation in their energy gaps. This phenomenon can be explained by the electron pairing effect and also be found in pure Cu_n clusters reported by Die *et al.*[40] After one Au atom in each of the Au_{n+1} clusters is replaced by a Gd atom, the energy gaps of the newly formed Au_nGd clusters are narrower than those of Au_{n+1} clusters except $Au_{12}Gd$ and $Au_{15}Gd$ that may be related to their peculiar structures in comparison with Au_{13} and Au_{16} clusters. Especially, the energy gaps of Au_8Gd, $Au_{10}Gd$, and $Au_{14}Gd$ are close to zero. The decrease of HOMO–LUMO energy gap implies the increase of metallic bonding and decrease of chemical stability of the Au_nGd cluster. This means that Au_nGd small clusters promise to be used as new catalysts with more reactive and even metallic properties.

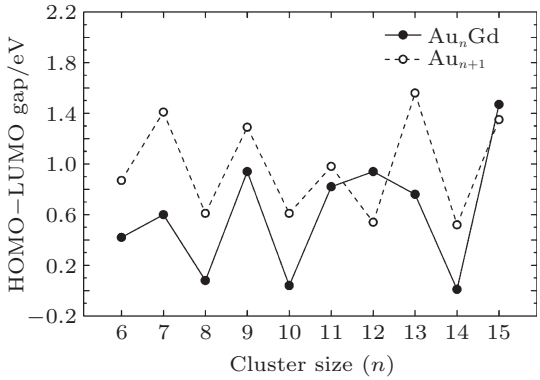


Fig. 7. Calculated HOMO–LUMO energy gaps of the ground state Au_nGd and pure Au_{n+1} clusters.

4. Conclusions

In this paper, we have systematically investigated the structural, electronic, and magnetic properties of Au_nGd ($n =$ 6–15) small clusters by performing first-principles calculations and evolutionary simulations. Our results indicate that the 2D-3D crossover for Au_nGd occurs in advance in comparison with pure Au_{n+1} clusters and the structural stability of Au_nGd is significantly enhanced due to the stronger interaction between Gd and Au atoms. In all of the Au_nGd clusters considered here, Au_6Gd has the largest magnetic moment with 7.421 μ_B due to its reduced coordination number and higher symmetry. The calculated DOS shows that the Gd-4f electrons are mainly responsible for the high magnetic moments of Au_nGd clusters, and in Au_6Gd and $Au_{12}Gd$ clusters the spin polarized effects from the Au-6s and Au-5d electrons are not ignored and further enhance their magnetism. In comparison with pure Au_{n+1} clusters, the chemical stability of Au_nGd clusters with the narrower HOMO–LUMO energy gaps decreases, which indicates that Au_nGd small clusters have promise to be used as catalysts with the enhanced reactivity.

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