55-atom clusters of silver and gold: Symmetry breaking by relativistic effects

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Abstract

Anionic 55-atom clusters of gold and silver are studied using density functional theory, scalar relativistic ab initio pseudopotentials and self-consistent generalized gradient corrections. An almost perfect icosahedron is found to be the clear ground state of Ag_{55}^-, and its electronic density of states agrees almost perfectly with recently measured high-resolution photoelectron spectra, up to the magnitude of the splitting of the highest free-electron shells by the I_h crystal field. A comparison between theory and a recent experiment allows one to assign icosahedral-based structures also for the Ag_{57}^- cluster. On the other hand, the Au_{55}^- cluster has several close-lying low-symmetry isomers with a washed-out electron shell structure. This qualitative difference between silver and gold clusters is related to the strong relativistic bonding effects in gold.

Key words: electronic structure, noble metal nanoparticles, relativistic effects
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1 Introduction

The optimal structure of a metal nanocluster is a delicate balance of several factors whose relative importance is size-dependent. Generally the smallest simple metal clusters are known to exhibit strong size-dependent variations in the energetic stability, reflected in the abundance spectra. [1] These variations

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result from an arrangement of the delocalized valence electrons into a collective ("jellium") shell structure due to the quantum confinement, whereby filling of a major angular momentum shell leads to an extra stability of that "magic" cluster size. On the other hand, the stability of the larger (from several hundred to several thousand atoms) clusters is expected to originate from special structures of either atomically closed-shell configurations or exhibiting the lattice symmetry of the corresponding bulk matter with surface facet orientations and areas that optimize the surface free energy. [2] The characteristics of the electronic structure evolve from the molecular-like (discrete levels) to bulk-like (electronic bands) behaviour as the size of the nanocluster increases. Understanding the intricate connection between the atomic and electronic structures represents an important preliminary step for the possible use of metal nanoclusters in future nanotechnological applications.

Silver and gold nanoclusters are intensively studied for their chemical and optical properties, and are promising candidates for applications e.g. in catalysis,[3,4] labeling [5] or photonics.[6] Previous photoelectron and optical spectroscopy studies and density functional calculations have characterized in detail noble metal clusters of up to about 21 atoms. [7–14] On the other hand, large particles of hundreds or thousands of atoms have been studied by electron microscopy and electron diffraction. [15,16] In those studies a variety of ordered structures with diverse symmetries (icosahedral, decahedral, octahedral) have been found. For medium-size clusters (about 50 atoms and up) the theoretically interesting questions pertain to the extent by which the elecron shell model could be applied and to the magnitude of the relativistic effects which were previously found to cause anomalous structures of small gold clusters of up to about 12 atoms. [11–13] The only existing UV photoelectron study [17] of medium-size silver and gold clusters gave some evidence for the existence of free electron shell structure in both metals but the resolution of the data was not high enough to enable detailed comparisons between the elements.

Here we show through density-functional calculations that anionic 55-atom (1.1 nm diameter) nanoclusters of silver and gold adopt drastically different structures, which can be related to the profound differences in the nature of chemical bonding. While the unambiguous ground-state of Ag_{55}^- is almost a perfect icosahedron, displaying a strong splitting of the free electron shells by the icosahedral lattice field, Au_{55}^- has several low-lying low-symmetry isomeric structures, with a washed-out free electron shell structure. These results are supported by the most recent high-resolution photoelectron spectroscopy data. [18] This qualitative difference is attributed to strong relativistic effects in the interatomic bonding in gold.

