

Alternative Low-Symmetry Structure for 13-Atom Metal Clusters

C. M. Chang^{1,*} and M. Y. Chou²

¹*Department of Physics, National Dong Hwa University, Hualien 974, Taiwan, Republic of China*

²*School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332-0430, USA*

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The atomic geometry, electronic structure, and magnetic moment of $4d$ transition-metal clusters with 13 atoms are studied by pseudopotential density-functional calculations. We find a new buckled biplanar structure with a C_{2v} symmetry stabilized by enhanced s - d hybridization. It has a lower energy than the close-packed icosahedral or cuboctahedral structure for elements with more than half-filled d shells. The magnetic moments of this buckled biplanar structure are found to be smaller than those of the icosahedral structure and closer to available experimental results.

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Small atomic clusters are known to exhibit novel electronic, magnetic, optical, and chemical properties [1], and have stimulated intensive research efforts in recent years. Enhanced stability against dissociation or fragmentation has been found in clusters of particular size. These clusters are called “magic” clusters [2–7]. Two major factors have been identified for the origin of these magic clusters: electronic shell closure [3] in alkali- and noble-metal clusters and atomic or geometric closed shells [2,5] in rare-gas clusters and others. In the latter case, the 13-atom cluster is the most studied aggregate, for it corresponds to the first geometric shell closing for both the icosahedral and cuboctahedral structures. Recently, it has been demonstrated by laser-vaporization and time-of-flight mass spectrometry [6] that 13 is a common magic number for many transition-metal clusters including Fe, Ti, Zr, Nb, and Ta. However, it is still difficult to directly determine the atomic arrangements of such small clusters experimentally.

Accurate first-principles calculations can in turn provide reliable information about the geometrical structures of small clusters. The ground-state structure for most 13-atom metal clusters studied previously was predicted to be either an icosahedron (Ni_{13} [8], Rh_{13} [9], Pd_{13} [10], Al_{13} [11], and Nb_{13} [12]) or a cuboctahedron (Pt_{13} [13] and Au_{13} [14]). However, none of the calculations have searched the entire configuration space. High-symmetry compact structures are not necessarily the ground state, since the bonding in small metal clusters can be different from that in the bulk. A recent calculation for Cu_{13} , Ag_{13} , and Au_{13} clusters has found many isomers with energies lower than that of an icosahedron [15], while in another calculation, the neutral Au_{13} and anionic Au_{13}^- clusters are found to prefer a 2D planar structure due to strong relativistic effects [16]. Therefore, the question worth asking is whether this is a more general phenomenon than for noble metals only, and whether one can identify a trend or understand the mechanism behind it.

In this Letter, we describe the results of an extensive study of the structure and energetics of 13-atom clusters

for the whole series of $4d$ transition metals by first-principles total-energy calculations and molecular dynamics (MD) simulations. To our surprise, a new buckled biplanar structure for this magic cluster size is found to be a competitive alternative to more compact arrangements such as the icosahedral structure. For late transition-metal clusters, this low-symmetry structure is even more favorable than an icosahedron. This result would not come from any pairwise potential and is a direct consequence of the electronic properties.

The first-principles calculations based on density-functional theory (DFT) [17] were performed using the Vienna *Ab initio* Simulation Package (VASP) [18] with a plane-wave basis and Vanderbilt-type ultrasoft pseudopotentials [19]. The kinetic energy cutoffs used were the maximal default values recommended by the pseudopotential database, which ranged from 120 to 205 eV for the $4d$ transition metals considered here. For the exchange-correlation functional, we used the spin-polarized generalized gradient approximation (GGA) [20]. A cubic supercell with a side dimension of 20 Å was employed in the calculation. The Brillouin zone integration was approximated by a $3 \times 3 \times 3$ Monkhorst-Pack k -point mesh [21] in the total-energy

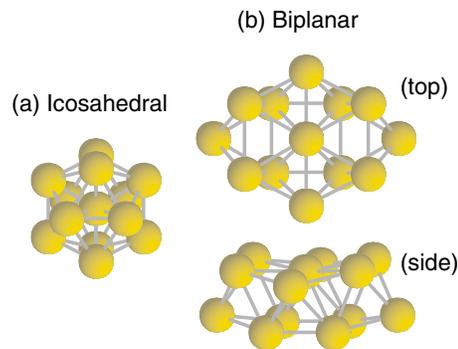


FIG. 1 (color online). Atomic arrangements of (a) the icosahedral and (b) the new buckled biplanar (BBP) structures for 13-atom clusters.

