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Theoretical study of structure and segregation in 38-atom Ag-Au nanoalloys

B.C. Curley[1], G. Rossi[2], R. Ferrando[2], and R.L. Johnston[1,a]

[1] Theoretical Chemistry, School of Chemistry, University of Birmingham, Edgbaston, Birmingham, UK
[2] Istituto Nazionale per la Fisica della Materia (INFM) and Istituto dei Materiali per l'Elettronica ed il Magnetismo/Consiglio Nazionale delle Ricerche (IMEM/CNR), Dipartimento di Fisica dell'Università di Genova, via Dodecaneso 33, I16146 Genova, Italy

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Abstract. Ag–Au bimetallic "nanoalloy" clusters with 38 atoms have been studied using a Gupta many-body potential combined with a genetic algorithm search technique. Clear changes in structure are observed as a function of Ag/Au composition and there is a clear tendency for surface segregation of the Ag atoms. Cluster stability is found to increase with increasing number of Au-Au and Ag-Au bonds and the segregation has been rationalised in terms of bonds strengths and elemental surface energies.

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1 Introduction

There is continuing interest in metal clusters because of their application in fields such as catalysis and nanoelectronics [1]. The desire to fabricate materials with well defined, controllable properties and structures, on the nanometre scale, coupled with the flexibility afforded by intermetallic materials, has engendered considerable research in bimetallic metal clusters or "nanoalloys" [2]. One of the major reasons for interest in nanoalloy particles is the fact that their chemical and physical properties may be tuned by varying the composition and atomic ordering, as well as the size of the clusters. Their surface structures, compositions and segregation properties [3] are of particular interest as they are important in determining chemical reactivity (especially catalytic activity [4]) and optical and electronic properties [5]. Nanoalloy clusters are also of interest as they may display structures and properties which are distinct from those of the pure elemental clusters.

There have been a large number of experimental studies of Ag-Au bimetallic particles, dating back to the 1960s [6, 7]. Core-shell $\mathrm{Ag}_{core}\mathrm{Au}_{shell}$ and $\mathrm{Au}_{core}\mathrm{Ag}_{shell}$ particles may be generated by chemical deposition of one metal onto a preformed cluster of the other. Optical measurements on these core-shell clusters have shown that the appearance of the surface plasmons (collective oscillations of the valence electrons) of the bimetallic particles are broad and complex. On the other hand, homogeneously alloyed $\mathrm{Ag}_x\mathrm{Au}_{1-x}$ clusters (generated, for example, by laser vaporization of bulk Ag-Au alloys) show a single plasmon resonance (as for the pure metals) with the plasmon frequency varying fairly linearly (for a given cluster size) with composition between that of the pure Ag and pure Au clusters. In fact, the UV-visible spectrum is generally used to distinguish between "core-shell" and "alloyed" Ag-Au clusters. It should be noted, however, that even though a cluster is "alloyed" there may still be some degree of surface segregation. In 1998, Han et al. reported the formation of 4 nm-diameter dodecanethiol-derivatised Ag-Au nanoalloys by reduction of a solution containing a mixture of Ag and Au salts [8]. A single plasmon resonance was observed, with a frequency varying linearly with Ag/Au composition, which indicates homogeneous alloying. However, surface-sensitive probes (X-ray photoelectron spectroscopy and FT-IR spectroscopy), indicated that the surfaces of these particles are actually enriched in Ag.

2 Methodology

2.1 Gupta potential

It is at present infeasible to perform ab initio calculations for large clusters of hundreds or thousands of atoms if large areas of configuration space are to be searched. There has, therefore, been much interest in developing empirical atomistic potentials for the simulation of such species. Empirical potentials, such as the Gupta potential [9], are derived by fitting experimental data to values calculated using a potential of an assumed functional form. The Gupta potential, which is based on the second moment approximation to Tight Binding theory, is written in terms of repulsive (V^{r}) pair and attractive many-body (V^{m}) terms,

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[a] e-mail: `r.l.johnston@bham.ac.uk`

Table 1. Gupta parameters for Au, Ag and Ag-Au (parameters supplied by C. Mottet).

