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Structure and electronic properties of small gold clusters

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Structure and electronic properties of small gold clusters

U.N. Kurelchuk, O.S. Vasilyev, P.V. Borisyuk

National Research Nuclear University MEPhI, Kashirskoye sh., 31, Moskva, 115409

E-mail: unkurelchuk@mephi.ru

Abstract. Structure and electronic properties of small Au nanoclusters study was performed using density functional theory with pseudopotential in relativistic approximation. Density of states of the valence band, projected density of states was calculated, Bader charge density analysis is presented. The spatial behavior of the density of states was studied. Charge-momentum spatial anisotropy observed in symmetrical nanoclusters, electronic states on Fermi level of 1nm clusters founded to be caused mostly by $d_{5/2}$ surface states.

1. Introduction

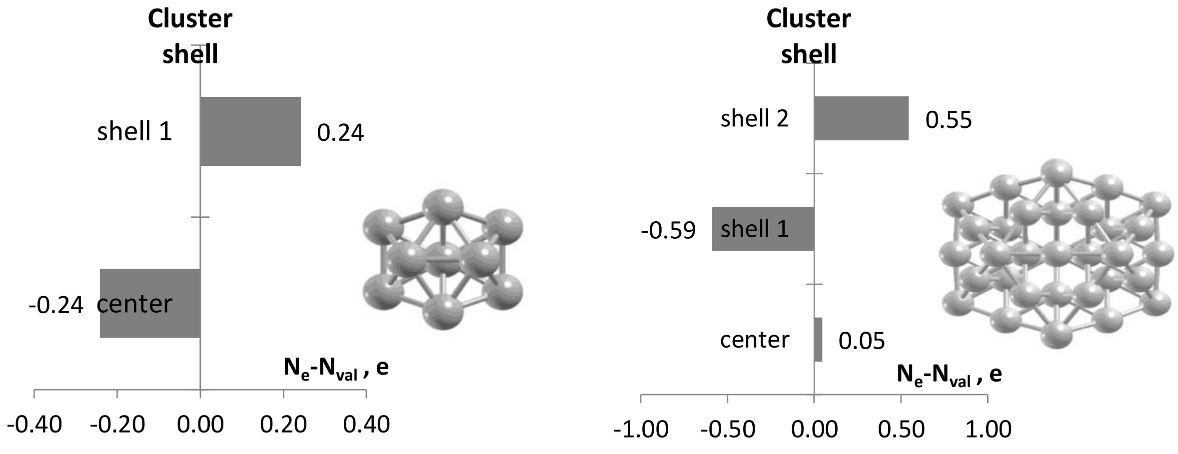
Porous films and heterogenic structures, formed from metallic nanoparticles, can be considered as new perspective materials for high-effective thermoelectric devices. The efficiency of thermoelectric generation in thermoelectric material is expressed by the dimensionless function figure of merit $ZT=S^2\sigma T/k$. Here S is thermoelectric power (Seebeck coefficient), electrical conductivity σ, and thermal conductivity $k=k_{el}+k_l$ composed of electronic and phononic parts. Till nowadays it has been developed and used several ways to increase ZT of traditional thermoelectric materials (such as such as $CsBi_4Te_6$, Bi_2Te_3, Sb_2Te_3. Layering and alloying, doping with nanoparticles, using nanostructured semiconducters, was aimed at decreasing thermal conductivity k using disordering to diminish phononic transport, and increasing keeping the same value of the thermopower S (which appears quite high in several semiconductors). But using nanoparticles is limited by critically degeneration of electrical conductivity in semiconductor nanoparticles with decreasing their sizes [1-6]. At the same time, it was observed for metal nanoclusters, that they stay conductive down to ~1nm size and manifestation of semiconductor properties at lower sizes [7]. Also from experimental results for films composed from metallic clusters smaller than 1 nm^3 volume, the Seebeck coefficient S was indirectly measured and founded to be about 10 times higher than in corresponding bulk materials [8]. These encouraging phenomena lead us to suggest that one can reach an extremely increasing ZT of thermoelectric material by properly composing nanoclustered species from metallic clusters with tuned electronic properties. The thermoelectric properties generally depend on electronic properties in the complex law, which can be simply approximate by Mott's law for simple metals. It shows how the conductivity σ and thermopower S depends on the electronic density of states (DOS) behaviour near the Fermi energy E_f (the steeper the DOS the higher is S), states occupation at E_f. Band structure features and anisotropy effects on S and σ directly too. In this sense, d-metals with highly localized or correlated d-electrons, relativistic effects, and generally complex electronic structure seems to be good resource to reveal and use the features of their nanoparticles quantum properties, and construct from them the structures with especial electronic properties [9]. As it has been known, the quantum-size effects can reveal extraordinary fine effects of atom electronic structure, and size-geometry-quantum properties is interdependent. For example, it has been known that color of bulk gold caused by relativistic effects [10], spin-orbit interaction make the small $Pt_{n<5}$ nanoclusters flat [11,12]. Thus, modeling the small structures electronic properties one cannot neglect the relativistic effects that become essential. Moreover, an extraordinary electronic phenomena of such structures can lead to unexpected practical usage like spin Seebeck and invers Hall effect [13,14]. In the sense of thermoelectric efficiency, there is evidence that spin Seebeck effect can potentiate an electronic (charge) Seebeck effect [14] in structures combined from particles with special relativistic and magnetic properties. Another whish is the technological clearance in forming nanostructures, i.e. chemical inactivity and nonmagnetic, at least on laboratory conditions research, so the noble d-metals are appropriate to investigation and fine-engineering, particularly gold, because of highest spin-orbit splitting among them (to evidential exploring of the fine structure). Thus, research of dependency of the size, geometry, electronic and spin properties of metals, with initially complex electronic structure, can be essential to predict and tune the properties of nanostructures formed from this clusters.

