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Ab initio random structure search for 13-atom clusters of fcc elements

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Abstract

The 13-atom metal clusters of fcc elements (Al, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au) were studied by density functional theory calculations. The global minima were searched for by the ab initio random structure searching method. In addition to some new lowest-energy structures for Pd₁₃ and Au₁₃, we found that the effective coordination numbers of the lowest-energy clusters would increase with the ratio of the dimer-to-bulk bond length. This correlation, together with the electronic structures of the lowest-energy clusters, divides the 13-atom clusters of these fcc elements into two groups (except for Au₁₃, which prefers a two-dimensional structure due to the relativistic effect). Compact-like clusters that are composed exclusively of triangular motifs are preferred for elements without d-electrons (Al) or with (nearly) filled d-band electrons (Ni, Pd, Cu, Ag). Non-compact clusters composed mainly of square motifs connected by some triangular motifs (Rh, Ir, Pt) are favored for elements with unfilled d-band electrons.

(Some figures may appear in colour only in the online journal)

1. Introduction

Nanoclusters can exhibit properties very different from both smaller atoms or molecules and larger bulk materials, and have stimulated intensive research effort in recent years due to various potential applications [1, 2]. It is well known that the physical and chemical properties depend strongly on the structure of a system. Therefore, the fundamental step is precise determination of the geometrical structure of the clusters [3], which has attracted significant interest and activity in this field. Atomic clusters can have a structure that is prohibited by the crystallographic translational-symmetry rules (e.g., icosahedra and decahedra with noncrystalline five-fold symmetry) and thus have very complex configurational spaces even for 13-atom clusters, which have been extensively studied in the last decade [4–27].

Recently, several strategies for global optimization combined with ab initio calculations have been employed to determine the lowest-energy structures for 13-atom transition metal clusters, such as the basin-hopping Monte Carlo [4], conformational space annealing [5], taboo search in descriptor space [6] and traditional molecular dynamics simulations [7–9]. With these techniques, nanoclusters composed of 13 atoms have been observed to stabilize in lower symmetry structures that are very different from their bulk counterparts [6–11]. Among these lowest-energy clusters, some still have very compact structures while others prefer non-compact ones. There seems to exist a tendency that compact structures are favored for the early and late transition metals while open structures are favored for elements in the middle of the transition metal series [7, 8]. This is similar to the trend of their bulk counterparts that the early and late transition metals form compact hexagonal close-packed (hcp) and face-centered cubic (fcc) structures, respectively, while less compact body-centered cubic (bcc) structures are formed for the elements in the middle of the transition metal series. However, it has been noted that some of the 13-atom clusters are much more compact than the others while their bulk counterparts have the same compact fcc structures. For example, the Al₁₃ cluster prefers the distorted icosahedral structure [10, 12], which is still very compact, but the Rh₁₃ and Ir₁₃ clusters prefer cubic-like open structures [6, 7, 9, 16, 17].
25]. The reason why some of the 13-atom clusters are much more compact than the others while their bulk counterparts have the same compact fcc structures is still unknown.

In this paper, we report the results of density functional theory calculations for 13-atom metal clusters of fcc elements. We have employed the recently developed ab initio random structure searching (AIRSS) method [28], which has been shown to be very efficient in generating new and unanticipated structures of solids, point defects, surfaces and clusters [28–30], to search for the lowest-energy structures. Most importantly, in addition to discovering some new lowest-energy structures via the AIRSS method, we have demonstrated a connection between the compactness of the lowest-energy structures and the ratio of the dimer-to-bulk bond length of these fcc elements. Elements without d-electrons or with (nearly) filled d-band electrons have a higher ratio of the dimer-to-bulk bond length and prefer to form compact clusters with triangular motifs. On the other hand, the unfilled d-band elements that have a lower ratio of the dimer-to-bulk bond length prefer non-compact structures composed of square and triangular motifs.