Parameter	Au-Au	Ag-Au	Ag-Ag
A /eV	0.2096	0.1488	0.1031
p	10.139	10.494	10.85
q	4.033	3.607	3.18
r_0 /Å	2.885	2.8885	2.8921
ζ /eV	1.8153	1.4874	1.1895

which are obtained by summing over all (N) atoms:

$$V_{\mathrm{clus}} = \sum_{i}^{N} \left\{ V^{\mathrm{r}}(i) - V^{\mathrm{m}}(i) \right\} \tag{1}$$

where:

$$V^{\mathrm{r}}(i) = \sum_{j \neq i}^{N} A\left(a,b\right) \exp\left(-p\left(a,b\right)\left(\frac{r_{ij}}{r_0\left(a,b\right)} - 1\right)\right) \tag{2}$$

and

$$V^{\mathrm{m}}(i) = \sum_{j \neq i}^{N} \zeta^2\left(a,b\right) \exp\left(-2q\left(a,b\right)\left(\frac{r_{ij}}{r_0\left(a,b\right)} - 1\right)\right)^{\frac{1}{2}}. \tag{3}$$

In equations (2) and (3), r_{ij} is the distance between atoms i and j and A, r_0, ζ, p and q are fitted to experimental values of the cohesive energy, lattice parameters and independent elastic constants for the reference bulk structure. The potential was parametrised as shown in Table 1. The average cluster binding energy is given by equation (4)

$$E_b = \frac{-V_{\mathrm{clus}}}{N}. \tag{4}$$

Excess energy is a term which is useful for comparing the stability of clusters and is given by equation (5). This quantity is the difference in energy of the cluster compared to the equivalent number of atoms in bulk lattice sites

$$E_{\mathrm{excess}}(\mathrm{Au}_n\mathrm{Ag}_m) = V_{\mathrm{clus}}(\mathrm{Au}_n\mathrm{Ag}_m) - (nE_{\mathrm{coh}}(\mathrm{Au}) + mE_{\mathrm{coh}}(\mathrm{Ag})). \tag{5}$$

Complexity increases on going from pure metal clusters to bimetallic nanoalloys due to the presence of two different types of atoms, which leads to different isomers, based on the permutations of the unlike atoms, as well as geometrical isomers. The term "homotops" was introduced by Jellinek and co-workers to describe A_aB_b nanoalloy isomers with a fixed number of atoms ($N = a + b$), composition (*a/b ratio*) and the same geometrical arrangement of atoms (at least prior to relaxation) but which are related by the permutation of some or all of the unlike atoms [2,10].

2.1.1 Birmingham cluster genetic algorithm BCGA

The genetic algorithm (GA) is a search technique [11,12] which uses the principles of evolution to find solutions to a problem. GAs are stochastic, which allows them to search multidimensional parameter space more effectively than deterministic approaches such as hill climbing. This is because the GA investigates many different solutions simultaneously and each investigation learns about a different region of the surface. To do this the GA uses operators which are analogous to the natural processes of evolution such as mating (crossover), mutation and natural selection. GAs belong to the class of evolutionary algorithms, which also includes differential evolution and genetic programming. The BCGA program has been described in detail elsewhere [13]. A range of Ag-Au clusters have been investigated using the BCGA. Ag-Au clusters of composition approximately 1:1 were studied for 5-55 atoms and some interesting nuclearites identified from a plot of the average binding energy as a function of nuclearity. "Magic numbers" were identified for nuclearities 13, 19, 38 and 55. Some nuclearites were then investigated as a function of composition. Detailed results and analysis for 38-atom Ag-Au nanoalloys are presented here.

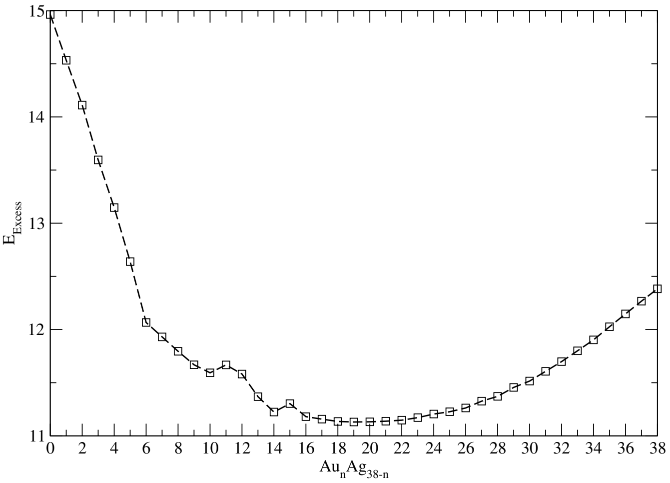

Fig. 1. E_{excess} (eV) as a function of gold content.

Using the GA search technique, each nuclearity had its composition varied systematically and optimum solutions found. To further understand the solutions provided by the GA, the number and type of bonds between the metals were investigated. This was achieved by performing a statistical analysis on 800 randomly generated structures which were correlated to the number of specific bonds in each structure, i.e. numbers of Ag–Ag, Au–Au and Ag–Au bonds.

