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Amorphous structures of Cu, Ag, and Au nanoclusters from first principles calculations

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We have carried out first-principles density functional calculations for clusters of the coinage metals containing thirteen atoms (M_{13} , where $M = \text{Cu, Ag, or Au}$). We find that for this geometric “magic number” the low energy isomers are actually disordered, forming almost a continuous distribution as a function of energy. © 2002 American Institute of Physics. [DOI: 10.1063/1.1524154]

Nanometer-sized metallic clusters play a central role in catalysis^{1–4} and nanotechnology.^{5–8} Clusters of the coinage metals, Cu, Ag, and Au, have been used in a wide range of demonstrations.^{2–8} While there has been considerable development in both cluster beams and associated techniques,^{8–10} the unambiguous determination of the 3D atomic structures of clusters remains elusive.^{4,11,12} As a result, theoretical methods play a prominent role in generating structural models of the cluster morphology.^{12–26} Conventional treatments rely on the application of sophisticated search algorithms, combined with empirical potentials that mimic metallic interactions, to generate sets of low energy structures (isomers) for clusters of different sizes.^{19–24} These calculations are often followed by first principles calculations of the most stable structures. The clusters obtained in this way, which constitute a basis for the interpretation of experimental results,^{11,12,27,28} tend to be highly symmetric.^{16,19–23} Recently, however, an increasing amount of evidence has emerged to suggest that structural disorder could be a common feature of nanometer scale clusters.^{24,26,29,30} In particular, amongst the coinage metals, gold has shown a tendency towards formation of amorphous structures.^{24,26}

Atomic clusters show both electronic and geometric magic numbers.^{4,8} The first geometric magic number is 13. Previous theoretical studies of M_{13} (where $M = \text{Cu, Ag, or Au}$) with empirical potentials indicated that the most stable structure was either an icosahedron [Fig. 1(l)] or a cuboctahedron [Fig. 1(k)].^{16,19–23} In both cases, the cluster geometry consists of a central atom surrounded by twelve neighbors that form a closed shell, which confers a special stability. First principles calculations have recently shown that at certain sizes (including 13) gold could adopt amorphous geometries.^{24,26}

The aim of the present study was to conduct first-principles calculations on a wide range of cluster isomers and thus to explore the relationship between structure and energetics. We did not restrict our search to symmetrical clusters but instead included amorphous structures as a starting point for the geometry optimisations (Fig. 1). We soon discovered that for all three coinage metals it was remarkably easy to find isomers which are more stable than the symmetrical isomers, even though they are quite disordered.

We did not attempt to find *the* global minimum isomer since this would imply a more refined search strategy, with a prohibitive computational cost for first principles calculations, but we scanned a broad sample of isomers (about 30) for each metal. In order to make comparisons we investigated the same geometries for Cu, Ag, and Au. Specifically, the optimized structures obtained for Ag were used as the initial geometries for Cu and Au.

The calculations employed density functional theory with plane-wave basis sets and pseudopotentials.³¹ We used the VASP³² code and utilized the ultrasoft pseudopotentials that form part of the code.³³ Pseudopotentials were generated with a reference configuration $d^{10}s^1$ (d states are treated as valence states in the calculations) and based on scalar relativistic wave functions with relativistic core effects taken into account. We chose the generalized gradient approximation due to Perdew *et al.* for the exchange-correlation energy.³⁴ This method and pseudopotentials have already been tested for Cu, Ag, and Au.^{33,35} The energy cutoff was 233 eV for Cu and 180 eV for Ag and Au and we did spin-polarized calculations at the Γ point of the Brillouin zone. The method is easier to implement if used in a three dimensional periodic arrangement which exploits periodic boundary conditions.³¹ A cubic box with a 15 Å lattice parameter was employed. The energy cutoff and the size of the vacuum region surrounding the cluster were checked to ensure convergence of the energies to within 2 meV/atom. All the geometries were fully relaxed until the forces acting on the atoms were less than 5 meV/Å.

