Trends and Properties of 13-Atom Ag–Au Nanoalloys I: Structure and Electronic Properties

Hector Barron,† Lucas Fernández-Seivane,‡ H.-Ch. Weissker,†† and Xóchitl López-Lozano*,†

†Department of Physics & Astronomy, The University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas 78249-0697, United States
‡Aix Marseille University, CNRS, CINaM UMR 7325, 13288, Marseille, France
*European Theoretical Spectroscopy Facility

ABSTRACT: We present a systematic study of the structures and the electronic and magnetic properties of 13-atom Ag–Au nanoalloys, using spin-polarized ab initio calculations based on density functional theory. To this end, we use all possible chemical configurations of four different initial symmetries as starting structures: icosahedra, decahedra, cuboctahedra, and the buckled biplanar (BBP) cluster. Mixing is energetically favored; there is no indication of segregation. We find a general tendency to minimize the number of Au–Au bonds. Many of the clusters undergo strong morphology changes. The resulting structures of lowest energy, independent of the starting geometry, are distorted biplanar clusters. The cuboctahedra are a rather stable local minimum against geometry changes following the introduction of the mixing. All the lowest-energy structures have a Kohn–Sham HOMO–LUMO gap of about 0.2 eV and a total spin of 1 μB. Higher total spin values are found for some of the icosahedra and decahedra, but they have an energy much higher than that of the lowest-energy structures of the respective compositions. The quasi-particle gap is about 3.7 eV across the composition range. It does not vary appreciably with the composition and structural details of the clusters.

INTRODUCTION

Bimetallic nanostructures are of great interest from both the fundamental and the technological points of view not only because of their potential to improve the catalytic properties of nanocatalysts1−5 but also because of the possibility of tuning their optical properties by changing the composition and the chemical configuration.6−9 The properties of the nanostructures, and hence their performance for applications, depend critically on their size, shape, and composition, as well as on the chemical configuration, as shown by the differences of the properties of random alloys and core–shell structures of equal composition.6,7 The two noble metals Ag and Au are known and used for their surface plasmon resonances. However, the two materials are optically very different. While in the Ag particles, the resonance persists down to very small sizes,10 it is strongly extenuated in Au particles below about 2 nm.7,11−14 In the bulk phase, Au and Ag form solid solutions at any composition.15 Moreover, they have practically the same lattice constants, 4.08 Å for Au and 4.09 Å for Ag. They present, therefore, a convenient system to study the effect of alloying on the structure and the properties of nanoparticles.

The introduction of chemical mixing complicates the calculation of the properties of alloy clusters. In addition to the morphology, the chemical configuration, i.e., the exact distribution of the different species, becomes a parameter that greatly increases the parameter space.9 Many studies have been carried out to consider the effect of the chemical configuration. Different homotops6,16,17 of a fixed structure have been treated with Monte Carlo techniques, mostly using empirical potentials. Other techniques include genetic algorithms and basin hopping.6,18 These studies have often profited from the fact that for relatively “large” NPs, magic-number closed-shell structures are particularly stable and often remain so in the case of mixing.18−20 By contrast, these bigger structures are not amenable to a full optimization using density functional theory because the numerical effort is too large. On the other hand, for very small structures, a relatively large number of studies have reported the lowest-energy structures of some systems, e.g., of Ag–Au,21−33 Ag–Ni,34 and Ag–Cu.35,36

In the present work, we focus on the size of 13 atoms, which is of particular interest because a number of closed-shell high-symmetry “magic” structures exist which are precursors of larger, stable high-symmetry structures. We consider the 13-atom icosahedron, decahedron, and cuboctahedron. These structures are particularly interesting because they can be considered building blocks that can be compounded into bigger structures.35,36 However, it is known that none of these high-symmetry clusters is the lowest-energy structure for the size of
13 Ag or Au atoms. For that reason, we include the buckled biplanar (BBP) cluster in our study, which has been shown to be more stable than icosahedra, cuboctahedra, and decahedra. The structures are shown in Figure 1.