3 Results and discussion

3.1 Structures

Figure 1 shows a plot of excess energy as function of composition for 38-atom Ag-Au clusters. There is an obvious trend and some notable deviations from it. These anomalous points coincide with structural changes that occur at these compositions. According to the GA: at $\mathrm{Au}_5\mathrm{Ag}_{33}$

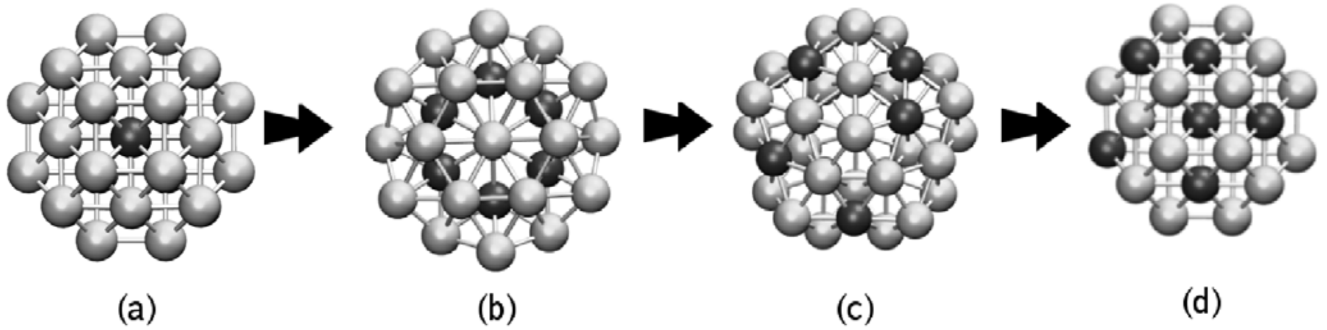

Fig. 2. Change in low energy minimum structures for selected 38-atom Ag-Au clusters as a function of increasing Au content. Light spheres = Ag, dark spheres = Au: (a) $Ag_{37}Au_1$, (b) $Ag_{32}Au_6$, (c) $Ag_{27}Au_{11}$, (d) $Ag_{23}Au_{15}$.

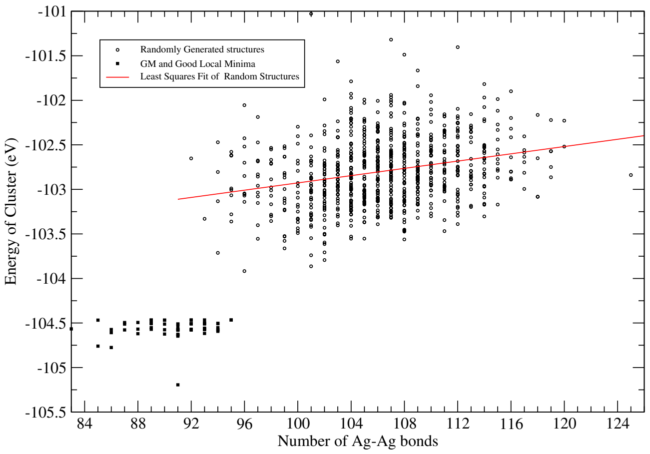

Fig. 3. Correlation of cluster potential energy with number of Ag–Ag bonds for $Ag_{32}Au_6$ clusters.

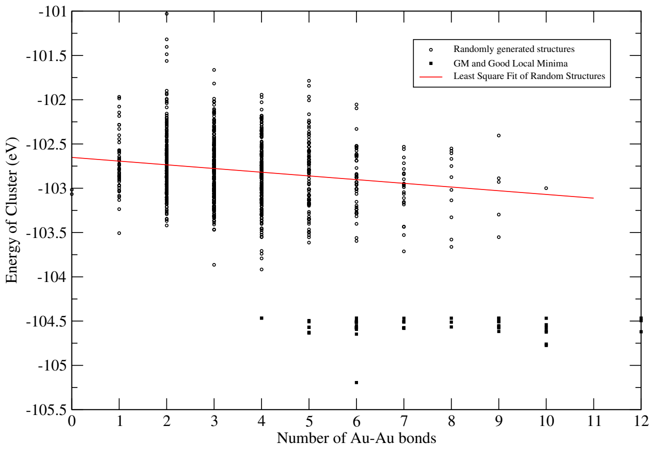

Fig. 4. Correlation of cluster potential energy with number of Au–Au bonds for $Ag_{32}Au_6$ clusters.

the structure changes from truncated octahedron (TO) to pancake-like; at $Au_{11}Ag_{27}$ the pancake structure changes to decahedral; and, finally, at $Au_{13}Ag_{25}$ the structure returns to TO and remains TO until the pure gold cluster. Structural transitions stand out nicely when using E_{excess} but the pancake to decahedral transition is particularly prominent. In fact, the decahedral structures, although low in energy, are not global minimum structures, as extending the pancake motif into higher gold compositions generated lower energy structures for $Au_{11}Ag_{27}$ and $Au_{12}Ag_{26}$. This made the transition points still notable but less prominent. Figure 2 show the structure of low energy minima found for Ag-Au clusters with 38 atoms.

