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Au_N clusters ($N=32,33,34,35$): Cagelike structures of pure metal atoms

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Based on the density functional theory, we demonstrate that Au_N clusters can have cagelike structures. The cage consisting of 32 Au atoms has an icosahedral symmetry with a large energy gap of 1.56 eV, suggesting high stability and chemical inertness. The calculations show that the cagelike structure is stabilized by the relativistic effect.

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There has been a surge of interest in searching for stable clusters as building blocks of nanostructured materials and electronic devices. Highly symmetrical clusters with cagelike structures have inspired physicists and chemists with great interest, because it can exhibit unusual stability and reactivity, which are very important as the building blocks, since carbon atoms, besides the planar graphite and diamond structure, are found able to condense into very stable cagelike structures, such as C_{60}, C_{70}, and C_{20} clusters.[1] Searching for the carbon-free clusters with a cagelike structure has attracted much attention in the last decade. Although some carbon-free clusters, such as $Na_{12}In_{48}$[2] and Si_{20},[3] have been found, they are components in three-dimensional solids and not free standing. Very recently, an inorganic fullerene-like molecule is successfully synthesized, the large cagelike molecule is, however, also stabilized by its surrounding ligands.[4]

It is generally believed that clusters consisting of metal atoms prefer compact structures; thus we would not expect metal atoms to form a cagelike structure, which is essentially a curved two-dimensional structure. Even for IV elements other than carbon, such as Si or Ge, the cagelike structures have never been observed! It was theoretically shown that pure Si (Ge) clusters with cagelike structures are not stable, but can probably be stabilized by doping metal atoms.[5,6]

Gold is a typical noble metal. Photofragment recorded with reflection time-of-flight mass spectrometry has shown a size distribution with an enhanced abundance of Au_N^+ clusters, at steps of $N=3,9,19,21,35,\ldots$, corresponding to the magic number 2, 8, 18, 20, 34 predicted by the jellium model.[7,8] The significant role played by the relativistic effect in the structures and bonding of small Au clusters is beginning to be realized. One of its important consequences is that small Au clusters, at least up to 13 atoms, favor planar structures, while in most of other metal clusters the planar structure would usually be transferred to a three-dimensional structure at 5–7 atoms.[9–12] One can expect that the relativistic effect probably continues to play a role in the structures and bonding of large Au clusters, which might make Au clusters have structures different from the compact ones. Recently, a tetrahedral structure of the Au_{20} cluster was found by the photoelectron spectrum combined with the relativistic density functional calculation.[13] Since all 20 atoms are located on the surfaces without even a single inner atom, Au_{20} can be considered as four triangle Au_{10} planes merged together, a quasi two-dimensional structure. Simple calculations show that, other larger tetrahedral Au clusters (Au_{35}, Au_{58}) are energetically unstable.[14] It is intriguing to know what possible structures of larger Au clusters could be, can the quasi two-dimensional structures exist in large Au clusters? In this paper, we predict that the Au_N ($N=32,33,34,35$) clusters can unexpectedly have cagelike structures, which can incorporate up to 3 Au atoms inside without a strong deformation.

The calculations are based on the density functional theory (DFT) with generalized gradient approximation (GGA)[15] implemented in the VASP code.[16] Only the valence electrons are treated explicitly and their interactions with ionic cores are described by the ultra-soft pseudopotentials[17,18] with a scalar relativistic effect included. The wave functions are expanded in plane waves with an energy cutoff ~230 eV. We use a simple cubic cell of 30 Å edge length with a periodic boundary condition, and the Γ point approximation for Brillouin zone sampling. For comparison, we have also used the ADF and Dmol3 codes,[19,20] where the relativistic effect can be explicitly included. Table I shows the calculated bond length and binding energy for the bulk structure and dimer. The difference of the dimer length between the relativistic and nonrelativistic calculation is as large as 10%, which suggests that therelativistic effect is really important. The results from VASP are essentially the same as what is obtained from the relativistic ADF and Dmol3, indicating that the present ultra-soft pseudopotential method can correctly predict the binding properties of gold. Our calculations on the Au_2 show that the spin-polarization has a minor effect, ~0.001 Å for the bond length and ~0.001 eV for the binding energy. So all the calculations reported below are spin nonpolarized.