2. Computational methods

First-principles calculations based on density functional theory (DFT) [31] were performed using the plane-wave-based Vienna ab initio simulation package (VASP) [32]. The interactions between the ions and valence electrons were treated by the projector augmented-wave (PAW) method [33] in the implementation of Kresse and Joubert [34]. The kinetic energy cutoffs used were the maximal default values recommended by the pseudopotential database. For the exchange–correlation energy functional we used the spin-polarized generalized gradient approximation (GGA) as proposed by Perdew et al [35]. A cubic supercell of 20 Å size was used in the calculation to ensure negligible interactions between clusters. Due to the large cell used in the calculations, the Brillouin zone integration was approximated by a single Γ-point. The global minima of the 13-atom clusters were searched for by the ab initio random structure searching (AIRSS) [28] method with the following strategies. (I) Firstly, we used three different schemes to generate the initial positions for the atoms in the clusters: (1) distribute atoms randomly within a small cubic box of side length 10 Å inside a large cubic supercell of side length 20 Å; (2) randomly add atoms, one by one, into a cubic box of side length 20 Å with a constraint that the added atom, say the ith atom, should be located within a reasonable distance of the previously generated cluster of i − 1 atoms; (3) impose various symmetry constraints (such as the C3 or C4 rotational symmetries) in generating the building blocks (such as the triangular or square motifs) of the clusters. (II) The generated clusters from the three previously described schemes were relaxed and optimized until the total energy was converged to 10−5 eV and the Hellmann–Feynman force on each atom was less than 0.01 eV Å−1. (III) The atomic positions of all the previous relaxed structures were further displaced randomly and the structures of the clusters were then optimized without symmetry constraints. This final step was to ensure that the previously obtained relaxed structures were not trapped in the saddle point (or lines) of the energy surface.

3. Results and discussion

First of all, in order to determine the global minimum structures, the AIRSS method was applied with about 200 randomly generated initial structures (including the three different schemes mentioned in section 2) for the 13-atom clusters of the nine fcc elements (Al, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au). The lowest-energy structures for the 13-atom clusters reported in previous studies [7] were all reproduced in these trials. Furthermore, we have also found new lowest-energy states that have lower energies than the previous reported ones for Au13 and Pd13 (which will be discussed later) within the 200 random trials. The relations between the number of nearest neighbors and the relative energy (with respect to the global minimum) of the fully relaxed structures are shown in figure 1. The numbers of nearest neighbors for the isomers within about 3% of the relative energy (figure 1) above the global minimum are all larger than 32 (ranged from about 32 to 42) for Al13, Ni13, Pd13, Cu13 and Ag13 clusters, and range mostly from 22 to 33 for Rh13, Ir13, Pt13 and Au13 clusters. From these distribution pattern, it seems that more compact-like structures with higher numbers of nearest neighbors are preferred for Al13, Ni13, Pd13, Cu13 and Ag13 clusters, while non-compact structures with fewer nearest neighbors are preferred for Rh13, Ir13, Pt13 and Au13 clusters.
The lowest-energy structures found in this study for these 13-atom clusters are shown in figure 2. The point group symmetries and the magnetic moments of these clusters are summarized in table 1. The total magnetic moments for all the clusters are obtained self-consistently during the spin-polarized structural optimization calculations without any constraints. We have also made some fixed magnetic moment calculations for several lower-energy structures for each element to ensure that we have found the magnetic moments of the lowest-energy states. The distribution of the magnetic moment shows even (odd) \( \mu_B \) for clusters with even (odd) numbers of electrons, which is expected for finite systems. From the random structure searching for Al\(_{13} \), Cu\(_{13} \), Ag\(_{13} \) and Au\(_{13} \) clusters, the spin state relaxed to 1 \( \mu_B \) per cluster for all the explored structures except the very high-energy states of Ag\(_{13} \) and Cu\(_{13} \) with 3 or 5 \( \mu_B \). These results represent the non-magnetic property of these clusters, and the moment exists only because the total number of electrons in the finite systems is odd. The total magnetic moment for Ni\(_{13} \) ranges mostly from 8 to 12 \( \mu_B \) with the lowest-energy state at 10 \( \mu_B \). For Pd\(_{13} \) and Pt\(_{13} \), the total magnetic moment ranges from 2–8 and 0–6 \( \mu_B \), respectively. The lowest-energy state for Pd\(_{13} \) is 8 \( \mu_B \), while the energies for the states with 0 and 2 \( \mu_B \) of the lowest-energy structure of the Pt\(_{13} \) cluster are almost degenerate. Although the lowest-energy structures for Rh\(_{13} \) and Ir\(_{13} \) are quite similar and have the same number of valence electrons, the distributions of the total magnetic moments for various structures are mostly in the ranges 7–17 \( \mu_B \) (with the lowest-energy state at 9 \( \mu_B \)) and 3–9 \( \mu_B \) (with the lowest-energy state at 3 \( \mu_B \)) for Rh\(_{13} \) and Ir\(_{13} \) clusters, respectively. We have also made non-spin-polarized calculations for several lower-energy structures for each element, and found that none of them have the tendency to reverse the relative stability of these lower-energy structures. These results are consistent with the previous report [20], which shows that the effect of the spin polarization on the structural stability is significant for the 3d Fe clusters but is less important for the 3d Ni clusters, and its effect decreases as the atomic number increases.