2 Methods

The atomic and electronic structures of silver and gold clusters were calculated with density functional theory (DFT) by using a Born-Oppenheimer molecular dynamics program [19] including self-consistent gradient corrections.[20] The $nd^{10}(n+1)s^1$ valence electrons of Ag (n=4) and Au (n=5) were described by scalar-relativistic norm-conserving pseudopotentials.[21] For Au, a non-relativistic pseudopotential was also made for comparison. The Kohn-Sham orbitals were expanded in a plane wave basis with a kinetic energy cutoff of 62 Ry. The method does not employ a supercell, i.e., a periodic image of the atoms, and is thus suitable for accurate calculations for charged finite clusters.[19] As extensive structural optimizations via simulated-annealing schemes in conjunction with a full determination of the electronic structure at each dynamic step are computationally not feasible for this size of d-metal clusters (having the total number of valence s- and d-electrons of about 600), we adopted an alternative strategy and utilized the already existing knowledge of possible structural candidates of nanosized metal clusters obtained through simulated annealing and genetic algorithms via classical pairwise and many-atom interatomic potentials. An extensive collection of these structures, known as the Cambridge Cluster Database (CCD), is publicly available on the World Wide Web.[22] For initial structural candidates we picked up 6 CCD structures representing different structural motifs: closed atomic shell icosahedral (IC), decahedral (DE), and cuboctahedral (fcc,CO) structures, and clusters optimized previously by classical Sutton-Chen (SC), glue (GL), and Morse (MO) potentials. These structures were then re-optimized with unconstrained Born-Oppenheimer MD simulations where the closest local energy minimum from the initial structure was located in a time scale of 1 ps by a damped dynamics via inclusion of a global friction force.

3 Results

The optimized structures for Ag_{55}^- and their electronic density of states (DOS) are shown in Fig. 1. The DOS spectra are shifted with the self-consistently calculated vertical detachment energy of the highest (HOMO) electron. From the six structures considered, the icosahedral cluster IC is the clear ground state, followed by the structures GL, MO, DE, SC, and CO and separated by 0.94 eV from the first isomer GL. According to the jellium model, Ag_{55}^- with 56 valence atomic s-electrons should exhibit the jellium electronic configuration $[1S^2 1P^6 1D^{10} 2S^2 1F^{14} 2P^6 1G^{16}]$ which is shy by 2 electrons from the major shell closing $[1G^{18}]$ at 58 electrons. The 6 peaks visible in the theoretical DOS spectrum for $3 < E < 5.5$ eV for the IC ground state consist of 38 electronic states, forming a sequence of degeneracies occupied by 6-10-6-8-6-2 electrons

(from top to bottom). The analysis of the collective orbital angular momentum character (with respect to the center of mass of the cluster) of these peaks, shown in the bottom panel of Fig. 2, reveals that two pairs of the peaks are due to crystal field splitting of the jellium 1G and 1F shells. Following the icosahedral I_h point group notation we can thus identify the 6 highest shells as $[G_g^6 H_g^{10} T_{1u}^6 G_u^8 T_{2u}^6 A_g^2]$ where the G_g^6 shell contains the HOMO state and two holes and is thus prone to the Jahn-Teller (JT) deformation. However, we found that during the unconstrained MD optimization the JT effect is not strong enough to significantly distort the icosahedral structure.

Recently, v.Issendorff and coworkers have measured the high-resolution photoelectron spectrum (obtained by a probe of 6.42 eV photons) of a cold beam of Ag_{55}^- clusters. [18] As can be seen in Fig. 1, the theoretical DOS of the IC ground state gives a very good match with the experimental result, apart from a slight underestimation (by 0.2 eV) of the binding energy of the first peak (electron detachment energy). The only other cluster structure that would give a close match with the experiment is the CO structure, but it is high in energy compared to the IC ground state (2.35 eV) and is not likely to be present in the beam (the estimated beam temperature is 150 - 250 K [18]); furthermore, in that case all the other structures should be expected to be present as well, which would not produce such a pure peaked structure of the PES as shown in Fig. 1. We thus conclude that the experiment and our calculation together point to an existence of an unambigous IC ground state for the Ag_{55}^- cluster.

Due to the clear stability of the IC Ag_{55}^- cluster it is natural to look for possible structures for the neighbouring cluster sizes based on the 55-atom icosahedron. We have studied the case of the Ag_{57}^- cluster since it completes the free-electron shell at 58 electrons, or specifically the G_g^8 subshell of the I_h group. Several close-lying isomers are found; for those isomers the additional 2 atoms must occupy various positions on the surface of the 55-atom icosahedron. Three such structures are shown in Fig. 3 along with their calculated DOS spectra and the experimental data. [18] We see that none of the structures alone yields a DOS that would match the experimental PES curve. However, even at the low temperature of the experiment we expect that the mobility of the two adatoms is high enough that several isomeric forms of Ag_{57}^- contribute to the observed PES spectrum. Fig. 3 shows quite convincingly that even the three structures we studied here are adequate to reproduce almost all the fine details of the experimental result (see the curve marked "Av" in Fig.3; this curve is a simple average of the theoretical curves A-C).

