

STRUCTURAL PROPERTIES OF BIMETALLIC CLUSTERS FROM DENSITY FUNCTIONAL CALCULATIONS

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Received 6 September 2004

Revised 17 November 2004

The structural properties and energy ordering of the lowest lying isomers of bimetallic $(\text{CuAu})_n$ and $(\text{PtPd})_n$, $n=5-22$ clusters have been investigated by means of density functional theory (DFT) in the generalized gradient approximation (GGA). The initial cluster geometry optimization is performed by using a genetic algorithm with the many body Gupta potential. This technique provide a distribution of the lowest energy cluster structures, that are further reoptimized using the DFT-GGA methodology. The energy ordering of isomers obtained with the Gupta potential does not agree, in general, with the one obtained using DFT-GGA for the two bimetallic clusters investigated. However, the lowest energy structures of the $(\text{CuAu})_n$ nanoalloy show icosahedral patterns in agreement with the results obtained with the model potential. For the $(\text{PtPd})_n$ clusters segregation effects are found, where the Pt atoms are forming the cluster core and the Pd atoms are on the cluster surface, in agreement with previous calculations using the many body Gupta potential.

Keywords: Bimetallic clusters; genetic algorithms; nanoalloys.

1. Introduction

The structural, dynamical, electronic, and other physical and chemical properties of bimetallic clusters are of great interest nowadays.^{1,2} This is not only due to the fact that they may show an enhancement in some specific behavior with respect to that existing in the corresponding pure metal clusters, but also because there are potential applications of these systems in, for example, nanocatalysis^{1,2}.

Until now, a very limited number of theoretical studies have been performed on the structural properties of bimetallic clusters.^{1,2,3} Most of these studies are based on the use of semiempirical many body potentials to model the metallic bonding. These model potentials contain parameters that are usually obtained by fitting to

experimental data of the corresponding alloys in the bulk phase, if available.^{1,2,3} Alternatively, they may be obtained by averaging the parameters of the pure bulk metallic components.⁴ These potentials are then utilized in cluster structure calculations using global (genetic)^{3,4,5} or local^{6,7} optimization techniques to obtain the lowest-energy isomers for a given cluster size and composition.

The reliability of the resulting most stable structures of bimetallic clusters obtained with the above approach depends on the capability of the many body potential (with parameters fitted to bulk properties) to model the metallic bonding existing in the nanoalloy. At present, there is not enough available information to evaluate the accuracy of this approach. On the other hand, the lowest energy structures of bimetallic clusters are generally more difficult to find than for the pure metallic clusters due to the existence of homotops (structural forms of a bimetallic cluster that have the same geometry, but differ by the placement of the two types of atoms at the sites of that geometry), as well as geometrical isomers^{2,3}. One of the objectives of the present work is to study the validity of the above theoretical methodology, by calculating the lowest energy structures of bimetallic clusters using a first principles method (density functional theory).

In the initial stage of our approach, a distribution of the lowest energy isomers of bimetallic clusters (with a given size and composition) is obtained by using the many body Gupta potential and a global (genetic algorithm) optimization technique. In the second stage, some of the more relevant isomers of this distribution (the ten most stable isomers, for example) are used as initial configurations in a further local structural reoptimization, using the forces calculated from density functional theory. This approach has been broadly used in previous studies on pure metal clusters showing an evident effectiveness.⁸

By comparing the energy ordering and the structural properties of the cluster isomers obtained in the two mentioned stages, it will be possible to validate the accuracy of the semiempirical potential to model bimetallic nanoclusters.

In the present work two different bimetallic clusters are investigated: $(\text{CuAu})_n$ and $(\text{PtPd})_n$, with $n=5-22$. One of the motivations to study these systems is that there exist several theoretical studies on their structural properties^{1,3,4,5,6}. For the Cu-Au bimetallic clusters, most of these studies are based on the use of the Gupta model potential with parameters fitted to the bulk copper and gold, and to the Cu_3Au alloy^{1,3,5,6}. Interesting trends in the structural properties of the most stable isomers of these systems have been found using such an approach. For example, in $\text{Cu}_{n-x}\text{Au}_x$ ($n=13,14$) clusters, icosahedral like structures were obtained as the lowest lying isomers for all concentrations¹. Icosahedral packing was also found for the most stable isomers of larger Cu_xAu_y ($x/y = 3, 1, 1/3; x + y < 57$) clusters³. On the other hand, only one study on $(\text{PtPd})_n$, $n=5-28$, bimetallic clusters using the Gupta potential with parameters obtained from the averaging of Pt-Pt and Pd-Pd parameters has been published recently⁴. The lowest-lying isomers of these clusters show that decahedral structures are more abundant than icosahedral

ones, in contrast with the behavior obtained for pure Pt and Pd clusters⁴. In addition, segregation is obtained in Pt-Pd clusters, with most having Pt-rich cores and Pd-rich surfaces.⁴

Since interesting trends in the structural properties of Cu-Au and Pt-Pd bimetallic clusters have been obtained using the semiempirical approach mentioned above, it is valuable to compare these predictions with those obtained in this work from DFT calculations. In section 2, the theoretical background is briefly described. The results and a discussion of the energetics and structural properties of the bimetallic clusters are presented in section 3. Section 4 contains a summary of this work.