calculations where all the atoms are allowed to relax following the Hellmann-Feynman forces. The cluster geometry is optimized without symmetry constraints until the total energy is converged to 10^{-5} eV in the self-consistent loop and the force on each atom is less than 0.02 eV/Å. We have also carried out finite-temperature MD simulations for selected clusters in order to search for possible structures. Only the Γ point is used in these MD simulations, and the atomic motion is described by using the Nosé dynamics [22] for a canonical ensemble. The time step used for integrating the atomic equations of motion is one femtosecond.

We first studied the well-known high-symmetry arrangements such as the icosahedral [Fig. 1(a)], cuboctahedral, and decahedral structures. For Pd_{13} , the icosahedron, which has the highest compactness for 13-atom clusters, is most stable among these three geometries. The decahedral structure, which can be obtained from an icosahedron by rotating the top pentagonal cap by 36° (thus transforming the ten triangular faces between the top and bottom pentagonal caps into five square faces) is 0.30 eV higher in energy than the icosahedral structure. The cuboctahedron, which maintains the face-centered-cubic (fcc) geometry, has the highest energy among the three structures— 1.01 eV above that of the icosahedron. These results are consistent with that of a recent first-principles calculation [10] in which an icosahedron was found to be more stable than a cuboctahedron for Pd_{13} . We next performed first-principles MD simulations at 300 K for Pd_{13} . With an initial geometry of a cuboctahedron, the simulation generated a surprising structure that has never been reported previously. Instead of transforming into an icosahedron, the atoms rearranged themselves to yield a new buckled biplanar (BBP) structure with a C_{2v} symmetry, as shown in Fig. 1(b). Its total energy evaluated at 0 K is 0.02 (0.52) eV lower than that of an icosahedron based on a spin-polarized (non-spin-polarized) calculation. As can be seen in Fig. 1(b), this BBP structure has seven atoms in

the top layer forming a hexagonal array, and six atoms in the bottom layer consisting of a central square of four atoms plus two side atoms. It is a much more open and extended structure than an icosahedron. The layers are slightly bent and the atoms of either layer are not exactly on the same plane.

In order to determine if this is a common low-energy structure for 13-atom metal clusters, we have systematically compared the energy of this BBP structure with that of an icosahedron for the $4d$ transition-metal series. In each total-energy calculation, the atomic positions are fully relaxed. The calculated total energy with respect to that of an icosahedron is summarized in Table I. We can see clearly that the 13-atom clusters of early transition metals (Y_{13} , Zr_{13} , Nb_{13} , Mo_{13}) prefer the icosahedral structure, while those of late transition metals (Tc_{13} , Ru_{13} , Rh_{13} , Pd_{13} , Ag_{13} , and Cd_{13}) may prefer the BBP structure. Therefore, the BBP structure seems to be favored only when the d shell is more than half-filled. From the MD simulations at 300 K for Pd_{13} , Ru_{13} , and Rh_{13} for a few ps, this BBP structure seems to be thermally stable and the shape is well kept in the simulation.

In the total-energy calculation for the icosahedral structure, atoms are relaxed without symmetry constraints. Except for Nb_{13} and Mo_{13} , most clusters exhibit little deviation from the ideal icosahedral symmetry. In the bulk, Nb and Mo do not favor close-packed structures and choose the body-centered cubic structure instead. Therefore, it is not surprising that icosahedral Nb_{13} and Mo_{13} show significant distortions after being allowed to relax. The results listed in Table I for icosahedral Nb_{13} and Mo_{13} are those of fully-relaxed (distorted) geometries. Without distortions, the ideal icosahedral structure for Nb_{13} (Mo_{13}) is 0.49 (1.16) eV higher in energy than the fully relaxed BBP structure, and has a magnetic moment of 0.54 (0.79) μ_B /atom and an average nearest-neighbor (NN) distance of 2.74 (2.65) Å.