Let us now turn to the case of gold. ¿From computations we find several close-lying low-energy, low-symmetry structures (SC, GL, MO) that are energetically better than the symmetric icosahedral, cuboctahedral or decahedral structures. The calculated DOS spectra of the low-symmetry structures are in a qualitative agreement with the experimental result (Fig. 1) in such that the

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"s-band" is highly structured and no clear shell structure can be seen. Other studies have also found an abundance of disordered isomers for 55-atom gold clusters [23] and it is possible that the true ground state was not found here. Furthermore, the fact that our calculation does not include the spin-orbit effects makes the direct comparison to experiment more problematic. Anyway, we can clearly conclude that structures with a closed atomic shell are not favoured by Au_{55}^-. This result is in line with previous photofragmentation studies which indicated that 55 is a geometric magic number for silver but not for gold. [24,25]

So why does the Au_{55}^- cluster behave so differently from Ag_{55}^-? The answer is found by comparing the results of a nonrelativistic pseudopotential with those of a scalar-relativistic one (see Fig 2). It turns out that a fictitious, nonrelativistic Au_{55}^- behaves very similarly to Ag_{55}^-, having a clear ICO ground state and an almost identical DOS. Only in the scalar-relativistic calculation the lower symmetry isomers are preferred, which is due to a change in the nature of the interatomic bonding. The Au atom is known to be "the most relativistic element below Fermium",[26] displaying a strong outer shell (6s) contraction and a reduced 5d–6s energy gap; from our calculations we find that the ($5d_{5/2}$ - 6s) energy gap is 1.21 eV for an Au atom and the corresponding ($4d_{5/2}$ – 5s) gap in an Ag atom is 5.72 eV. This leads to significant s-d hybridization and direct d-d bonding effects, which for instance are also responsible for anomalous, planar ground-state structures of anionic Au_N^- clusters up to about $N = 12$. [11–13] The most obvious consequences of these relativistic effects is a shortening of the interatomic bond lengths and a drastic increase of the bulk modulus. In a calculation of the Au_2 potential energy curve we have obtained an increase of the curvature from 5.3 eV/Å^2 to 11.6 eV/Å^2 when including relativistic effects. The same trend was reported earlier for the calculated bulk modulus of crystalline Au, where a relativistic treatment increased the value from 108 GPa to 182 GPa.[27] A recent general study of metal cluster structures demonstrated that it is mainly this high bulk modulus which leads to the different behaviour of gold and silver clusters.[23]

4   Acknowledgments

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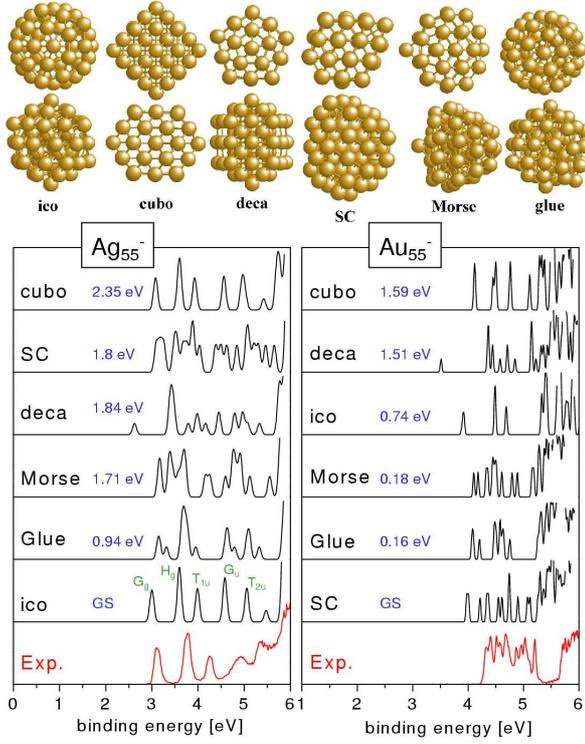[27] C. Elsässer, et al., J.Phys.: Condens. Mat. 2 (1990) 4371.