In order to derive general trends, we consider all possible chemical configurations (homotops) of each possible composition as starting structures for ionic relaxation using density functional theory (DFT). It turns out that in many cases the chemical mixing perturbs the structures so strongly as to induce strong morphology changes. For this reason, the discussion of the effect of alloying on the different types of clusters of Figure 1 gives way to the discussion of trends in the overall behavior of 13-atom nanoalloys. On the basis of the comprehensive sampling of the different chemical configurations, we derive tendencies followed by the 13-atom nanoalloys. The paper is organized as follows. In Model Structures and Computational Details, we describe the geometries and the set of possible chemical configurations as well as the technical details of the calculations. In Results, the structures of the relaxed clusters that are lowest in energy for any given composition as well as the role of the different bond types in the alloying are discussed. The electronic and magnetic properties are reported and discussed before Conclusions are drawn.

■ RESULTS

Description of the Structures. The relaxed lowest-energy structures of each composition are shown for the different starting geometries icosahedra, cuboctahedra, BBP clusters, and decahedra in Figures 2, 3, 4, and 5, respectively. The absolute composition is smaller when the symmetry of the system is higher. The numbers and the symmetry groups are reported in Table 1. The number of homotops is smallest for the icosahedron with the largest number of symmetry operations. For the BBP, which has only 4 symmetry operations, the number is as high as 2208.

The spin-polarized density functional theory (DFT) calculations were performed with the SIESTA code using the generalized gradient approximation of Perdew–Burke–Ernzerhof (PBE). Norm-conserving Troullier–Martins pseudopotentials with scalar relativistic correction were used with 11 valence electrons per atom. The wave functions were expanded in a double-$\zeta$ polarized basis set (D$\zeta$P). A 160 Ry cutoff for the density integration grid and a density matrix convergence criterion of $10^{-4}$ were chosen. A simple cubic superlattice with a cell size of 30 Å was used. The clusters were relaxed starting from the geometry of the pure clusters after the designation of the atoms as Ag or Au had been carried out as described above. Using the conjugate gradient minimization method, all atoms were allowed to relax until the forces were smaller than 0.005 eV/Å.

Table 1. Number of Homotops for Each of the Structures for a Given Composition

<table>
<thead>
<tr>
<th>symmetry group</th>
<th>symmetry operations</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ico</td>
<td>$I_h$</td>
<td>120</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td>8</td>
<td>15</td>
<td>22</td>
<td>30</td>
</tr>
<tr>
<td>Cubo</td>
<td>$O_h$</td>
<td>48</td>
<td>1</td>
<td>2</td>
<td>5</td>
<td>13</td>
<td>27</td>
<td>42</td>
<td>54</td>
</tr>
<tr>
<td>Deca</td>
<td>$D_{5d}$</td>
<td>20</td>
<td>1</td>
<td>3</td>
<td>10</td>
<td>24</td>
<td>53</td>
<td>87</td>
<td>114</td>
</tr>
<tr>
<td>BBP</td>
<td>$C_{2v}$</td>
<td>4</td>
<td>1</td>
<td>5</td>
<td>25</td>
<td>81</td>
<td>195</td>
<td>343</td>
<td>454</td>
</tr>
</tbody>
</table>

The numbers are symmetric for $n$ and $13 - n$, i.e., the composition $n = 5$, Ag$_5$Au$_8$, has naturally the same number of homotops as $n = 13 - 5 = 8$, Ag$_8$Au$_5$. In addition, the symmetry groups and the number of symmetry operations are given for the four cluster geometries.
minimum structures across the four starting geometries, all derived from the decahedra and BBP clusters as starting structures, are highlighted by the black frames. Interactive 3D PDF figures are available in the Supporting Information. All the pure structures retain their original morphology, while many of the alloy structures are very strongly distorted and, in many cases, change their morphology completely.

In detail, the behavior of the mixed clusters for the different starting structures is the following. For the icosahedra, the clusters with 10, 11, or 12 Ag atoms keep the original morphology, while all other mixed structures are relatively strongly distorted. Ag01Au12 actually switches to a cuboctahedron morphology. It is interesting to note that several of the clusters develop a hollow cage structure without a center atom. This is the case for the clusters with 3, 5, 7, 8, or 9 Ag atoms. Moreover, the clusters with 2, 4, or 6 Ag atoms essentially form bilayer structures, with an extra atom in the first and the last of these three cases. The energies of these three are not far from those of the corresponding BBP structures as discussed below.