In order to find out the ground state structure of the Au_N cluster, we have carried out an extensive search started with various initial structures, from either highly symmetrical structures or low symmetrical structures. The atomic structures are optimized by the conjugated gradient method, with a force convergence of 1.0×10^{-3} eV/Å . Surprisingly, the results show that the most stable structures of Au_N ($N=32,33,34,35$) clusters are cagelike. The cage consists of 32 atoms with an icosahedral symmetry (see Fig. 1), which can

TABLE I. Calculated properties of the Au dimer and solid with three different theoretical methods. d_0 (Å) and E_0 (eV) are the bond-length and the binding energy of the dimer, respectively, d_b (Å) and E_b (eV) are the shortest atomic distance and the binding energy of the gold solid, respectively. The VASP results are in close agreement with the data from relativistic ADF and Dmol3 methods.

		Dimer		Bulk	
		d_0	E_0	d_b	E_b
VASP	LDA	2.47	3.15	2.87	4.39
	GGA	2.52	2.63	2.96	3.19
Expt.[a]		2.47	2.30	2.88	3.81
		Dimer			
		Relativistic		Nonrelativistic	
		d_0	E_0	d_0	E_0
ADF	LDA	2.46	3.21	2.69	2.24
	GGA	2.52	2.71	2.75	1.88
Dmol3	LDA	2.44	3.03	2.70	1.90

[a] References21.

be obtained by capping one atom on each pentagon of a dodecahedron. There are only two different kinds of sites on the cage, i.e., 12 five-coordinated sites and 20 six-coordinated sites, and as a result, there are only two bond lengths, 2.74 Å for five-coordinated sites, and 2.85 Å for the six-coordinated sites, respectively.

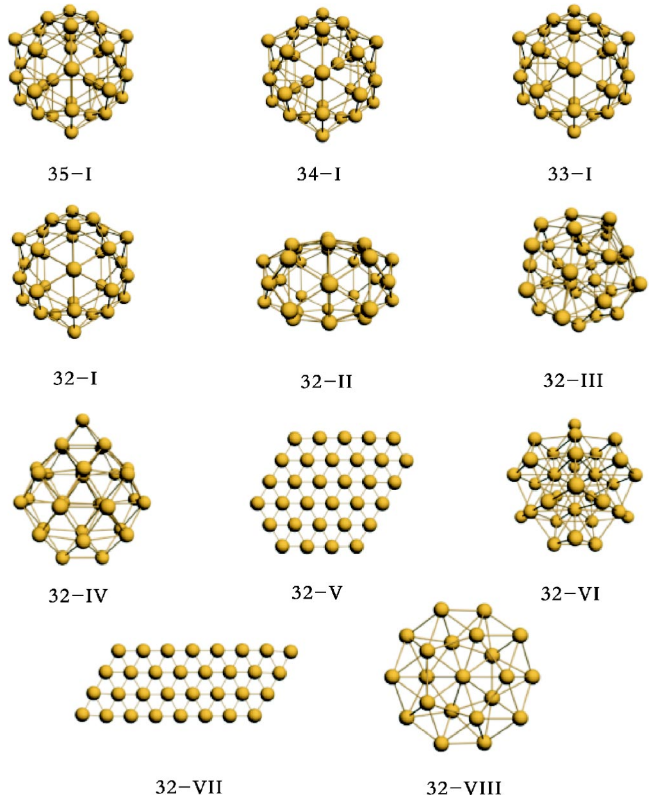

FIG. 1. Structures of Au_N (N=32,33,34,35).

TABLE II. Optimized structures of the Au_{32} cluster: point group symmetry, binding energies E_b(eV) relative to that of the cagelike structure with icosahedral symmetry, the number in the bracket being the binding energy per atom, HOMO-LUMO gap E_g (eV), N_b, number of bonds, R_0(Å) average bond length.

Structure	Symmetry	E_b	E_g	N_b	R_0
I	$I_h(cage)$	0.000(2.618)	1.558	90	2.778
II	$D_{6h}(cage)$	0.940(2.588)	0.847	90	2.782
III	C_1	1.696(2.565)	0.311	105	2.854
IV	C_{1v}	1.942(2.556)	–	104	2.852
V	*Planar*	3.168(2.519)	–	76	2.734
VI	T_d	4.000(2.493)	–	99	2.854
VII	*Planar*	4.160(2.488)	0.512	73	2.731
VIII	D_{5h}	6.080(2.428)	0.318	130	2.944

