RAPID COMMUNICATIONS

PHYSICAL REVIEW B **79**, 041405(R) (2009)

Structure of large gold clusters obtained by global optimization using the minima hopping method

Kuo Bao,[1,2] Stefan Goedecker,[2] Kenji Koga,[3] Frédéric Lançon,[4] and Alexey Neelov[2]
[1]*State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, China*
[2]*Department of Physics, Universität Basel, Klingelbergstrasse 82, 4056 Basel, Switzerland*
[3]*National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan*
[4]*INAC, SP2M, Laboratoire de Simulation Atomistique (L_Sim), CEA, F-38054 Grenoble, France*
(Received 11 November 2008; published 29 January 2009)

The energetic ground state of gold clusters with up to 318 atoms consists of complex geometries that have only a limited resemblance to the perfect icosahedra, decahedra, and octahedra that are encountered for some magic numbers. The structure changes in most cases completely by the addition of a single atom. Other low-energy structures are so close in energy that their Boltzmann weight is not negligible at room temperature.

DOI: 10.1103/PhysRevB.79.041405 PACS number(s): 61.46.Bc

Since the structure determines the functionality of any material, the knowledge of the structure is the first step to understand any property of a condensed-matter system. Clusters are a particularly interesting system both scientifically and technologically. It is well known that for small clusters of less than 30 atoms the structure can drastically change by the addition of a single atom. Size-selected clusters offer thus the possibility to obtain a large variety of structures with possibly widely different functionalities. It has, for instance, been revealed that the reactive properties of Au_{55} are drastically different from other gold clusters.[1]

Global geometry optimization has been performed in a systematic way for up to 80 atoms[2] and for selected clusters up to 75 atoms.[3] For such a small number of atoms, most clusters are amorphous, i.e., they have no simple structure. In some cases such an amorphous structure can be rationalized by a transformation of an icosahedron.[4] This feature is independent of the exact form of the potential which is the Rosato Guillopé Legrand (RGL) potential[5] in our case, the Sutton-Chen potential in Ref. 2, or the Gupta potential in Ref. 3. We extend these studies to much larger cluster sizes for which we no longer find amorphous ground-state geometries. A global optimization for these large structures is significantly more difficult because these large nonamorphous clusters have a multifunnel landscape with an extremely high number of local minima. In order to determine the structure of large clusters containing a few hundred atoms, educated guesses of low-energy structures were until now made instead of systematic global optimization. This procedure was used for metallic clusters in many publications. Both for model Lennard-Jones clusters[6] as well as for gold clusters described by various potentials,[7–9] they all arrived at the same conclusion. For small clusters icosahedral structures are energetically the lowest; for medium size clusters decahedral structures are best; and for large clusters finally truncated octahedra (TOh). This evolution of the shape was explained by the fact that the ratio of surface-to-volume atoms is decreasing as the cluster size increases. Icosahedra (Ih) are terminated everywhere with the energetically most favorable (111) surfaces and they are nearly spherical, but the internal atoms have a lot of strain. The truncated octahedra on the other hand have in the center the perfect fcc crystalline structure but (100) facets with large surface energy. The decahedra have an intermediate behavior. The size range within which each of the structural motifs is lowest in energy was called a window by Baletto *et al.*[8] The cluster sizes at which the transition between the different structural motifs takes place depends on the element.[10] For gold, the transitions happen already at rather small cluster sizes.[8] Our global optimization results give a more complex picture. Even though certain structural motifs dominate around certain sizes, there are no well-defined windows within which only one structural motif would exist. Instead the structural types change upon the addition of one or a few atoms. As one increases the number of atoms, one thus alternatingly encounters a certain number of different structural motifs.

In this study we have obtained the structure of gold clusters with up to 318 atoms by global optimization using the minima hopping method.[11,12] Minima hopping is a highly efficient global optimization method which can in particular reliably find the global minimum for multifunnel landscapes. Gold clusters are multifunnel systems since each structural motif corresponds to a funnel. Standard genetic algorithms that were used for smaller cluster sizes would fail in this context because of their strong preference for the icosahedral funnel and their inability to escape from a wrong funnel.[13] Since global optimization on the density-functional level is not possible for such large cluster sizes, we have used the RGL interatomic potential with the parameters of Ref. 8. This potential has become virtually a standard for studies of systems with a large number of metal atoms and has been used in hundreds of publications to describe numerous properties.[14]

Figure 1 shows our central result, namely, the energies of all the ground-state configurations of the clusters for which we did a global geometry optimization together with their structural motif. We distinguish the following structural motif illustrated in Fig. 2:

(i) Amorphous. No detectable structure.