For the Al\(_{13} \) cluster, the lowest-energy structure is the distorted icosahedron, which is consistent with previous results [10, 12]. A recent study has shown that the calculated density of states for the icosahedral Al\(_{13} \) cluster reproduces the experimental photoelectron spectra [12]. The lowest-energy structures for Cu\(_{13} \) and Ag\(_{13} \) clusters have the same morphology (figures 2(c) and (f)) and are consistent with previous results [7]. For Au\(_{13} \) clusters, it has been shown that a planar structure is preferred due to the relativistic effect [11]. In this study, by the AIRSS method, we find that the lowest-energy state for the Au\(_{13} \) cluster is indeed a planar structure (as shown in figure 2(i), which is a close-packed structure in two-dimensional space with C\(_{3v} \) symmetry), but with lower energy by 30 meV than the previously reported triangular-like structure with C\(_{3v} \) symmetry [11]. The energy difference (and all the energy differences reported hereafter) is obtained by our own calculations, i.e., the previous reported structures are re-optimized within our calculations with the same exchange–correlation energy functional.

We also discover another two lowest-energy structures for Ni\(_{13} \) (figure 2(b) and Pd\(_{13} \) (figure 2(e)) clusters, which are lower in energy by 95 and 13 meV respectively than the previously reported ones by Piotrowski et al [7]. Interestingly, the lowest-energy state for Ni\(_{13} \), which has also been reported by Aguilera-Granja et al [21], has

<table>
<thead>
<tr>
<th>Point group</th>
<th>Ir</th>
<th>Rh</th>
<th>Au</th>
<th>Pt</th>
<th>Ni</th>
<th>Pd</th>
<th>Ag</th>
<th>Cu</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu_B ) (( \mu_B ))</td>
<td>C(_{6v} )</td>
<td>C(_{6v} )</td>
<td>C(_{1v} )</td>
<td>C(_{7v} )</td>
<td>C(_{7v} )</td>
<td>C(_{1v} )</td>
<td>C(_{2v} )</td>
<td>C(_{2v} )</td>
<td>~C(_{3v} )</td>
</tr>
<tr>
<td>E(<em>{B</em>{13}} ) (eV/atom)</td>
<td>3.37</td>
<td>3.66</td>
<td>3.97</td>
<td>4.28</td>
<td>5.48</td>
<td>5.65</td>
<td>5.66</td>
<td>5.69</td>
<td>6.26</td>
</tr>
<tr>
<td>( r_{B_{13}} ) (( \mu_B ))</td>
<td>2.41</td>
<td>2.44</td>
<td>2.72</td>
<td>2.59</td>
<td>2.36</td>
<td>2.69</td>
<td>2.85</td>
<td>2.46</td>
<td>2.77</td>
</tr>
<tr>
<td>( r_{B_{13}} ) (( \mu_B ))</td>
<td>2.74</td>
<td>2.72</td>
<td>2.95</td>
<td>2.81</td>
<td>2.49</td>
<td>2.78</td>
<td>2.95</td>
<td>2.57</td>
<td>2.86</td>
</tr>
<tr>
<td>( E_{B_{13}} ) (eV/atom)</td>
<td>−7.32</td>
<td>−5.91</td>
<td>−2.98</td>
<td>−5.54</td>
<td>−4.77</td>
<td>−3.70</td>
<td>−2.49</td>
<td>−3.47</td>
<td>−3.53</td>
</tr>
</tbody>
</table>
a triangular-pyramid-like structure which is composed of a triangular pyramid with 1–3–6 atoms in the A–B–C stacking of the (111) face of the fcc crystal. The other three atoms are capped at the B-site stacking at the basal plane of the triangular pyramid. This lowest-energy structure for the Ni13 cluster with C3v symmetry has a magnetic moment of 10 \( \mu_B \) (0.77 \( \mu_B \)/atom), which is consistent with the experimental result of \( \sim 0.8 \mu_B \)/atom [36]. The icosahedral Ni13 cluster is higher in energy by 0.24 eV than the lowest-energy structure and has a moment of 8 \( \mu_B \) (0.62 \( \mu_B \)/atom), which is a little too low when compared with the experimental value. For the Pd13 cluster, the previously reported lowest-energy bilayer structures with \( C_3v \) [17, 27] and \( C_5 \) [7, 9, 27] symmetries are also generated in our searching, and the \( C_5 \) structure with a magnetic moment of 6 \( \mu_B \) is lower in energy by 101 meV than the \( C_3v \) structure with a magnetic moment of 6 \( \mu_B \), which is consistent with the previous study [27]. The new lowest-energy state with \( C_1 \) symmetry found in this study (figure 2(e)), which is lower in energy by only 13 meV than the sepet \( C_5 \) bilayer structure, has a total spin magnetic moment of 8 \( \mu_B \) (0.62 \( \mu_B \)/atom), which is a little higher than the experimental value (<0.4 \( \mu_B \)/atom) [37].