Figure 1 also shows other isomers for Au_{32} clusters found in our structure search. Structure II is another cagelike structure with D_{6h} symmetry, but its binding energy is 0.94 eV lower than that of the icosahedral one. The main difference between the icosahedral cage structure and D_{6h} structure is the relative position of pentagons. In the D_{6h} cagelike structure, there also exist 12 five-coordinated sites and 20 six-coordinated sites, but five-coordinated atoms are connected together, forming six pairs, which is known energetically unfavorable in the fullerenes. Structure III is a compact structure without any symmetry. Although its binding energy is the largest among all the compact structures, the binding energy difference between the cage structure and this compact structure is still as large as 1.69 eV (see Table II). Structure IV can be roughly considered as a fragment of fcc gold with relaxed bond lengths, the binding energy is about 2 eV lower than that of the icosahedral one. Since the planar structures have been found in the small Au clusters, we have calculated a planar structure for Au_{32} shown as Structure V in Fig. 1, its binding energy is about 3.1 eV lower than the icosahedral one. Structure VI is another cluster of high symmetry (T_d).

Three kinds of structures, i.e., planar, cagelike and compact structures, have different bond lengths and bond numbers. The bond lengths of all the calculated clusters are listed in Table II. As it is known, the higher the dimensionality, the longer the bond length and the more the number of bonds. The planar structure has the shortest bond length (2.73 Å) with only 73–76 bonds, while the quasi two-dimensional cagelike structure has a bond length of 2.78 Å with about 90 bonds. However, in the compact structure, the bond length is increased by 0.7 Å compared with the cagelike structure, with about 100 bonds.

The icosahedral Au_{32} cluster can accommodate only three inner Au atoms, the fourth atom inserted into the cage will largely distort the cage and make the structure unstable. The binding energy difference between Au_{32} and Au_{33} is only 1.6 eV, much smaller than the binding energy per atom of Au_{32}, which indicates that the cagelike structure of Au_{32} is very unfavorable to accept one more atom. Our calculation shows when inserting Au atoms into the cage, the first atom

TABLE III. Calculated properties for the selected Au clusters. R_0(Å) is the average bond length, E_b(eV) is the binding energy per atom, E_g(eV) is the HOMO-LUMO gap, while the number labeled by + indicating the HOMO-LUMO gap if the cluster positively charged; the first order and second order energy differences are defined as $\Delta_1 E = E_N - E_{N-1}$, $\Delta_2 E = 2E_N - E_{N-1} - E_{N+1}$. The large values of $\Delta_1 E$ ($\Delta_2 E$) indicate high stability for both Au_{32} and Au_{34}.

Cluster	R_0	E_b	E_g	$\Delta_1 E$	$\Delta_2 E$
7	2.718	1.997	–		
10	2.720	2.224	1.277		
20	2.850	2.495	1.796		
30	2.763	2.549	0.877		
31	2.771	2.577	0.351(+)	3.427	−0.458
32	2.778	2.618	1.558	3.885	2.235
33	2.793	2.588	0.688(+)	1.650	−1.760
34	2.810	2.613	1.532	3.410	0.835
35	2.824	2.612	1.181(+)	2.575	−0.126
36	2.820	2.614	0.768	2.701	
Bulk	2.955	3.19	–		

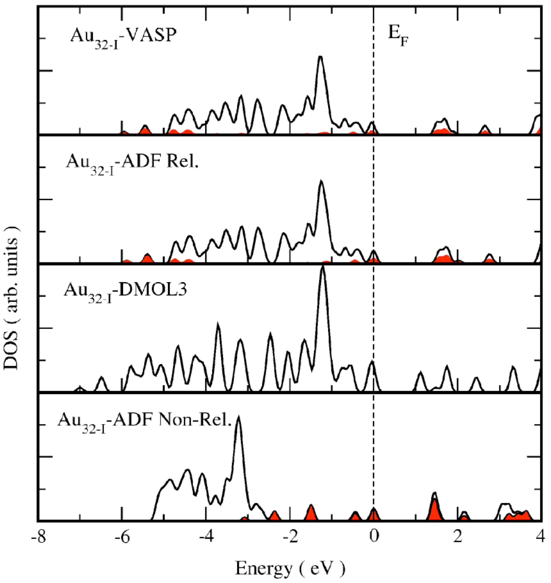

FIG. 2. Electronic density of states for the cagelike structure of Au_{32}. The results of Au_{32} from different methods are shown for comparison. The Fermi energy is shifted to zero, and the shaded area is the projected *s* component. The pseudopotential results are in close agreement with that of the relativistic ADF (ADF Rel.) and Dmol3.

is capped on a five-fold position, the second on another five-fold position but keeping the D_{5d} symmetry, and the third one drives the other two to form a triangle on an ecliptic plane, lowering the symmetry to D_{3h}.