(ii) Fivefold symmetry (fivefold). A significant subset of atoms has one fivefold symmetry axis. Marks decahedra (M-Dh) fall into this class as the special case where the subset comprises all the atoms of the cluster. The large majority of our structures are imperfect in the sense that the whole cluster is not invariant under rotations around the fivefold axis.

(iii) Single fcc (s-fcc). The cluster can be cut out of a fcc

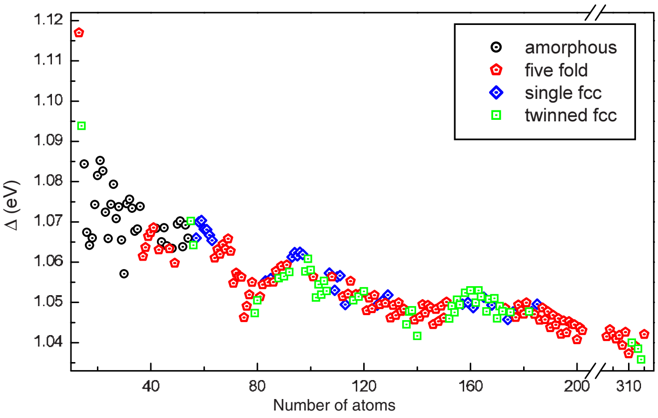


FIG. 1. (Color online) The quantity Δ of Eq. (1) for all the clusters that were studied. Among all the fivefold clusters only Au_{13} is an icosahedron.

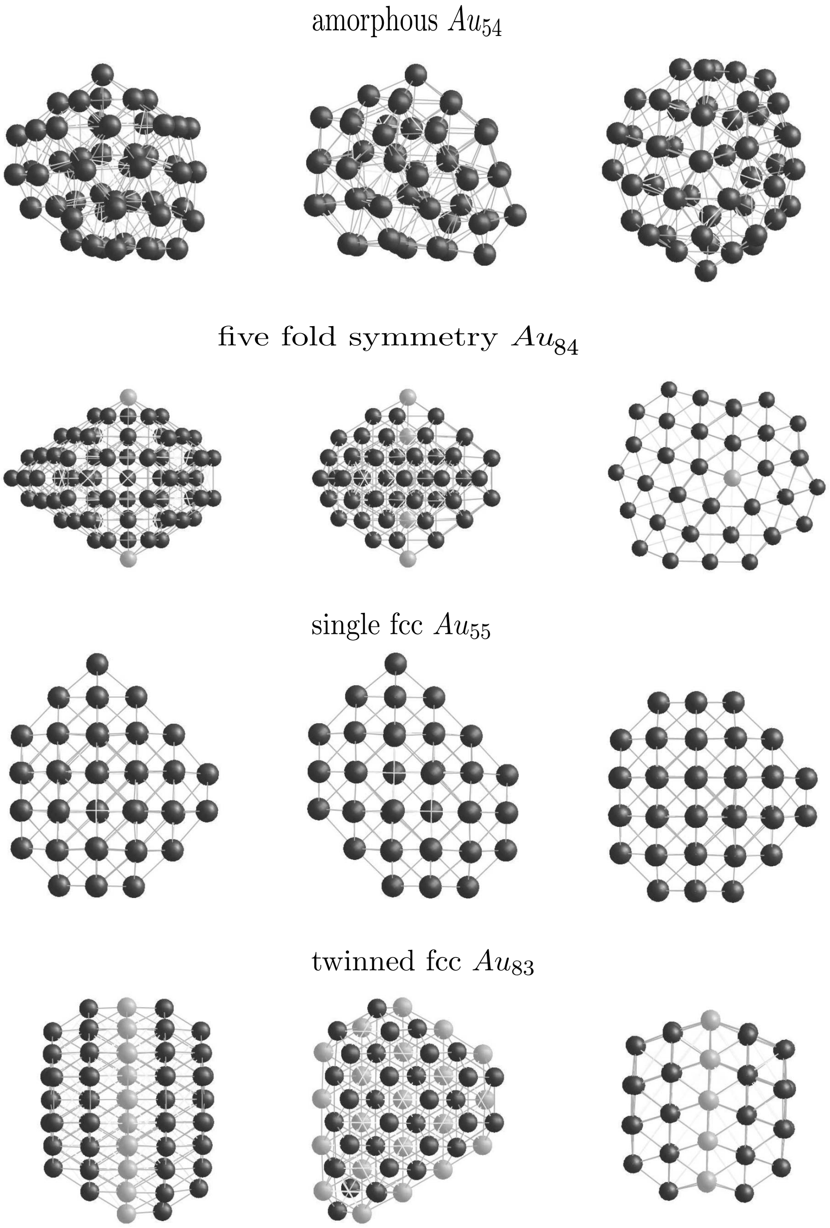
crystal. Perfect octahedra and truncated octahedra fall into this class as a special case.