The competition between the icosahedral and BBP structures reflects a delicate balance among various en-

TABLE I. Relative total energy per cluster of the buckled biplanar structure (BBP) with respect to the icosahedral structure (ICO). The spin magnetic moment per atom (μ_B /atom), and the average nearest-neighbor distance (a_{avg}) for both structures are also shown.

	Y_{13}		Zr_{13}		Nb_{13}		Mo_{13}		Tc_{13}	
	ICO	BBP								
Energy (eV)		1.59		1.89		4.00		0.67		-1.66
μ_B /atom	1.00	0.38	0.46	0.15	0.23	0.08	0.62	0.31	1.00	0.69
a_{avg} (Å)	3.39	3.32	2.90	2.90	2.93	2.69	2.70	2.58	2.58	2.53
	Ru_{13}		Rh_{13}		Pd_{13}		Ag_{13}		Cd_{13}	
	ICO	BBP								
Energy (eV)		-0.78		-0.13		-0.02		-0.84		-0.18
μ_B /atom	0.92	0.46	1.62	1.31	0.62	0.31	0.38	0.08	0.00	0.00
a_{avg} (Å)	2.59	2.53	2.67	2.60	2.75	2.69	2.89	2.85	3.42	3.32

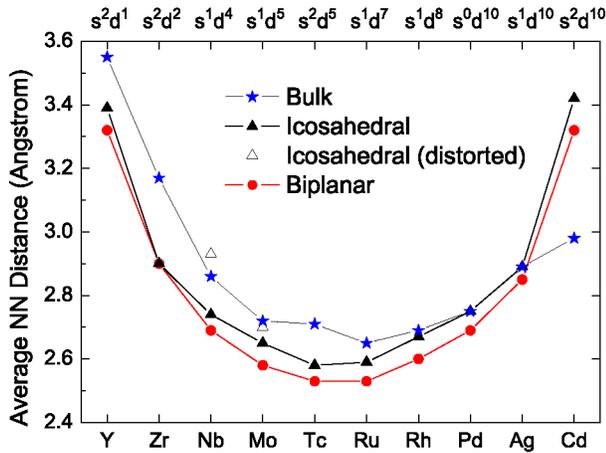


FIG. 2 (color online). Average nearest-neighbor (NN) distance for the icosahedral (filled triangles) and buckled biplanar (filled circles) structures for $4d$ 13-atom clusters compared with the bulk values (stars). The values for the low-energy distorted icosahedral structure of Nb_{13} and Mo_{13} are also shown (open triangles). The atomic valence electron configuration for each element is given at the top of the figure.

ergy terms. Being a more extended and open structure, the BBP arrangement has a lower electrostatic energy associated with the electron-electron and ion-ion repulsion, as well as a lower kinetic energy. On the other hand, the more compact icosahedral structure is designed to maximize the interaction between the electrons and the ionic cores. The number of NN pairs is 42 in an icosahedron, compared with 36 in the BBP structure. Without paying a high penalty in the Hartree energy, the latter can take a slightly smaller NN distance than the former in order to optimize the electron-ion interaction. The average NN distance in the BBP structure is therefore consistently smaller than that of the icosahedral structure (see Table I), although the difference is not substantial.

Figure 2 shows these average NN distances for the whole series compared with the bulk values. The shape of the curve also reflects the bonding characteristics in the transition-metal series. Since the d orbitals are only slightly screened by the outer s electrons, increasing the nuclear charge and adding more d electrons in the beginning of the series will cause stronger electron-ion interaction, increase cohesion, and decrease the NN distance. At a certain point near half-filled in the series, the electron-electron repulsion starts to outweigh the electron-ion interaction, the cohesive energy decreases, and the NN distance increases as the d shell gets filled. In clusters, one has much more degrees of freedom in arranging the atoms. Therefore, for late transition-metal clusters, it is expected that a structure with reduced electron-electron interactions may be favored, such as the BBP structure found in this work.