For the Pt13 cluster, the lowest-energy structure we have found, as shown in figure 2(h), has a \( C_5 \) symmetry with a spin magnetic moment of 2 \( \mu_B \). This result is consistent with the result of Piotrowski et al [7]. The structures reported by Wang and Johnson [9] and Sun et al [6] have also been found in this study, but their total energies are 90 and 230 meV higher respectively than the lowest-energy state shown in figure 2(h). The spin magnetic moment is 2 \( \mu_B \) for both cases, which is consistent with previous results [6, 9]. Although it is known that the spin orbit coupling (SOC) effect is strong enough to reverse the relative stability of structural isomers for small Pt clusters [22, 38], it is much less relevant for the Pt13 cluster, as was discussed by Błoński and Hafner [22]. They have shown that the Pt13 cluster exhibits only a small non-collinear effect and a Pt cluster of this size is close to a magnetic to non-magnetic transition. Furthermore, Piotrowski et al [7] have also discussed the SOC effect for Pt13 clusters, and found that the lowest-energy state (the same structure as ours) remains unchanged when SOC is included in the calculations although the relative stabilities of some of the higher-energy states do change accordingly.

The lowest-energy structures for the Rh13 and Ir13 clusters found in this study have similar simple-cubic-like structures with spin magnetic moments of 9 and 3 \( \mu_B \) respectively, which are consistent with previous results [6, 7, 9, 16, 25]. The magnetic moment for Rh13 (0.69 \( \mu_B \)/atom) is quite close to the experiment value (0.48 ± 0.18 \( \mu_B \)/atom) [37]. From figure 2, we can see that the lowest-energy isomers for Al13, Ni13, Pd13, Cu13 and Ag13 clusters are composed exclusively of triangular motifs which result in more compact-like structures, and the lowest-energy isomers for Rh13, Ir13 and Pt13 clusters are composed of square and triangular motifs which lead to non-compact structures.

In order to quantitatively describe how compact a cluster is, we employed the concept of the effective coordination number (ECN) and averaged bond length [7, 39, 40] to analyze the lowest-energy structures of these 13-atom clusters. The averaged bond length for the \( i \)th atom is defined as

\[
 d_{i,av} = \frac{\sum_{j=1}^{N} d_{ij} \exp[1 - (d_{ij}/d_{av})^6]}{\sum_{j=1}^{N} \exp[1 - (d_{ij}/d_{av})^6]},
\]

where \( N \) is the total number of atoms in the cluster. The initial value of \( d_{i,av} \) is taken as the shortest distance between atom \( i \) and all \( j \) (\( j \neq i \)) atoms, and then the final value is obtained self-consistently with a convergence criterion of \( 10^{-4} \) Å. Then, the ECN for the \( i \)th atom is calculated by

\[
 \text{ECN}_i = \frac{\sum_{j=1}^{N} \exp \left[1 - \left(\frac{d_{ij}}{d_{i,av}}\right)^6\right]}{N}.
\]