(iv) Twinned fcc (t-fcc). The cluster consists out of two fcc pieces "glued" together. Twinned octahedra where the two parts are joined together after a rotation have been introduced by Raoult[6] and later examined by Cleveland[15] who came to the conclusion that they are energetically not particularly favorable. In our case, the structures are in most cases not octahedrons but more irregular structures that just contain a microtwin.

The excess energy to form a cluster out of atoms in the perfect crystal relative to the number of surface atoms is denoted by Δ and defined as[10]

$$\Delta = [E(N) - N\epsilon_{\mathrm{coh}}]/N^{2/3}. \tag{1}$$

$E(N)$ is the energy of the cluster of N atoms and ϵ_{coh} is the cohesive energy per bulk Au atom. All energies are calculated with the RGL potential.


amorphous Au_{54}

five fold symmetry Au_{84}

single fcc Au_{55}

twinned fcc Au_{83}

FIG. 2. Illustration of our classification of the various cluster structures. One row always shows the different perspectives (along x, y, and z) axis of the same cluster. In the case of the fivefold structure, the atoms on the fivefold axis are shown in gray instead of black. In the case of the t-fcc structure, the atoms in the twin plane are shown in gray.

TABLE I. Energies of perfect magic number structures relative to the energy of the global minimum of the cluster with the same number of atoms found by global optimization. An energy of 0.0 indicates that the perfect structure is the global minimum. The indexing of the M-Dh is the one from Ref. 7.

Number of atoms	Magic number type	Global minimum type	Relative energy (eV)
13	Ih (1 shell)	Identical	0.0
38	TOh (4,1)	fivefold	0.04
49	M-Dh (2,1,2)	Identical	0.0
55	Ih (2 shells)	s-fcc	0.68
55	TOh (5,2)	s-fcc	1.22
75	M-Dh (2,2,2)	Identical	0.0
79	TOh (5,1)	Identical	0.0
101	M-Dh (2,3,2)	Identical	0.0
116	TOh (6,2)	s-fcc	0.41
140	TOh (6,1)	Identical	0.0
146	M-Dh (3,2,2)	Identical	0.0
147	Ih (3 shells)	fivefold	1.85
147	TOh (7,3)	fivefold	2.49
192	M-Dh (3,3,2)	Identical	0.0
201	TOh (7,2)	fivefold	0.007
309	Ih (4 shells)	fivefold	3.64
314	TOh (8,2)	Identical	0.0

Perfect Ih, M-Dh, and TOh exist only for certain magic numbers. Our global optimization results of Table I show that even in the case where a gold cluster has a magic number of atoms, the global minimum is frequently not this perfect structure. In the case where the global minimum is one of the perfect structures listed in Table I, it is not or not much lower in energy than less symmetric neighboring structures (Fig. 1).

Our results show that in most cases the structure of clusters that differ just by a single atom is completely different. Thus the rule that every atom counts is not only valid as hitherto believed for small clusters of a few dozen atoms that have amorphous structure but even for clusters of a few hundred atoms. Figure 3 shows an example where the structure changes from fivefold to s-fcc and t-fcc by the consecutive addition of atoms. Even in cases where the basic structural motif (fivefold, s-fcc, and t-fcc) is not modified by the addition of a single atom on its surface, whole regions change their structure and the shape of a cluster changes in general.

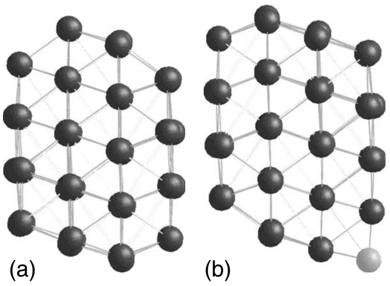


FIG. 4. The global minima structure of Au_{62} is shown in (a). (b) Taking away a weakly bound atom (shown in gray), we get the global minima of Au_{61} shown on the right-hand side.