In the case of the cuboctahedra, the pure structures as well as Ag01Au12 undergo a Jahn–Teller distortion but without any change in overall morphology. Likewise, the lowest energy (LE) structures with 2, 5, 6, 10, 11, or 12 Ag atoms keep the cuboctahedron morphology. The remaining structures distort into mostly 3-dimensional (3D) geometries. Ag07Au06 and Ag08Au05 can be described as bilayer structures, the energies of which are rather close to those of the structures relaxed from the BBP.

The BBP mixed clusters are all distorted to various degrees with the exception of Ag12Au01 which keeps the original morphology. However, most of the LE structures (and many of the other homotops) keep the 6-fold ring with a center atom that is present in the pure BBP and a second plane roughly parallel to it. The main type of deformation is a rather free sliding of the two planes with respect to each other. It is, nonetheless, remarkable to see that even the BBP structure that for the pure Ag and Au clusters is lowest in energy, at least compared to the icosahedral, cubo, and decahedral geometries, undergoes rather strong distortion when the alloying is introduced.

The two pure decahedra are much less stable than the pure BBP clusters. All the mixed decahedral clusters are very strongly distorted; they do not keep their symmetric geometry at all. In most cases, a bilayer structure is formed, with a distorted 6-atom ring with a center atom plus a second layer and, in some cases, one extra atom. Only the Ag05Au08 cluster forms a hollow, genuinely 3-dimensional structure that does not fit into the bilayer picture. The lowest-energy structures obtained from the decahedra are, therefore, rather similar to those obtained from the BBP clusters.

Energetics, Mixing, and Distortion. The excess energy of the bimetallic cluster is defined as

$$E_{ex}(\text{Ag}_m\text{Au}_n) = E(\text{Ag}_m\text{Au}_n) - mE(\text{Ag}) - nE(\text{Au})$$

(1)

where $E(\text{Ag}_m\text{Au}_n)$ is the configurational energy of the Ag$_m$Au$_n$ cluster and $E(\text{Ag})$ and $E(\text{Au})$ are the energies per atom of Ag.
and Au. For the latter energies, different references are possible. Choosing the bulk values for \(E(\text{Ag})\) and \(E(\text{Au})\), one obtains a representation which is independent of structure and geometry of the clusters. By contrast, one can define

\[
E_{\text{exc}}^\text{m}(\text{Ag}_m\text{Au}_n) = E(\text{Ag}_m\text{Au}_n) - mE(\text{Ag}_n)/N
- nE(\text{Au}_n)/N
\]

where \(E(\text{Ag}_n)\) and \(E(\text{Au}_n)\) are the energies of the global minimum structures of the pure \(N\)-atom clusters.\(^6\) In the present work, we use the BBP clusters as reference because they have the lowest energy compared with the other three structures and can be assumed to be close to the minima.

Figure 6 shows that, first of all, the excess energy \(E_{\text{exc}}\) of the lowest-energy structures independent of the starting geometry is negative for all compositions. The same holds for each type of starting structure separately if the excess energy is referred to the respective pure clusters. This indicates that mixing is favorable at all compositions, as it was expected in view of the bulk alloy.

Compositions of particular stability are characterized by the second difference of the excess energy\(^6\)

\[
\Delta_2(\text{Ag}_m\text{Au}_n) = E(\text{Ag}_{m-1}\text{Au}_{n+1}) + E(\text{Ag}_{m+1}\text{Au}_{n-1})
- 2E(\text{Ag}_m\text{Au}_n)
\]

\(\Delta_2\) is independent of the reference energies used to calculate \(E_{\text{exc}}^\text{m}\) and \(E_{\text{exc}}\), because the term subtracted from \(E(\text{Ag}_m\text{Au}_n)\) in eqs 1 and 2 is linear in the composition and therefore leaves the second derivative unchanged. The \(\Delta_2\) calculated for our lowest-energy structures (independent of the starting geometry) does not show any particular peaks; for our clusters, there is no composition of particular stability compared with the other compositions. This corresponds to the behavior of the bulk material.\(^15\)

The excess energy for all the starting geometries shown in Figure 6 is referred to the energy of the pure BBP clusters. One can, therefore, directly compare the energies of the different structures for a given composition. Our results show that over the whole range, the structures derived from either the decahedra or the BBP are the lowest among all our relaxed clusters and in most cases are energetically very close to each other. These LE structures are highlighted by the black frames in Figures 4 and 5. Together with the fact that these structures are formed by two planes with various degrees of distortion and respective shifts as described in the previous section, we can conclude that this type of arrangement is in general favorable for the 13-atom Ag–Au nanoalloy clusters.