2. Theoretical Background

The initial step to determine the lowest energy structures of bimetallic clusters is to perform a global optimization using the Gupta many body potential and a genetic algorithm. In order to compare our results with previous published calculations, we used the same parameters of the Gupta potential reported in Ref. 3 for the CuAu clusters, and the parameter set I described in Ref. 4 for the PtPd clusters. For the global optimization of the bimetallic cluster structures, a generalized version of the genetic-symbiotic algorithm utilized by our group in pure metal cluster calculations,^{9,10} was implemented.

The global optimizations provide a distribution of the lowest lying isomers of bimetallic clusters for a given size and composition. These isomers are locally re-optimized with a conjugate gradient procedure, using the forces obtained from a DFT-GGA calculation. We use the first-principles code SIESTA¹¹ with standard norm-conserving scalar-relativistic pseudopotentials¹² in their fully nonlocal form¹³. They were generated with the atomic valence-electron configurations $d^{10}s^1$ for the Cu and Au atoms, and d^9s^1 for the Pt and Pd atoms. In the present calculations we used double- ζ s , d -basis and single p polarization orbitals.

We use the GGA parametrization of Perdew, Burke and Ernzerhof¹⁴. Spin polarization is not considered. An unconstrained conjugate-gradient structural relaxation using the DFT forces¹⁵ was performed for several initial structures (typically ten).

3. Results and Discussion

A distribution of the lowest lying isomers of $(\text{CuAu})_n$ and $(\text{PtPd})_n$, $n=5-22$, bimetallic clusters was obtained using our genetic algorithm optimization method and the many body Gupta potential. A comparison of the lowest energy isomers obtained in this work with those reported in Refs. 3, 4, indicates a full agreement in the cluster geometry, as well as in the energy value for all sizes investigated of the two bimetallic clusters. This is a relevant result since due to the existence of permutational isomers (homotops)², in addition to the geometrical ones in bimetallic clusters, it is much more difficult to find the lowest energy isomer. Since by two different optimization methods (this work and those reported in Refs. 3, 4) the same lowest energy isomers





































Lowest energy isomers and binding energies				Lowest energy isomers and binding energies			
Cu_5Au_5	 2.669 2.918	 2.954	 2.936	Pt_5Pd_5	 4.059 4.213	 4.290	 4.289
Cu_6Au_6	 3.012 3.027	 3.099	 3.080	Pt_7Pd_7	 4.456 4.589	 4.589	 4.575
Cu_7Au_7	 2.919 3.163	 3.192	 3.189	$\text{Pt}_{10}\text{Pd}_{10}$	 4.671 4.793	 4.802	 4.800
Cu_8Au_8	 3.033 3.278	 3.278	 3.276	$\text{Pt}_{14}\text{Pd}_{14}$	 4.863 4.975	 4.975	 4.971
$\text{Cu}_{14}\text{Au}_{14}$	 3.292 3.503	 3.545	 3.540	$\text{Pt}_{19}\text{Pd}_{19}$	 5.032 5.118	 5.118	 5.107
$\text{Cu}_{20}\text{Au}_{20}$	 3.454 3.656	 3.660	 3.656	$\text{Pt}_{22}\text{Pd}_{22}$	 5.082 5.177	 5.177	 5.152

Fig. 1. (Left panel) Lowest energy structures and binding energies (in eV/atom) for bimetallic $(\text{CuAu})_n$, $n = 5, 6, 7, 8, 14$, and 20 , clusters. The darker spheres correspond to the Cu atoms. The left column shows the lowest energy structure calculated from the semiempirical Gupta potential. In this case, the displayed binding energies (BE) are obtained for that geometry before (top value) and after (bottom value) the DFT-GGA relaxation. The two most stable cluster configurations obtained in this work are shown in the middle (lowest energy isomer) and right (second lowest energy isomer) columns together with their corresponding BE values. (Right panel) Same as in left panel for bimetallic $(\text{PtPd})_n$, $n = 5, 7, 10, 14, 19$ and 22 , clusters. The darker spheres correspond to the Pt atoms. For $n = 7, 14, 19$, and 22 the lowest energy isomer obtained with both the semiempirical Gupta potential and DFT-GGA correspond to the same cluster geometry.

were obtained, the probability of missing the most stable ones is low.