If clusters that differ only by one atom would in general have similar structures, one could in most cases obtain the global minimum structure of the $N-1$ atom structure by taking away a weakly bound atom of the N atom global minimum structure. We have done this test and could obtain the $N-1$ ground state only in 48 cases out of 203. One such case is shown in Fig. 4.

It is well known that it is difficult to establish a relation between theoretical ground-state structures and experimental results, since in many cases the structure of clusters is determined by the kinetics of the growing process rather than by the energetics. Even if one assumes that thermodynamical equilibrium has been obtained in an experiment, relating experimental results to simulation results is not straightforward. The size of the clusters prepared for diffraction experiments can neither be controlled up to a single atom nor can the size be measured after the growth of the cluster with single atom accuracy in most cases. Therefore one has experimentally distributions of cluster sizes around a certain number of atoms. An additional factor that has to be considered is the fact that the energy separation between the geometric ground state and the second-lowest local minimum structure is very small. Figure 5 shows this energy difference for all our structures. It is of the order of the ambient thermal energy ($k_BT=0.025$ eV) and, therefore, at room temperature not only the global minimum will be encountered but also a few other low-energy configurations. Similar small energy differences were also found for a few selected small gold clusters by Soler *et al.*[16] and for silicon clusters by Hellmann *et al.*[17] using rather accurate density-functional and quantum Monte Carlo methods. The existence of a large number of

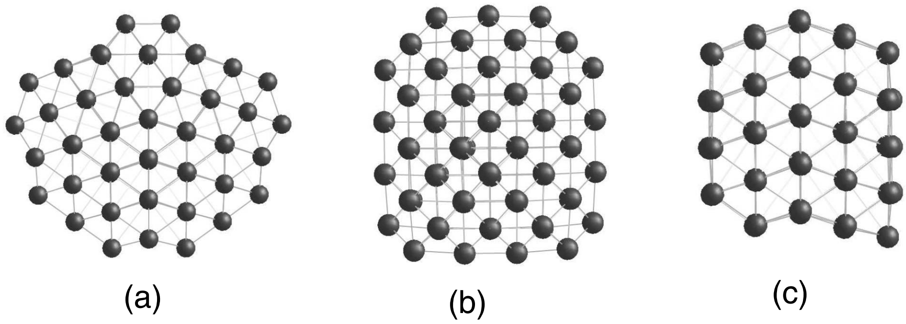


FIG. 3. The global minimum structure of fivefold Au_{91} (a), simple-fcc Au_{92}(b), and twinned-fcc Au_{93}.

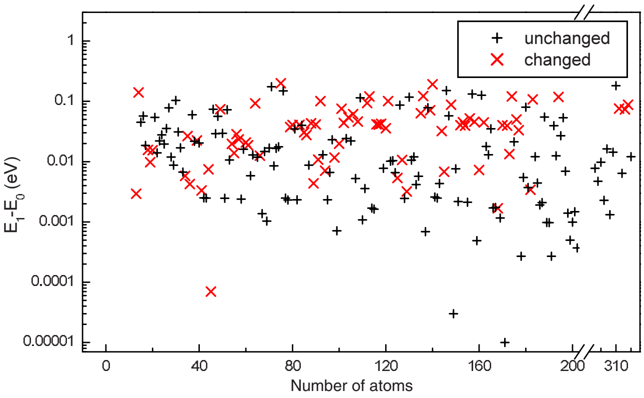


FIG. 5. (Color online) The energy difference between the global minimum and the second-lowest local minimum for all the clusters studied. If both minima share the same structure, this is indicated by a cross symbol (+); otherwise by a times symbol (×). For Au$_{55}$ we have, for instance, an amorphous structure, previously proposed to be the ground state (Ref. 3), which is only 0.014 eV higher in energy than our ground state.

structures that are energetically very close to the global minimum is also illustrated by the fact that within an energy interval of 0.1 eV above the global minimum, there are on average 12 configurations for the clusters studied in this work. All these facts show that in experiment one cannot expect to observe a single structure but rather a distribution of structures as it is indeed the case.[18,19]

Like for silicon clusters,[17] it is expected that entropy effects can change the energetic ordering, i.e., the order given by the free energy at room temperature or somewhat above is different from the energetic ordering at zero temperature. Highly symmetric configurations become disfavored with respect to less symmetric configurations at finite temperatures. We found many low-symmetry configurations that are very close in energy to high-symmetry global minimum configurations. For the M-Dh Au$_{192}$ cluster (Table I), there is, for instance, another configuration that is only 0.04 eV higher in energy and which has only one mirror plane. Even though this small energy difference is certainly not reliable given by the RGL potential, it is to be expected that density-functional theory (DFT) or even quantum Monte Carlo calculations would give low-symmetry configurations that are very close in energy to certain high-symmetry configurations.