The excess energy of the clusters contains two different contributions. First, there is the effect of alloying between Ag and Au, without allowing for strong distortions and changes of the geometry. This part is what governs bulk solid solutions like the Ag–Au alloy. Second, the distortion and, for big displacements, the change of geometry also reduce the energy. A telling example of the two effects is the curve of the cuboctahedra in Figure 6. The cuboctahedron-derived LE structures with 4, 7, or 8 Ag atoms deviate strongly from what would be a smooth excess energy curve as it is known for the bulk Ag–Au alloy.\(^15\) Analysis of the corresponding LE structures shows that they are very distorted, deviating far from the cuboctahedron’s morphology. If, however, one considers the lowest structures of those that in general retain the morphology of the cuboctahedron, one obtains a smooth curve for the excess energy. To highlight this fact, we connected the cuboctahedra that are little distorted by the solid line in Figure 6, printing the 5 strongly distorted clusters that are lower in energy as separate points.

In order to quantitatively distinguish between the two effects, chemical composition versus distortion, we use the excess energy of the unrelaxed clusters, i.e., the alloy clusters with the geometry constrained to the starting geometry. In these clusters, from now on referred to as "constrained", only the chemical mixing contributes to the mixing energy, while distortions are absent. We consider (i) the true excess energy of the LE structures, \(E_{\text{exc}}^\text{m}(\text{LE})\) and (ii) the constrained excess energy \(E_{\text{exc}}^\text{m}(\text{LE}_{\text{constr}})\) of the same LE structures, i.e., the energy of the constrained starting clusters that after relaxation become the LE structures. Moreover, we consider (iii) the constrained energy \(E_{\text{exc}}^\text{m}(\text{LE}_{\text{constr}})\) of the structures that have the lowest energy for the constrained cluster, i.e., in the first step of the calculations, before the ions have been moved. The energies are shown in Figure 7 for all the starting structures. The reference energies are the total energies of the respective pure clusters. Because of this, all curves are zero at the pure ends of the composition range.

The first observation is that \(E_{\text{exc}}^\text{m}(\text{LE}_{\text{constr}})\) of the constrained clusters is a rather smooth curve, resembling the parabola that characterizes the bulk alloy.\(^15\) In particular, in all four cases, the behavior is symmetric. Moreover, the differences between the four starting structures are rather small; the minimum energy lies between 0.11 and 0.13 eV. This is roughly twice the experimental value for the bulk alloy.\(^15\) By contrast, the \(E_{\text{exc}}^\text{m}(\text{LE})\) of the relaxed LE structures is very different. It is smallest for the BBP and cuboctahedra (with the exception of the few strongly distorted cuboctahedra discussed above). It is likewise small, of the same order, for the largely undistorted icosahedra with 10, 11, or 12 Ag atoms. For these three, the LE structures have also the lowest constrained energies. By contrast, it is larger for the strongly distorted icosahedra and largest for the decahedra, which are all strongly distorted as discussed above.

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**Figure 6.** Excess energy \(E_{\text{exc}}^\text{m}\) of the LE structures for each starting geometry, referred to the energies per atom of the pure Ag and Au BBP clusters. For the cuboctahedra, we omitted 5 strongly distorted relaxed clusters and instead connected the clusters that remained largely undistorted by the solid green line, which results in a smooth curve. The omitted cuboctahedron-derived structures are given by the separate, unconnected triangles (see text).
Moreover, Figure 7 shows that the lowest-energy structures are not, in general, those which have the lowest unrelaxed energy. This is most clearly seen for the cuboctahedra where both possibilities are realized: for the cuboctahedra with 1, 2, 4, 5, 10, or 12 Ag atoms as well as of course for the pure structures, the LE structures also had the lowest unrelaxed energy. These are, in general (with the exception of Ag04Ag09), clusters that do not change their structure but distort only slightly. By contrast, for the cuboctahedra with 3, 7, 8, or 9 Ag atoms, the ones that relax to become the strongly distorted LE structures have a much higher constrained energy. In other words, the cuboctahedron appears to be a rather stable local minimum structure compared to, in particular, the decahedra; only the configurations with a rather high first-step energy are efficient in leaving the minimum and distort strongly.