3.2 Segregation

From the results obtained using the GA, it is obvious that some sort of atomic segregation is occurring with these potential parameters. Figure 2 shows that there is a clear tendency for Ag atoms to segregate to the surface of the clusters. To help identify which interactions contribute most to structure stability, a statistical analysis was performed on the bonding interactions of clusters.

Figure 3 shows the potential energy (V_{clus}) of 800 randomly generated structures for $Ag_{32}Au_6$, plotted against the number of Ag–Ag bonds. The general trend for more stable clusters is that a reduction in the number of Ag–Ag bonds leads to a more stable cluster (more negative potential energy), the low energy structures found by the GA (shown as squares in Fig. 2) are consistent with this trend.

Figure 4 is a similar analysis, based on the number of Au–Au bonds, using the same 800 structures. Increasing the number of Au–Au bonds leads to an increase in stability of the clusters.

Finally, Figure 5 shows the correlation of V_{clus} with the number of Ag–Au bonds. There is again a general increase in the stability of clusters with an increase in the number of Ag–Au bonds.

4 Conclusions

From previous work [14], it has been shown that homotop stability — i.e. whether there is segregation or mixing (either ordered or random) of the unlike atoms — is determined by a number of factors, which (depending on the geometry, size and composition of the cluster and the nature of atoms A and B) may oppose or reinforce each other.

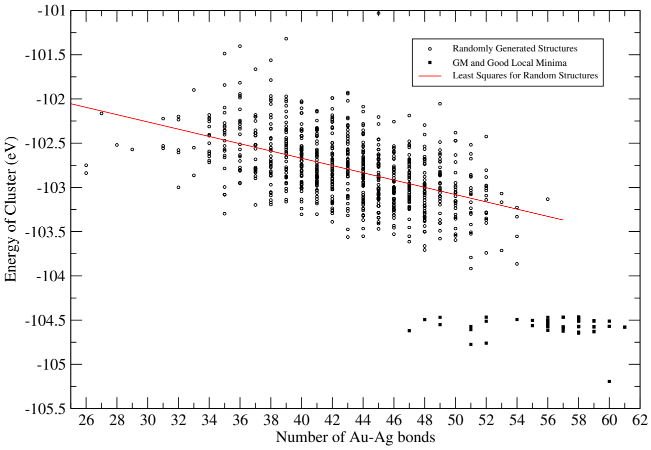

Fig. 5. Correlation of cluster potential energy with number of Ag–Au bonds for $Ag_{32}Au_6$ clusters.

Considering thermodynamic contributions to Ag-Au cluster stability, firstly, the M–M bond lengths in elemental Ag and Au are very similar (2.889 Å and 2.884 Å, respectively), so there will be no strain-induced driving force towards segregation. However the surface energy of Ag (78 meVÅ^{-2}) is less than that of Au (97 meVÅ^{-2}), which favours surface-enrichment by Ag. The cohesive energy of Ag (2.95 eV) is lower than that of Au (3.8 eV). This, coupled with the weak exothermic enthalpies of formation of the bulk Ag-Au alloys indicates that the metal-metal bond strengths are in the order Au–Au > Ag–Au > Ag–Ag, favouring core-enrichment by Au. As Au is more electronegative (2.4) than Ag (1.9), there should be some degree of electron transfer from Ag to the Au atoms. The ionic contribution to the Ag–Au bonding will favour Ag-Au mixing, as this increases the number of favourable Ag($\delta+$)–Au($\delta-$) interactions. It should be noted, however, that bulk Ag-Au alloys are solid solutions (randomly mixed, not ordered) for all compositions, which would seem to contradict charge transfer being a dominant factor in the bulk. The contribution of hetero-polar (“ionic”) bonding in Ag-Au alloy clusters has been studied (for small clusters, with up to 20 atoms) by Bonačić-Koutecký et al., using DFT calculations [15]. They found that there is indeed a certain amount of electron transfer from Ag to Au atoms. The structural and segregation properties of Ag-Au nanoalloys are currently being studied for a variety of nuclearities and compositions. As part of this work, we are also comparing the results of Gupta potential calculations with ab initio DFT calculations.

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