In Fig. 1 we show some of the stable isomers generated by our search together with the cuboctahedron and the icosahedron. We find that the cuboctahedron is more stable than the icosahedron for Ag and Au (by 16 and 79 meV/atom, respectively) and less stable for Cu (by 29 meV/atom). Empirical potentials invariably predict the icosahedron as the most stable isomer^{19–23} although previous first-principles studies of Au_{13} (Refs. 16 and 26) gave the cuboctahedron as more stable (80–100 meV/atom), in good agreement with our results. However, the most important result we obtain from our study is that the lowest energy isomers, illustrated in Figs. 1(a)–1(j), are highly asymmetric. The recently reported result for Au_{13} ,²⁶ with an energy gap of 110 meV

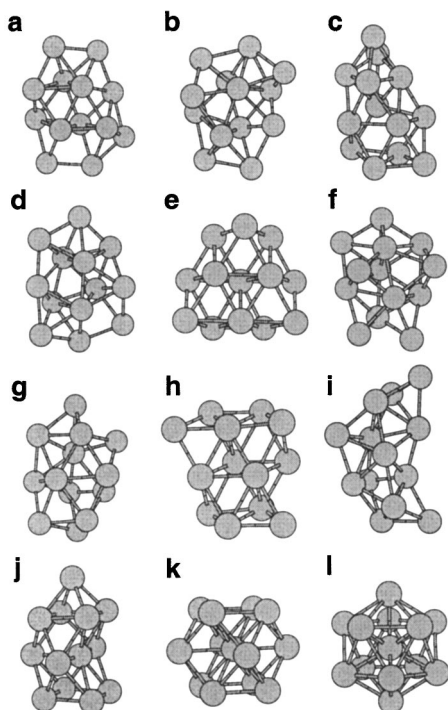


FIG. 1. The most stable Ag isomers from our density functional theory calculations. (a)–(j) Ten most stable isomers in order of decreasing stability, i.e., (a) is most stable, (k) cuboctahedron, and (l) icosahedron. Corresponding Au and Cu isomers have the same coordination structure although a slightly different stability order (see Fig. 2). Initial geometries for the optimization procedure were generated from distorted symmetric clusters (e.g., (h) was generated by distortion of (k), or by “cutting out” small clusters either (e) from a crystalline solid or (a)–(d) from melted structures.

between the most stable amorphous isomer of Au_{13} and the cuboctahedron (102 meV in the present work), is thus seen to be a *general feature* of all three coinage metal clusters.

In Fig. 2 we represent the energies of the most stable Cu, Ag, and Au isomers we obtained, corresponding to the structures shown in Fig. 1. It is apparent that the relative energy order is very similar for the three metals. This is at odds with previous calculations with empirical potentials, which revealed very different structural behavior for these metals.^{20,23} For example, it was predicted that Au might be amorphous at certain specific sizes but not Cu and Ag.^{23,24} By contrast, our results seem to suggest that the characteristics of the metal bonding are quite similar for Cu, Ag, and Au, reflecting the similarity in their electronic configurations ($nd^{10}(n+1)s^1$).

The distribution of energies shown in Fig. 2 is quite smooth. This is contrary to the traditional picture, in which one isomer (the icosahedron) is separated by a significant energy gap from the others.^{19,21} Indeed, we do not see any reason why this distribution could not be converted to an almost continuous function by adding more structures, since we did not find any special feature (see below) that lead us to think that our “global” minimum is unique in nature. Rather, it seems fairly easy to find isomers close in energy to those shown in Fig. 2. It is worth mentioning that the absence of a well separated, symmetrical global minimum for M_{13} seems to preclude the existence of a geometric magic number at this size. This agrees with mass spectral abundance

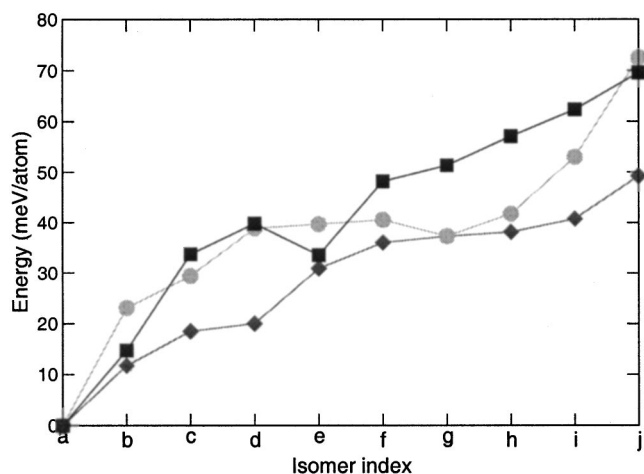


FIG. 2. Relative energies of the most stable isomers. Cu, Ag, and Au clusters are represented as squares, diamonds, and circles, respectively, with lines serving only as guides to the eye. Energies are relative to the global minimum. Isomer indexes (a)–(j) follow Fig. 1; they are ordered according to decreasing stability for silver clusters. The cuboctahedron and icosahedron, not included in the figure, have energies above the global minimum of 100 and 71 meV/atom for Cu, 75 and 91 meV/atom for Ag, and 102 and 181 meV/atom for Au.