This phenomenon can also be understood by considering electronic orbitals. In chemistry terms, once half of

the d orbitals are filled, the antibonding orbitals are occupied and the cohesion is weakened. Hence a cluster structure with enhanced s - d hybridization may become favorable for elements with more than half-filled d shells. These structures are often of lower dimensions. It has been reported in a recent study of Au_N^- ($N \leq 13$) [16] that planar structures are favored due to strong hybridization of the atomic $5d$ and $6s$ orbitals resulting from relativistic effects. Here we can compare the s - d hybridization indices [16] for the icosahedral and BBP structures defined by

$$H_{sd} = \sum_{I=1}^{13} \sum_{i=1}^{\text{occ.}} w_{i,s}^{(I)} w_{i,d}^{(I)} \quad (1)$$

where $w_{i,s}^{(I)}$ ($w_{i,d}^{(I)}$) is the square of the projection of the i th Kohn-Sham orbital onto the s (d) spherical harmonics centered at atom I , integrated over a sphere of radius equal to half of the shortest NN distance in each cluster. The spin index is implicit in the sum of orbitals i in Eq. (1). The results for these two structures are plotted in Fig. 3. In order to examine the generic features, the values for the undistorted icosahedral Nb_{13} and Mo_{13} are shown. It is clear that the BBP structure has consistently higher values of H_{sd} than the icosahedron. For late transition metals, s - d hybridization is energetically favorable; thus the lower-symmetry BBP structure can be stabilized.

The other interesting issue for small metal clusters is the magnetic properties. It is known that small metal clusters made of nonmagnetic elements in the bulk can actually become magnetic, the Rh clusters [23] being an example. Therefore, we have also calculated the spin magnetic moments for the $4d$ transition-metal clusters of 13 atoms in the two structures, and the results are

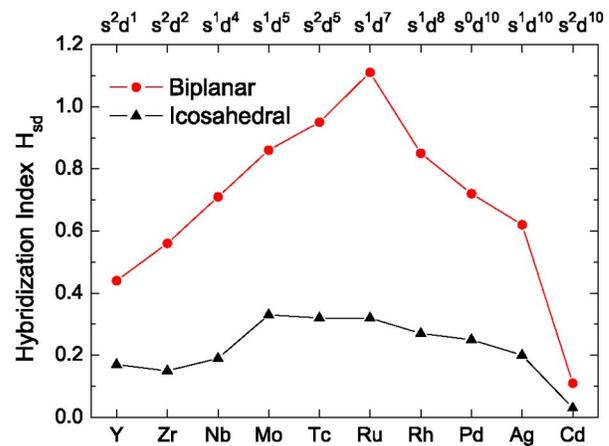


FIG. 3 (color online). The s - d hybridization index (see text) for the icosahedral (filled triangles) and buckled biplanar (filled circles) structures for $4d$ transition-metal 13-atom clusters. The values for icosahedral Nb_{13} and Mo_{13} are from the undistorted geometry. The atomic valence electron configuration for each element is given at the top of the figure.

summarized in Table I. Our values for icosahedral clusters Ru_{13} ($0.92 \mu_B/\text{atom}$), Rh_{13} ($1.62 \mu_B/\text{atom}$), and Pd_{13} ($0.62 \mu_B/\text{atom}$) are consistent with those of previous studies [10,24]. When compared with the experimental results of Ru_{13} ($< 0.29 \mu_B/\text{atom}$ [25]), Rh_{13} (0.88 [23] or 0.48 [25] μ_B/atom), and Pd_{13} ($< 0.40 \mu_B/\text{atom}$ [25]), we find the calculated values for icosahedrons are generally too high. However, as shown in Table I the spin magnetic moments of the BBP structure are consistently lower than those of the icosahedral structure, and the values for Ru_{13} ($0.46 \mu_B/\text{atom}$), Rh_{13} ($1.31 \mu_B/\text{atom}$), and Pd_{13} ($0.31 \mu_B/\text{atom}$) are closer to the experimental results, especially for Pd_{13} . The giant magnetic moments found in previous calculations [10,24] may not correspond to the correct ground state of the cluster.

We have also checked the energies of these two structures for selected transition-metal clusters in the $3d$ and $5d$ series. Ti_{13} and Hf_{13} (early $3d$ transition metals with the d shell less than half-filled) prefer the icosahedral structure with an energy difference of 1.84 and 2.03 eV, respectively. For the late transition-metal clusters in the $3d$ and $5d$ series, such as Co_{13} , Cu_{13} , Ir_{13} , Pt_{13} , and Au_{13} , the BBP structure is preferred and the energies are 0.91, 0.53, 2.49, 1.56, and 1.78 eV lower than that of an icosahedron, respectively [26]. From these results, it is expected that the trend also holds for $3d$ and $5d$ metal clusters.