The average bond length and the ECN for the cluster are defined as

\[
 r_{13} = d_{av} = \frac{1}{N} \sum_{i=1}^{N} d_{i,av}
\]

and

\[
 \text{ECN} = \frac{1}{N} \sum_{i=1}^{N} \text{ECN}_i.
\]

The exponential weighting function and the power 6 are used to ensure that the ECNs have the same values as the ordinary coordination numbers (CNs) for highly symmetric systems such as icosahedral clusters (CN = 6.46) and fcc crystalline solids (CN = 12) [7, 40].

The calculated ECNs and averaged bond lengths are summarized in table 1. According to the ECNs shown in this table, there seem to be two distinct groups. The effective coordination numbers for Al13, Ni13, Pd13, Cu13 and Ag13 clusters are roughly between the fcc truncated cuboctahedron (ECN = 5.54) and the most compact icosahedron (ECN = 6.46). The effective coordination numbers of the other group, which is composed of Ir13, Rh13, Au13 and Pt13 clusters, are much lower (ECN ≤ 4.28). Figure 3(a) displays a roughly linear relationship between the ratio of the binding energy per ECN of the clusters to the bulk energy and the ratio of the averaged bond length of these clusters to their bulk NN distance. This implies a simple correlation between the bond length and the bond strength. That is, the averaged bond strength is reinforced, as compared to the binding of the bulk, for clusters with lower ECN, which corresponds to having shorter averaged bond length. In other words, the clusters minimize their energy by building up stronger binding, i.e. shorter bond lengths, with the surrounding neighboring atoms at the expense of a reduction in coordination number.

Since the clusters serve as a natural bridge between the macroscopic bulk limit and the microscopic limit of atoms and molecules, we have also calculated the ratio of the dimer bond length to the bulk nearest neighbor (NN) distance for comparison. The calculated dimer bond length and the lattice constant of the bulk for these nine fcc elements are also
Figure 3. (a) The relationship between the averaged binding energy per ECN (normalized to the bulk cohesive energy) and the ratio of the averaged bond length of the M\textsubscript{13} cluster to the bulk NN distance; (b) the relationship between the effective coordination number of the lowest-energy state of the M\textsubscript{13} cluster and the ratio of the dimer bond length to the nearest neighbor distance of the bulk. The lines are used for guiding the eyes only.

summarized in table 1. From the relationship between the effective coordination number of the M\textsubscript{13} (M = Al, Rh, Ir, Ni, Pd, Pt, Cu, Ag, and Au) cluster and the ratio of the dimer bond length to the bulk nearest neighbor distance as shown in figure 3(b), there seem to be two distinct groups (except for Au\textsubscript{13}) again. Elements that have higher dimer-to-bulk NN ratios (Al, Ni, Pd, Cu, and Ag) also have higher ECNs for their 13-atom clusters, i.e., compact-like structures are preferred. Among the five elements that prefer compact-like structures, Al has the highest ratio of dimer-to-bulk bond length and its ECN for the 13-atom cluster is very close to the value for the icosahedron, while Ni has the lowest ratio of dimer-to-bulk bond length and its ECN for Ni\textsubscript{13} is very close (just a little bit lower) to the value for the fcc cuboctahedron. On the other hand, elements that have lower dimer-to-bulk NN ratios (Rh, Ir and Pt) also have considerably lower effective coordination numbers (ECN < 4.5) and thus form non-compact lowest-energy structures, and their compactness increases as the dimer-to-bulk NN ratio increases. On further investigating the lowest-energy structures of the non-compact elements, i.e. Rh\textsubscript{13}, Ir\textsubscript{13} and Pt\textsubscript{13}, we notice that the structure of Ir\textsubscript{13}, which has the lowest dimer-to-bulk NN ratio, is composed of all square motifs apart from one triangular motif. As the dimer-to-bulk NN ratio increases from Ir to Rh to Pt, the proportion of triangular motifs in the lowest-energy 13-atom clusters increases.