experiments,³⁶ which only show evidence for electronic magic numbers ($n=8,20,34,\dots$). An almost continuous distribution of energies could imply the coexistence of several structural isomers. Furthermore, the distribution (and in consequence the measured properties) might depend on the temperature and also on the conditions in which the clusters are created, e.g., whether the formation process is thermodynamically or kinetically controlled.^{8,28}

The absence of significant energy gaps between isomers might also allow dynamic fluctuations of the cluster structure, i.e., liquidlike behavior. In fact, it has been argued that electronic and geometric magic numbers are indicative of liquidlike and solidlike clusters, respectively.¹⁹ In order to address this issue (partially) we have made first-principles molecular dynamics calculations, starting from our global minimum for Ag, at several temperatures. Even at temperatures as high as 700 K (Fig. 3) we do not observe structural transformations of the cluster. However, we point out that our simulations span only 6 ps, possibly a short period compared with that needed to surmount transition barriers.^{35,37} A complete study of this phenomenon would imply much longer simulations that are beyond the scope of this work.

We have tried to relate the energy of the optimized clusters to their structure, Fig. 4. We classify the isomers by using various geometrical parameters such as the average bond length, the average coordination number and others related to the shape of the clusters.¹⁴ A high average coordination number is important but not decisive in determining cluster stability [Fig. 4(b)]. It has to be balanced by a smooth distribution of coordination numbers. This is the reason why the symmetric clusters, having central atoms with a coordination number of 12, are not particularly stable. For example, transfer of one atom from the first cell of the cuboctahedron to a hypothetical second shell, thus reducing the coordination of the central atom, decreases the energy by 37

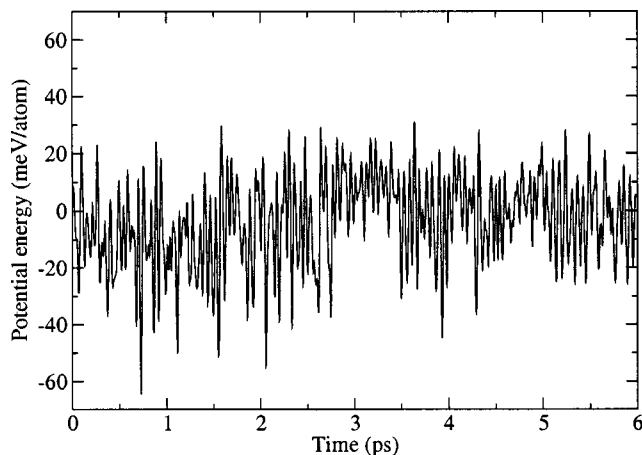


FIG. 3. Potential energy of the most stable Ag_{13} cluster [Fig. 1(a)] during a molecular dynamics simulation at 700 K. Energy values are relative to the average value for the whole simulation. Calculations were carried in the microcanonical ensemble with a time step of 3 fs and total simulation time of 6 ps. During the simulation the total energy (kinetic+ potential) remained constant to within 2 meV/atom.

meV/atom [Figs. 1(k)–1(h)]. This effect seems to be related to the stress experienced by the central atom by the external ones.¹³ Another remarkable property of metallic clusters is the possibility of expanding or contracting bond distances to reduce the energy.¹³ Radial distribution functions (not shown) for the asymmetric clusters show a well defined, although fairly broad, first peak at the characteristic metallic bond distance as well as other features at higher distances that can be described as amorphouslike.^{23,24} However, amorphous does not mean without any structure, and in practice the clusters tend to be polytetrahedral.¹⁹

Figure 4 also represents the cluster energy as a function of bond distances. Again, we find no simple relationship between this structural parameter and the energy. The same result holds when several possible combinations of parameters are considered. This result could help to explain why empirical potentials fail to predict the correct geometry for the global minimum energy structure. Empirical potentials use a small set of parameters, generally fitted to reproduce properties of the bulk material or some highly ordered clusters.^{20,21,23} It has been noted before that even slight changes in those parameters can give rise to important differences in predicted geometries.^{19,22} From our study, it seems that it is intrinsically difficult to describe metallic bond characteristics with simple analytical functions that depend on a few parameters. This is associated with the fact that many body effects play an important role in metallic interactions.¹³ It is also worth pointing out that search strategies tend to start geometry optimizations from approximately spherical clusters^{21,23} making it even more difficult to find distorted clusters such as the ones shown in Fig. 1.