One additional feature of our global optimizations is that we obtained a distribution of the lowest-lying isomers of each cluster size and composition. We used the 10 most stable isomers of this distribution for further local minimization using the DFT-GGA method. Figure 1 displays the cluster geometries calculated by this procedure. The left column of each panel shows the cluster geometry obtained using as initial condition the lowest energy isomer calculated from the genetic algorithm optimization with the many body potential. Two binding energy values are shown for this column. The top value corresponds to the binding energy before cluster relaxation, whereas the bottom value is the cluster binding energy obtained after the local conjugate gradient minimization with DFT. The middle and right columns of each panel in Fig. 1 shows the cluster geometry and the binding energies of the two lowest lying isomers calculated for each cluster size (the most stable isomer is shown in the middle column).

An analysis of the data shown in Fig. 1 indicates that only in the cases of $(\text{CuAu})_8$, $(\text{PtPd})_7$, $(\text{PtPd})_{14}$, $(\text{PtPd})_{19}$, and $(\text{PtPd})_{22}$, the lowest energy isomer obtained with the many body potential coincides with the one found using DFT-GGA. This is an interesting result because it indicates that in general, the most stable permutational isomers of the bimetallic clusters calculated at the level of DFT-GGA are not the same as those predicted by the semiempirical many body Gupta potential. This result is not unexpected, since as it was mentioned in the Introduction of this paper, the parameters of the potential were obtained by fitting to experimental properties of bulk copper and gold, and to the alloy Cu_3Au in bulk phase³. In the other case, the parameters of the potential were fitted to the properties of bulk Pt and Pd, and they were averaged to generate the parameters of the Pt-Pd interaction⁴.

On the other hand, although the lowest energy configuration of the bimetallic clusters calculated with the potential and the DFT-GGA method are generally not the same, it is interesting to note that the trends in the structural properties of the lowest energy isomers obtained by both methodologies are very similar. For example, the lowest energy isomers of the $(\text{CuAu})_n$, $n = 5, 6, 7, 8, 14$, and 20, displayed in the middle and right columns of Fig. 1 (left panel) show icosahedral patterns, in agreement with the trends described in Refs. 1, 3, 5. A comparison of the structures shown in the left and middle columns (left panel) of Fig. 1, except $(\text{AuCu})_8$, indicates that the difference between the two clusters is related to the distinct relative positions of the Cu and Au atoms on the cluster surface, but does not correspond to the existence of a different cluster geometry. In other words, different permutational isomers (homotops) are obtained as the global minima, depending on the theoretical methodology utilized in the modeling of the cluster bonding.

A similar situation occurs for $(\text{PtPd})_n$ clusters. In this case, icosahedral patterns are not characteristic of the lowest energy structures for $n = 5, 19$, and 22, although some local five fold symmetry is present in $n = 7$ and 14 (see right panel of Fig. 1). However, a general trend observed in the calculated lowest energy isomers of $(\text{PtPd})_n$ clusters is that their structure is characterized by a segregation phenomenon. In this case, it is found that Pt atoms (dark spheres in the right panel of Fig. 1) concentrate around the cluster core whereas the Pd atoms are preferentially on the cluster surface. This result confirms the trend predicted using the many body Gupta potential reported in Ref. 4, and shows that a much different structural pattern characterizes this nanoalloy, as compared with the solid solution existing in the bulk phase of this material.

4. Summary

A DFT-GGA study of the energetics and structural properties of bimetallic $(\text{CuAu})_n$ and $(\text{PtPd})_n$, $n = 5-22$, has been reported in this work. The results obtained for a given size show that the energy ordering of the lowest lying isomers predicted by DFT-GGA, in general, does not agree with the one obtained using

the many body Gupta potential. This difference might be due to failure of the parameters in the semiempirical Gupta potential to describe the metallic bonding existing in the nanoalloy. On the other hand, the trends in the structural properties corresponding to the existence of icosahedral patterns in the geometry of the lowest lying isomers of $(\text{CuAu})_n$ clusters, and the appearance of segregation effects producing cluster cores rich in Pt atoms and cluster surfaces rich in Pd atoms in Pt-Pd clusters, are in agreement with those obtained using the Gupta potential^{3,4}.

The results described in this work refer to structural properties of bimetallic $(\text{CuAu})_n$ and $(\text{PtPd})_n$ clusters. These calculations are not only useful to find interesting trends in the cluster geometries, but they are the initial step in investigating their thermal¹⁶, electronic, and catalytical properties. In fact, charge transfer effects in clusters of the type studied in this paper are expected to contribute to increasing the catalytical activity of bimetallic clusters.¹⁷

Acknowledgments

This work was supported by DGAPA-UNAM Project IN104402, CONACYT-México Project 43414-F, and the DGSCA-UNAM Supercomputing Center. EMF acknowledges a FPU grant from MECyD-Spain, and thanks the members of the Instituto de Física, UNAM for their hospitality at the initial steps of this work.

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