To quantify these qualitative statements, we have determined the morphology of all the relaxed clusters. In order to do this, all the atoms in the relaxed alloy clusters have been replaced by the same type. Thereafter, the symmetry has been determined with a tolerance of 0.2 Å for the positions and 8.0° for the angles after the point group operations. In this way, a cluster that is only slightly distorted by the alloying and has kept its basic morphology will still be recognized to have approximately the initial point group symmetry. Strongly distorted clusters that have changed their morphology will have a different symmetry or no symmetry at all.

The result of this analysis is shown in Figure 8 for the cuboctahedron and the decahedron; the BBP and icosahedra are presented in the Supporting Information. The relative stability of the cuboctahedra as a local minimum is confirmed by the fact that 96% of all the relaxed alloy clusters have kept

Figure 7. Excess energy for all clusters. Shown are the constrained energy $E_{\text{exc}}^{\text{constr}}(\text{LE})$ (green) and the final energy $E_{\text{exc}}^\ast(\text{LE})$ for the lowest-energy structures (black), as well as $E_{\text{exc}}^{\text{constr}}(\text{LE}_{\text{constr}})$, the unrelaxed energy of the lowest-energy structures of the first step, i.e., without relaxation (red). The energies are referred to the energies of the respective pure clusters.

Figure 8. Symmetries indicating the morphology of the relaxed clusters (see text). 96% of the cuboctahedra keep their original morphology (symmetry $O_h$ and only slightly distorted), while this is the case of only 14% of the decahedra (symmetry $D_{5h}$ and only slightly distorted). The label “other” stands for clusters which had any other symmetry than that of the starting structure.

Moreover, Figure 7 shows that the lowest-energy structures are not, in general, those which have the lowest unrelaxed energy. This is most clearly seen for the cuboctahedra where both possibilities are realized: for the cuboctahedra with 1, 2, 4, 5, 10, or 12 Ag atoms as well as of course for the pure structures, the LE structures also had the lowest unrelaxed energy. These are, in general (with the exception of Ag04Ag09), clusters that do not change their structure but distort only slightly. By contrast, for the cuboctahedra with 3, 7, 8, or 9 Ag atoms, the ones that relax to become the strongly distorted LE structures have a much higher constrained energy. In other words, the cuboctahedron appears to be a rather stable local minimum structure compared to, in particular, the decahedra; only the configurations with a rather high first-step energy are efficient in leaving the minimum and distort strongly.

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The result of this analysis is shown in Figure 8 for the cuboctahedron and the decahedron; the BBP and icosahedra are presented in the Supporting Information. The relative stability of the cuboctahedra as a local minimum is confirmed by the fact that 96% of all the relaxed alloy clusters have kept
the cubo morphology, and only 2% have distorted in such a way as to have no symmetry. By contrast, the decahedral starting morphology is kept by only 14% of the clusters, while 47% of the decahedron-derived relaxed clusters have lost all symmetry. The relative magnitude of the excess energy hence gives a measure of the distortion that the clusters undergo with respect to the starting structures. In particular, the difference between the constrained energies and the final energies of the relaxed LE structures provides quantitative information. From Figure 7 we conclude that the contribution of the distortion to the excess energy is rather small for the BBP clusters as well as for those of the cuboctahedra and the icosahedra where the LE structures are also those which have the lowest constrained energies; it is larger for the strongly distorted cuboctahedra and the icosahedra. It is largest for the decahedra, which is consistent with the finding that all the mixed decahedra distort so strongly as to lose the reference to the initial structures.