The cagelike Au_{32} and Au_{34} clusters have a gap between the highest occupied molecular orbital(HOMO) and the lowest unoccupied molecular orbital(LUMO) as large as 1.5 eV, as shown in Table III, which is comparable to the gap of 1.80 eV recently found in the tetrahedral Au_{20} cluster and larger than that of all other known coinage metal clusters. Such a large HOMO-LUMO gap implies that Au_{32} and Au_{34} should be chemically very inert. If we re-call that DFT always underestimates the energy gap, we can expect that these cagelike structures would have even larger gaps. As shown in Table II, all other isomers have either no gap or only a small gap of 0.3–0.5 eV, suggesting a lower stability. It is interesting to note that, within our nonspin polarized calculations, the neutral Au_{35} has no HOMO-LUMO gap due to the odd number of valence electrons, however, the positively charged cluster shows a significant gap of 1.18 eV, indicating high stability as observed in the experiment.[8,23]

We have also performed similar calculations for Ag_{32} and Cu_{32} clusters, in which the relativistic effect is much less important. A compact structure which is more stable than the cage structure can be easily found. We have carefully checked the stability of the cagelike structure by ADF and Dmol3 codes with a relativistic effect, and confirmed that the cagelike structure of Au_{32} predicted by VASP is indeed stable against ADF and Dmol3 re-optimization. We have recalculated the binding energies of the Au_{32} cluster for the cage structure and the amorphous structure using a nonrelativistic ADF code. The results show the amorphous structure becomes energetically more stable. All these results strongly suggest that the relativistic effect stabilizes the cage structure of Au_{32}, while for Ag and Cu with much less relativistic effect, the cage structure is not stable. A similar difference between Au and Ag(Cu) was also observed on the surface reconstruction.[22] In fact, it was shown that the planar structure of small Au clusters is also due to the relativistic effect.[9]

Figure 2 displays the electronic density of states (DOS) for the icosahedral cage structure of the Au_{32} cluster. For comparison, the results from ADF and Dmol3 methods are also shown. The shaded parts denote the partial DOS contributed by the *s* electrons. The DOS from the ultra-soft pseudopotential is in close agreement with the results from relativistic ADF and Dmol3, which further indicates that the relativistic effect is properly accounted for in ultra-soft pseudopotential calculations. Significant differences between the relativistic and nonrelativistic results can be clearly observed. In the nonrelativistic calculation, the partial DOS is essentially *s*-like, and *s*-*d* hybridization is very weak. The relativistic effect pushes the *s* band more close to *d* band, resulting in a strong *s*-*d* hybridization which increases the bandwidth of *d* orbitals up to 1–2 eV.

We have also calculated the DOS for two isomers of Au_{32} (Au_{32-II} and Au_{32-III} as shown in Fig. 1) and also for Au_{33}, Au_{34} and Au_{35}, shown in Fig. 3. We can find that all the cagelike clusters show quite similar DOS. While comparing the DOS of icosahedral Au_{32} with that of its isomers, the visible difference can be observed. In the amorphouslike structure, the band-width is about 1 eV wider. The global shape is also less structured. Even though, there is no HOMO-LUMO gap in the amorphous structure, the density of states is very low near the Fermi level.

In Fig. 4, the binding energies of planar or cagelike structures are compared with that of the compact structures, which clearly demonstrated that the binding energies of the compact structures are lower than that of planar or cage structures. This strongly suggests that the relativistic effect is