In this work we have explored the low energy isomers of the coinage metal clusters, M_{13} ($\text{M}=\text{Cu}$, Ag or Au). We find that the low energy isomers for the three metals are disordered and form almost a continuous distribution of energies from the global minimum. This means that the structures observed in experiments are likely to depend on the tempera-

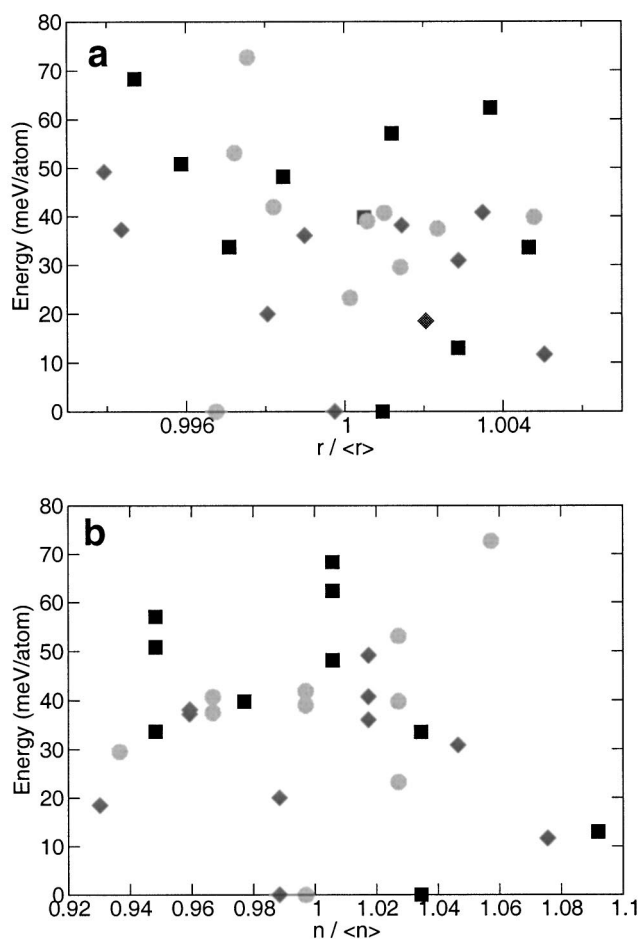


FIG. 4. Energy-structure relationship for the most stable isomers. Cu, Ag, and Au are represented by squares, diamonds, and circles, respectively. (a) Energy vs bond distance. On the x axis we plot the mean bond distance, r , for each isomer in Fig. 1; i.e., (a)–(j), relative to the ensemble average over all the isomers, $\langle r \rangle$. To calculate r for each isomer we have taken an average of the two shortest bond distances for every atom (Ref. 14). In the figure $\langle r \rangle$ is 2.40, 2.77, and 2.75 Å for Cu, Ag, and Au, respectively. (b) Energy vs coordination number. In this case the x axis shows the mean coordination number, n , for each isomer in Figs. 1(a)–1(j) relative to the ensemble average over all the isomers, $\langle n \rangle$. To calculate n we have considered that two atoms are coordinated if the distance between them is shorter than the value of 1.15 $\langle r \rangle$ calculated previously. In the figure $\langle n \rangle$ is 5.35, 5.29, and 5.09 for Cu, Ag, and Au, respectively.

ture and cluster growth conditions, which may have repercussions for the interpretation of experiments in the nanometer regime. From a theoretical point of view, we find that the traditional empirical potentials tend to overestimate the tendency of nanoclusters to adopt symmetric structures and fail to describe adequately metallic bond characteristics. Our work, and especially the similar pattern of behavior found for Cu_{13} , Ag_{13} , and Au_{13} contributes to the view that amorphous structures may be a common feature of nanometer scale systems.^{24,26,29,30} Strictly, our results apply only to free clusters. However, they may have also implications for other finite systems such as supported and passivated clusters,^{8,11,38} which lie at the heart of projected technological applications.

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