Unlike the $E_{\text{exc}}^{\text{const}}(\text{LE}_{\text{const}})$ of the constrained clusters, the curve of the excess energy of the LE structures, $E_{\text{exc}}^{\text{LE}}$ is not symmetric in all cases. Most clearly for the cuboctahedra and the decahedra, there is a pronounced asymmetry, in particular comparing both limits of the composition range. The difference from the unrelaxed energies shows that one or a few Ag atoms are more efficient in distorting an almost pure Au cluster than vice versa, a conclusion that is supported by inspection of the

Figure 9. Excess energy as a function of the relative number of Au–Au bonds and Ag–Ag bonds for the constrained (left panels) and the final relaxed clusters (right panels) obtained for the BBP clusters. The straight lines are fits to the points. Their slopes, which indicate the tendency to increase or decrease the energy with the number of the respective bonds, are shown in the lower panels for all three bond types. The results for the other starting structures, including the figures for the mixed bonds that are not shown in this figure for the BBP, are presented in the Supporting Information.
LE structures in particular for the icosahebra and cuboctahedra (Figures 2 and 3, respectively).

**Bonds and Alloying.** The negative excess energy $E_{\text{exc}}$ of the alloyed clusters indicates that mixing is favorable, in analogy to the bulk Ag–Au alloy. Several factors influence segregation, mixing, and ordering in free-standing nanoalloys. They are (i) the relative strengths of the different types of bonds, (ii) the surface energies of the respective elements, (iii) the relative sizes of the atoms, (iv) charge transfer, and (v) potentially specific electronic or magnetic effects that might stabilize certain sizes or distributions. For the very small 13-atom clusters, it is difficult to predict the respective importance of these influences, in particular because the total number of bonds varies between the different final geometries and because it is not possible to define a surface and an interior of the clusters.

In order to quantify the influence of the number of the different bonds (Au–Au, Ag–Ag, and mixed Ag–Au), we show the correlation between the excess energy and the number of the bonds in Figure 9. The energy is shown as a function of the ratio of the bond numbers to the total number of bonds. The straight lines are linear fits, the slopes of which, shown in the lower panels, indicate the correlation between the bond numbers and the excess energy.

We find a very clear trend to minimize the number of Au–Au bonds, which holds over the complete composition range as shown by the positive slope of the fit lines. In other words, the Au atoms tend to sit in places as far separated as possible. Clearly, this means that mixing is favored because it implies that the number of mixed Au–Ag bonds is large. It is interesting to note that this finding holds for both the constrained starting structures and for the final relaxed clusters. Moreover, the result is qualitatively the same for all starting structures. We conclude that the effect is basically independent of the precise structure and depends solely on the nature of the bonds. The minimization of the number of Au–Au bonds is in agreement with the findings of Tafoughalt et al. who reported the same for very small clusters.

Unlike for the Au–Au bonds, the tendency for the Ag–Ag and the mixed Ag–Au bonds changes over the composition range. While on the Au-rich side, the number of Ag–Ag bonds is likewise minimized, it is maximized on the Ag-rich side. This is shown by the decrease in the slope of the fit lines over the composition range, starting from positive values and tending to negative values for Ag-rich clusters. The tendency to form the mixed Ag–Au bonds likewise changes over the composition range, but conversely to the Ag–Ag bonds. We note that for these bonds as well, the results do not differ qualitatively between the constrained and the final relaxed structures.

**Electronic Properties.** The Kohn–Sham HOMO–LUMO gaps of the clusters are shown in Figure 10a. Interestingly, almost all the LE structures have gap values around $0.2 \text{ eV}$, and the variations are very small. Exceptions are the pure Ag and Au icosahedra as well as the icosahedra with 11 or 12 Ag atoms. These four clusters have retained the basic icosahedral structure. Moreover, they are the only ones of the LE structures for a given starting geometry that show a higher magnetization than $1 \mu_B$ (Figure 11). The similarity of the gap values for clusters with very different structures as well as their constancy over the composition range are remarkable and indicate that, details apart, the Kohn–Sham gap value of about $0.2 \text{ eV}$ is a general feature of the 13-atom Ag–Au alloy clusters.

![Figure 10](image)

**Figure 10.** (a) Kohn–Sham HOMO–LUMO gap of all structures. The lowest-energy structures are shown by the filled symbols and connected with lines. The symbols are shifted along the x axis for better visibility. (b) Quasi-particle gap from $\Delta$SCF calculations for the LE structures of each geometry. Note that the energy axis spans the same interval, although at energies much higher than in (a).