Given the fact that the error bars of the RGL potential are larger than the energy differences between the global minimum structure and other low-energy structures, we can certainly not claim that the global minima structures that we found are the true global minima structures. What is, however, true and does not depend on the exact form of the interatomic potential is that there exist completely different types of structures that are very close in energy. This is due to the fact that a cluster cannot satisfy all the conditions that would lead to a lowering of the energy, namely, a small surface area, mainly (111) surfaces, few grain boundaries, and little strain in a fcc-like core region. This competition between features that lead to an energy lowering is qualitatively correctly described by the RGL potential. Favoring one condition at the expense of another in this competition by global rearrangements of the structure gives similar energies.

Even if it were computationally feasible to do density-functional calculations for all the large cluster configurations we studied, the accuracy of the density-functional calculation would not be sufficient either to predict the correct energetic ordering of energetically similar structures. Already for small gold clusters where the isomers differ in energy much more than in our case, the energetic ordering depends, for instance, on the density functional that is used.[20]

Taking out an atom is a significant perturbation which induces, in many cases, a complete structural change in the entire cluster. This is due to the fact that the change in the binding energy $E(N)-N\epsilon_{\mathrm{coh}}$, i.e., $E(N+1)-E(N)-\epsilon_{\mathrm{coh}}$, is on the order of 0.15 eV for the cluster sizes we studied, which is larger than the typical energy difference between the global minimum and the second-lowest local minimum (see Fig. 5).

The fact that taking out a single or a few atoms in our global geometry optimization induces a structural change can also be understood by a geometric argument. All our low-energy structures have the property that they have rather smooth surfaces. Taking out one or several atoms will at some point lead to nonsmooth surfaces that have steps or holes and thus to cluster shapes that are energetically unfavorable.

We thank the Swiss National Science Foundation and the CSC (China Scholarship Council) for the financial support of our research work and the CSCS for computing time.

---

[1] H.-G. Boyen *et al.*, Science **297**, 1533 (2002).
[2] J. Doye and D. Wales, New J. Chem. **22**, 733 (1998).
[3] K. Michaelian *et al.*, Phys. Rev. B **60**, 2000 (1999).
[4] E. Apra *et al.*, Phys. Rev. Lett. **93**, 065502 (2004).
[5] V. Rosato *et al.*, Philos. Mag. A **59**, 321 (1989).
[6] B. Raoult *et al.*, Philos. Mag. B **60**, 881 (1989).
[7] C. Cleveland and U. Landman, J. Chem. Phys. **94**, 7376 (1991).
[8] F. Baletto *et al.*, J. Chem. Phys. **116**, 3856 (2002).
[9] F. R. Negreiros *et al.*, Phys. Rev. B **76**, 205429 (2007).
[10] F. Baletto and R. Ferrando, Rev. Mod. Phys. **77**, 371 (2005).
[11] S. Goedecker, J. Chem. Phys. **120**, 9911 (2004).
[12] S. Roy *et al.*, Phys. Rev. E **77**, 056707 (2008).
[13] B. Hartke, J. Comput. Chem. **20**, 1752 (1999).
[14] A. Angulo and J. Noguez, J. Phys. Chem. A **112**, 5834 (2008).
[15] C. L. Cleveland *et al.*, Phys. Rev. Lett. **79**, 1873 (1997).
[16] J. M. Soler *et al.*, Phys. Rev. B **61**, 5771 (2000).
[17] W. Hellmann *et al.*, Phys. Rev. B **75**, 085411 (2007).
[18] K. Koga *et al.*, Phys. Rev. Lett. **92**, 115507 (2004).
[19] Z. Y. Li *et al.*, Nature (London) **451**, 46 (2008).
[20] E. Apra *et al.*, Phys. Rev. B **73**, 205414 (2006).