In order to understand the reason why some of the fcc elements prefer compact-like structures while the others prefer non-compact ones in the 13-atom clusters, we calculated the projected densities of states (DOSs) of the nine lowest-energy clusters, as shown in figure 4. From this figure together with figure 2, we can see that compact structures are preferred for Al, which is an element without d-electrons, and Cu, Ag, Ni, and Pd clusters, which have filled or nearly filled d-electrons, while non-compact (open) structures are preferred for Rh, Ir and Pt clusters, which have unfilled d-electrons. Interestingly, a similar correlation between the type of structure (compact or open) and the relative number of d and sp electrons was also discussed by Aguilera-Granja \textit{et al} [20]. From the study of the late isoelectronic 3d (Fe, Co, Ni) and 4d (Ru, Rh, Pd) transition metal clusters of 13 and 23 atoms [20], Aguilera-Granja \textit{et al} have found that compact structures are preferred by the 3d Fe and Ni clusters in comparison to the open structures of the 4d Ru and Rh clusters. This trend (with exceptions for Co and Pd clusters) indicates a more metallic character in the bonding of the 3d ones and a tendency towards a more covalent and directional bonding in the 4d ones. They have also shown that the number of localized d-electrons relative to the delocalized sp ones is larger in the 4d clusters than in their 3d counterparts, and more d-electrons with fewer sp electrons (when compared to their 3d counterparts) favors more covalent directional bonding of the cubic structures for Ru\textsubscript{13} and Rh\textsubscript{13}. This trend is similar but not exactly the same as our findings. In [20], the discussions are focused on the trend between the 3d and 4d clusters that have different bulk structures.
However, in this paper we focus on elements that all have the compact fcc bulk structure. From the projected DOSs for the 13-atom clusters presented in figure 4, we can see that, for elements without d-electrons (Al) or with (nearly) filled d-electrons (Cu, Ag, Ni, and Pd), the charge distribution can be more spherical-like around the atoms, and they thus prefer non-directional bonding and tend to maximize the number of bonds. Actually, the authors of [20] have also argued that Pd_{13} clusters, in which the d states are close to being fully occupied, prefer a compact structure when compared with Rh_{13} clusters, which prefer cubic-like open structures. This is consistent with our results. On the other hand, the projected densities of states show unfilled d-electrons for Rh, Ir and Pt clusters, and, thus, the charge distribution would be more directional-like and prefer stronger directional-like bonding. Therefore, the lowest-energy states for Rh_{13}, Ir_{13} and Pt_{13} clusters comprise many square motifs which resemble the directional bonding property. Furthermore, as shown in figure 4, the d-electrons in the Ir cluster interact most strongly (largest effective d-band width) among these nine elements, followed by Rh and Pt clusters. These are the three with open structures. Thus, the open structures seem to be stabilized by the strong interaction of unfilled d orbitals, which is consistent with previous results [20]. When comparing with figure 3, we find that elements without d-electrons or with (nearly) filled d-electrons have a larger dimer-to-bulk NN ratio and their corresponding lowest-energy 13-atom clusters prefer compact-like structures, while elements with unfilled d-electrons have a much lower dimer-to-bulk NN ratio and their corresponding lowest-energy 13-atom clusters prefer non-compact structures.

4. Summary

In summary, we report a theoretical study of 13-atom metal clusters of fcc elements by density functional calculations. The global minimum configurations were searched for by the ab initio random structure search, and we have found new lowest-energy structures for Pd_{13} and Au_{13} clusters. We have also found that elements with a higher ratio of dimer-to-bulk nearest neighbor (NN) bond length would have higher effective coordination numbers (ECNs) for the lowest-energy structures of the 13-atom clusters (except for Au_{13} which prefers a 2D planar structure). From the relationship between the ECN and the ratio of dimer-to-bulk NN bond length, we can identify two distinct groups for the lowest-energy structures: (1) compact-like structures preferring triangular motifs for elements without d-electrons (Al) or with (nearly) filled d-electrons (Ni, Pd, Cu, Ag); (2) non-compact structures consisting of square and triangular motifs for unfilled d-band elements (Rh, Ir, Pt).

Acknowledgments

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