![Figure 11](image)

**Figure 11.** Electronic spin of all clusters. The excess energy per atom is referred to the BBP clusters as in Figure 6. The spin is given by the symbol size as indicated in the legend.

In general, the Kohn–Sham HOMO–LUMO gap is suitable to discuss the variation of the gaps depending on different parameters like, in our case, the composition. However, the relevant physical quantities are either the electronic gap, referring to single-electron excitations as produced by photoemission and inverse photoemission experiments, or the optical gap that would be measured in an absorption experiment.

The electronic (or quasi-particle) gap can be approximately calculated, using the so-called $\Delta$SCF method, as the difference of the ionization potential $I$ and the electron affinity $A$, which in...
turn are calculated as total energy differences between the neutral and singly charged clusters, \( I = E(n - 1) - E(n) \) and \( A = E(n) - E(n + 1) \). The electronic gap

\[
E_{qp} = I - A = E(n - 1) + E(n + 1) - 2E(n)
\]

is generally larger than the Kohn–Sham HOMO–LUMO gap because it contains the self-energy correction which opens the gap and is strongly size-dependent.46

The electronic gaps of the LE structures for each starting geometry, calculated according to eq 4, are shown in Figure 10b for the cuboctahedra, decahedra, and BBP clusters. The results for the icosahedron-derived clusters are not shown because in this case some of the neutral clusters have a high-spin ground state as shown in the following section, and it is not easily clear to which charged states the respective excitations correspond. Moreover, we exclude a few points where the calculation of one of the charged clusters did not converge.

As expected, the electronic gaps are much larger than the Kohn–Sham gaps. The self-energy correction, calculated as the difference between the quasi-particle gap and the Kohn–Sham gap, is about 3.5 eV. This corresponds roughly to energies obtained for other systems of similar size, in particular for Si and Ge clusters, although in those cases the Kohn–Sham gaps are much larger than for the AgAu cluster.46,47 The values spread over a range of only about 0.2 eV, i.e., the overall variation is only 5% of the total value. The clear conclusion of this is that although the self-energy corrections depend strongly on the size, they are very insensitive to the composition and the precise structure of the AgAu alloy clusters. Only a weak tendency for the electronic gap to decrease with increasing Ag content is seen.

Magnetic Properties. \( \text{The total spin polarization is shown for all clusters by the symbol size in Figure 11. Practically all the LE structures have a total spin of 1} \mu_B, \text{the minimum value given the odd number of electrons. Exceptions are the pure icosahedra, with a total spin of 5} \mu_B, \text{which is in agreement with the studies of other groups,}^{48,49} \text{as well as the icosahedra} \text{Ag}_{\text{B}}\text{Au}_{\text{A}} \text{and} \text{Ag}_{\text{B}}\text{Au}_{\text{C}}, \text{with a total spin of 3} \mu_B. \text{All these maintain the icosahedral morphology. Comparison with Figure 10 shows that these are also the four icosahedra-based structures that deviate from the common gap value of about 0.2 eV. The finding that all the LE structures, which mainly present double-plane structures, have a total spin of 1} \mu_B \text{is similar to the results of Gruber et al. who reported 5} \mu_B \text{for the pure Au icosahedra but 1} \mu_B \text{for all planar and “amorphous”} \text{Au}_{\text{A}} \text{clusters.}^{49}

Figure 11 shows that all the BBP and cuboctahedra (with one exception) have a total spin of 1} \mu_B. \text{Apart from the four cases discussed above, only some of the icosahedra- and decahedra-derived structures show a spin of 3 or 5} \mu_B, \text{respectively. It must be noted, however, that they are all rather high in energy. Therefore, the general conclusion for the 13-atom AgAu clusters is that they are not magnetic. The exceptions, the icosahedra} \text{Ag}_{\text{B}}\text{Au}_{\text{A}}, \text{Ag}_{\text{B}}\text{Au}_{\text{C}}, \text{and} \text{Ag}_{\text{B}}\text{Au}_{\text{D}}, \text{where the spin-polarization clearly stabilizes the structures, have energies far higher than the minimum structures derived from the BBP clusters and the decahedra, as is clear from Figure 6.}