Fig. 1. Structures and density of electronic states (DOS) of Ag and Au clusters obtained via density functional calculations. Top: Six candidate structures (displayed are the fully relaxed optimal structures for gold) for Ag_{55}^- and Au_{55}^- representing different structural motifs: closed atomic shell icosahedral (ico), decahedral (deca), and cuboctahedral (fcc, cubo) structures, and clusters optimized previously by classical Sutton-Chen (SC), Glue, and a short ranged Morse potentials. Bottom: DOS of the six structures (black curves) compared to the experimental photoelectron spectra (red curves) for Ag (left panel) and Au (right panel). The numbers denote the energy difference to the most stable structure. In plotting the DOS, each discrete state is broadened by Gaussians with a width parameter of 0.05 eV for Ag and 0.025 eV for Au.
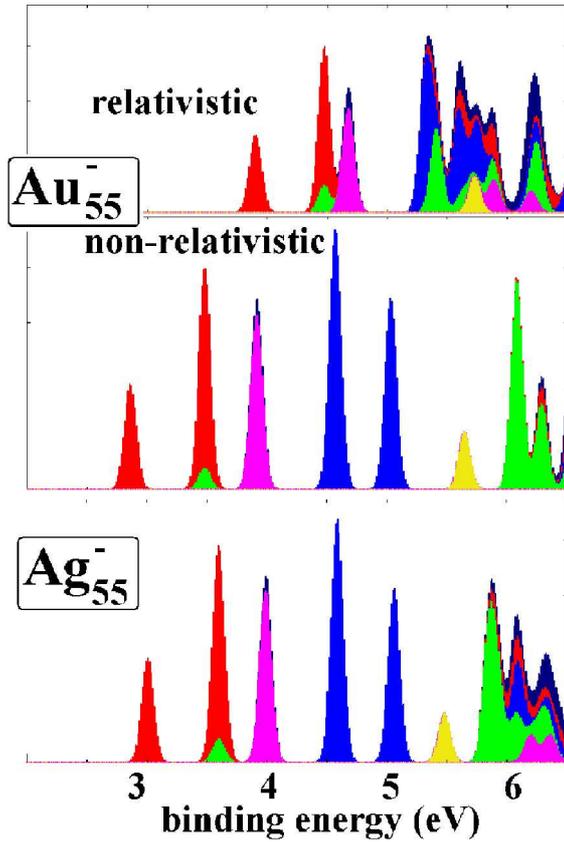
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Fig. 2. DOS of the icosahedral Au_{55}^- cluster calculated with a scalar-relativistic (top) and a non-relativistic (middle) pseudopotentials as compared to the DOS of the icosahedral Ag_{55}^- (bottom). The colours denote that angular momentum character (from s-state to h-state) of the states, as analyzed with respect to the cluster center of mass. The coding is as follows: s-yellow, p-purple, d-green, f-blue, g-red and h-black.
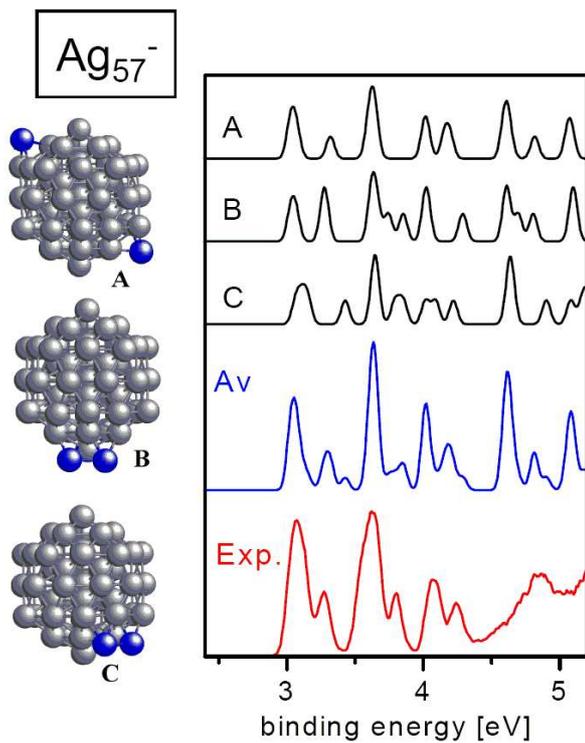
Fig. 3. Three relaxed icosahedral-based candidate structures (A,B,C) of Ag_{57}^- (left hand side) and the related DOS (black curves on the right hand side) as well as an average of A,B and C (blue curve, marked with "Av") and the experimental photoelectron spectrum (red curve). C is the ground state structure, followed by A (energy difference of 0.23 eV) and B (0.63 eV).