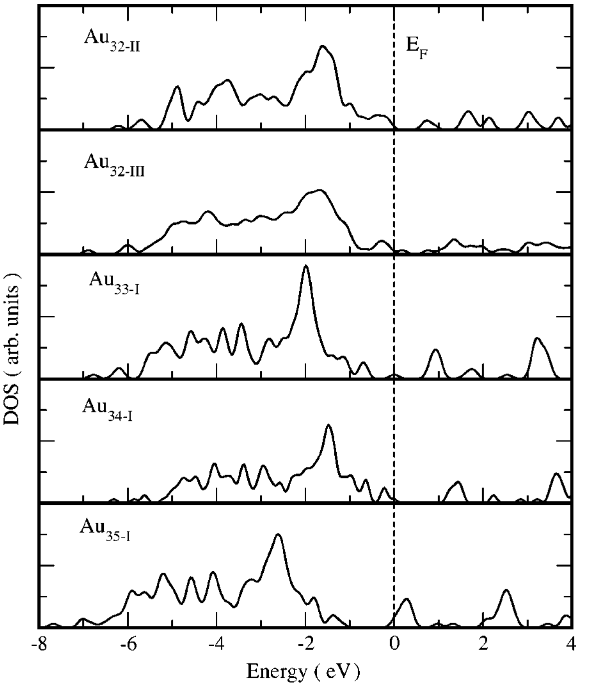

FIG. 3. Electronic Density of states for the cagelike structure of Au$_N$ (N=33,34,35) and two isomers of Au$_{32}$. The Fermi energy is shifted to zero.

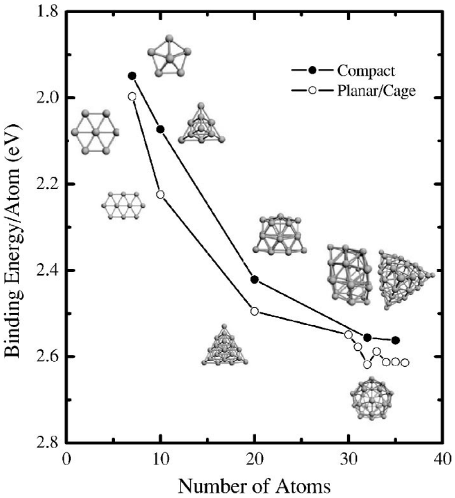

FIG. 4. Binding energies for the Au clusters. The solid dots are for the compact structures and the circles for either planar or cage structures. The compact structure of Au$_{20}$ has a symmetry of C$_{2v}$. The compact structure of Au$_{32}$ is Structure IV with C$_{1v}$ symmetry; the compact structure of Au$_{35}$ is a distorted tetrahedral structure. The binding energies of the compact structures are lower than that of the planar or cage structures in all the studied clusters.

still very important in these clusters. We have put the tetrahedral Au$_{20}$ in the planar category since it can be considered as four planar Au$_{10}$ glued together and no central atom exists. We have found that a one- or two atom-missed cage structure is stable against conjugated gradient optimizations; the results for the Au$_{31}$ and Au$_{30}$ shown in Table III are for the structures with one or two five-coordinated-atom missed. All these selected clusters prefer either planar or cage structure, those properties are shown in Table III. The structures of the small clusters are perfectly planar, the structure of Au$_{20}$ is tetrahedral, while for the Au$_N$ with N=32,33,34, 35, the structures are cagelike. The structure of Au$_{36}$ with four atoms inside the cage is energetically unfavorable, what we show in Fig. 4 and Table III is the structure obtained by capping one Au atom on the surface of Au$_{35}$. Particularly, one can notice that, as the number of Au atoms increases, the energy difference between compact and cagelike structure does not vanish, thus a larger cagelike cluster could probably exist. This might somehow be related to why gold nanotubes can be formed.[25,24] Although all the calculated clusters (shown in Fig. 4) prefer a quasi two-dimensional structure, we cannot exclude the possibility that all other clusters in the size interval 10–30 will have a quasi two-dimensional structure, since the cagelike structure can only be formed with a specific number of atoms.

In summary, we have found that Au$_N$ (N=32,33,34,35) clusters can surprisingly have cagelike structures, which are stabilized by the strong relativistic effect, while the Ag$_N$ or Cu$_N$ cluster does not. The stability of the icosahedral cage of Au$_{32}$ is confirmed by the ultra-soft pseudopotential method (VASP), relativistic ADF and Dmol3 codes. The comparison of the binding energies between the compact structure and planar structure implies that such a relativistic effect may still affect the structure and bonding properties of larger clusters. We find that a large HOMO-LUMO gap exists in Au$_{32}$ and Au$_{34}$. Such an icosahedral cage would provide another interesting kind of cluster other than carbon fullerenes for further studies, especially deserves the delicate experimental investigations, such as high resolution photoelectron spectroscopy.

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