In summary, we have performed first-principles molecular dynamics simulations and total-energy calculations to study the structures and energetics for the whole series of $4d$ transition-metal clusters with 13 atoms. Instead of the high-symmetry icosahedral, cuboctahedral, and decahedral structures, we find another low-lying structure with a buckled biplanar arrangement that has a C_{2v} symmetry. This novel buckled biplanar structure for 13-atom clusters has a shorter average nearest-neighbor distance than the icosahedron and is commonly favored by late transition metals with more than half-filled d shells. The spin magnetic moments of the buckled biplanar structure are generally smaller than those of the icosahedral structure, and are in better agreement with existing experimental values. In addition, the buckled biplanar structure has a larger and more irregular surface area, which is likely to enhance the catalytic reactivity of the cluster. This subject is currently being further investigated.

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*Electronic address: cmc@mail.ndhu.edu.tw

- [1] *Quantum Phenomena in Clusters and Nanostructures*, edited by S. N. Khanna and A. W. Castleman (Springer-Verlag, Heidelberg, 2003).
- [2] O. Echt *et al.*, Phys. Rev. Lett. **47**, 1121 (1981).
- [3] W. D. Knight *et al.*, Phys. Rev. Lett. **52**, 2141 (1984).
- [4] K. E. Schriver *et al.*, Phys. Rev. Lett. **64**, 2539 (1990).
- [5] T. P. Martin *et al.*, Chem. Phys. Lett. **172**, 209 (1990).
- [6] M. Sakurai *et al.*, J. Chem. Phys. **111**, 235 (1999).
- [7] O. C. Thomas *et al.*, J. Chem. Phys. **114**, 5514 (2001).
- [8] M. Calleja *et al.*, Phys. Rev. B **60**, 2020 (1999).
- [9] B. V. Reddy *et al.*, Phys. Rev. B **59**, 5214 (1999).
- [10] M. Moseler *et al.*, Phys. Rev. Lett. **86**, 2545 (2001).
- [11] J. Akola *et al.*, Phys. Rev. B **58**, 3601 (1998); B. K. Rao *et al.*, Phys. Rev. B **62**, 4666 (2000).
- [12] V. Kumar *et al.*, Phys. Rev. B **65**, 125403 (2002).
- [13] N. Watari *et al.*, J. Chem. Phys. **106**, 7531 (1997).
- [14] O. D. Häberlen *et al.*, J. Chem. Phys. **106**, 5189 (1997).
- [15] J. Oviedo and R. E. Palmer, J. Chem. Phys. **117**, 9548 (2002).
- [16] H. Häkkinen *et al.*, Phys. Rev. Lett. **89**, 033401 (2002); H. Häkkinen *et al.*, J. Phys. Chem. A **107**, 6168 (2003).
- [17] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
- [18] G. Kresse and J. Hafner, Phys. Rev. B **49**, 14251 (1994); G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).
- [19] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990); G. Kresse and J. Hafner, J. Phys. Condens. Matter **6**, 8245 (1994).
- [20] J. P. Perdew, *Electronic Structure of Solids '91*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991); J. P. Perdew *et al.*, Phys. Rev. B **46**, 6671 (1992).
- [21] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
- [22] S. Nosé, J. Chem. Phys. **81**, 511 (1984).
- [23] A. J. Cox *et al.*, Phys. Rev. Lett. **71**, 923 (1993).
- [24] B. V. Reddy *et al.*, Phys. Rev. Lett. **70**, 3323 (1993).
- [25] A. J. Cox *et al.*, Phys. Rev. B **49**, 12295 (1994).
- [26] Similar to Au_{13}^- (Ref. [16]), we also find that Au_{13} prefers planar structures due to relativistic effects. A C_s triangular structure and a D_{6h} six-capped hexagonal "star" have energies 0.74 eV and 0.03 eV lower than that of the biplanar structure, respectively. These 2D planar structures are not favored by other 13-atom transition-metal clusters.