■ CONCLUSIONS

We have investigated the effect of alloying on the structure and the electronic properties of 13-atom Ag–Au nanoalloys using spin-polarized DFT calculations. To derive general trends and tendencies, we have used all possible chemical configurations of bimetallic icosahedra, cuboctahedra, decahedra, and buckled biplanar clusters as starting structures. While in some cases the starting structures remained unchanged up to small distortions, for many structures the chemical disorder induced strong distortions and morphology changes during the relaxation. Most of the lowest-energy structures found with our approach consist of biplanar structures that are more or less distorted and where the two planes are shifted against each other. A tendency of some of the structures to produce hollow cages was likewise observed, although not for the LE structures.

The strongest changes occurred for the decahedra which are already the most unstable structures for the pure Ag and Au clusters. They almost completely lose the “memory” of the starting structures, producing clusters that are similar to those obtained from the BBP.

The structure most stable against the effect of the chemical disorder is the cuboctahedron where the LE structures retain their morphology for 9 out of 14 compositions, including the pure clusters. In total, 96% of the alloy cuboctahedra retain their morphology, while this is the case for only 14% of the decahedra.

The excess energy is negative throughout the composition range, indicating that mixing is favorable. No signs indicating segregation have been found. The excess energy curves are approximately symmetric, indicating no particular composition of high stability. However, some asymmetry is found close to the pure ends of the composition range in the cases of the decahedron and the icosahedron, indicating that one or a few Ag atoms in an Au cluster are inducing stronger effects than vice versa. The excess energy of the constrained relaxed starting structures is strictly symmetric for all structures, and the values are greater than the respective experimental bulk values by a factor of about two. In general, the LE structures do not have the lowest energy for the starting geometries when compared to the other homotops of a given composition. Therefore, no prediction can be made based on a screening of the starting structures using static calculations.

In all cases, the clusters have the clear tendency to minimize the number of Au–Au bonds, while the trend for the Ag–Ag and the mixed Ag–Au bonds varies monotonously from the Au-rich to the Ag-rich compositions.

The Kohn–Sham HOMO–LUMO gap of all the relaxed structures, including the LE structures, has a value of about 0.2 eV, with only a small spread. The only notable exceptions are the pure Ag and Au icosahedra, which have a total spin of 5} \mu_B, as well as the icosahedra} \text{Ag}_{\text{B}}\text{Au}_{\text{A}} \text{and} \text{Ag}_{\text{B}}\text{Au}_{\text{C}}, \text{with 3} \mu_B. \text{These clusters are the lowest icosahedra of the respective compositions, but they are not the LE structures. All the absolute LE structures of our calculations have a total spin of 1} \mu_B. \text{Apart from the icosahedra just mentioned, only some of the decahedron-} \text{and icosahedron-derived clusters have a total spin higher than 1} \mu_B, \text{but they have very large energies compared to the LE structures.}

The quasiparticle gap is \( \sim 3.7 \) eV for all clusters. It is surprisingly insensitive to the composition and the details of the geometry, varying only by \( \sim 5\% \) of its total value over the composition range.

■ ASSOCIATED CONTENT

Supporting Information

Figures showing the excess energy versus the number of bonds for the relaxed and constrained (unrelaxed) icosahedra,
decahedra, and cuboctahedra-derived clusters; symmetry analysis of the relaxed icosahedra and BBP-derived clusters for each composition; and interactive 3D pdf versions of Figures 2–5 showing the lowest-energy relaxed structures for each composition for each of the starting structures icosahedron, cuboctahedron, decahedron, and BBP. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

Corresponding Author
*E-mail: Xochitl.LopezLozano@utsa.edu.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We gratefully acknowledge discussions with Christine Mottet. H.B., L.F.S., and X.L.L. acknowledge funding from NSF-DMR-1103730, NSF-PREM DMR-0934218, and UTSA-TRAC FY2011-2012. This work received computational support from Computational System Biology Core, funded by the National Institute on Minority Health and Health Disparities (G12MD007591) from the National Institutes of Health, the Texas Advanced Computing Center (TACC) at The University of Texas at Austin, and HPC resources from GENCI-IDRIS (Grant 2012-096829). Moreover, we acknowledge support from the European Union through the COST Action MP0903.

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