In this work we study the size, spatial, charge, and electronic structure dependences for small Au nanoclusters.

2. DFT study of nanoclusters electronic properties

We define starting configurations of nanoparticals up to 1.1 nm size in a follow way. Configurations Au_{13} and Au_{55} were defined as icosahedrons, as has been showed by molecular dynamical simulations that structures is the most energetic-preferable and stable form of the d-metallic nanoparticles up to 1-2 nm [15,16]. Density functional theory (DFT) geometric optimization of structures was performed. DFT study of Au nanoclusters was performed in GGA Perdew-Burke-Ernzerhoff approximation of the exchange-correlation energy [17], uncluding spin-orbit interaction for the noncollinear start spin orientation and nonmagnetic initial state in plan wave basis set using periodic DFT code Quantum Espresso [18]. The interaction of valence electrons with the core is described with the full-relativistic ultrasoft Vanderbilt pseudopotential including semicore states in valence with core correction for atomic state Au(5d10 6s1 6p0) [19]. Relaxation was carried out until the forces reached 0.01 eV/A. In the periodic paradigm, single nanoclusters was placed at the center of a cubic pseudocell to provide a vacuum layer of 15-20 A between neighboring clusters. Calculations of wave functions and energy states for relaxed clusters, the total and projected density of electronic states, and Bader analysis of the converged charge density was carried out [20]. Then effective atomic charge, defined as the difference between calculated Bader charge N_e i.e. number of the valence electrons spatially associated with the selected atom, and N_{val} – number of electrons defined as valence in atomic pseudopotential, was calculated.

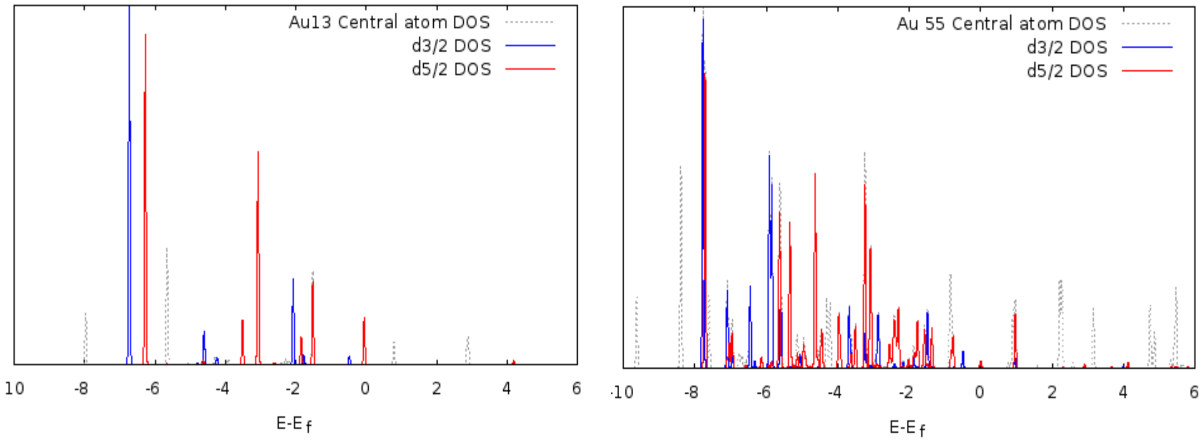
Icosahedral clusters has a shell spatially structure: Au_{13} consists of a central atom and 1st shell, formed from 12 atoms placed on icosahedral vertexes, in Au_{55} a 2nd shell of 42 atoms is added. In Fig.1 showed the scheme of clusters structure and diagrams of the effective charge distribution. In diagrams the shell effective charge as sum of the atomic effective charges of the shell atoms is plotted on the abscissa, the cluster shell numbers is plotted on the ordinates. It follows from the Bader analysis, that the neighboring shells has opposite charge. In Au_{13} found an even redistribution of the electron density between the center and the shell, with electron “leak” from center to surface, so the central atom in Au_{13} has an effective charge of -0.24 e, and shell +0.24 e. In Au_{55} founded that the charge is redistributed mostly between the surface shells till the central atom has negligible charge, and the extra electronic density about +0.55e founded to be located on surface.



Au_{13} Au_{55}

Fig. 1. Nanoclusters Au_{13} and Au_{55} structure and effective atomic charge distribution. The abscise in diagram shows the "shell effective charge" as sum of the atomic effective charges of the shell atoms. The ordinates shows the cluster shell number. For Au_{13}: center, shell 1 - 12 icosahedral vertexes. For Au_{55}: center, shell 1 - 12 icosahedral vertexes, shell 2 - surface atoms.

Consider the density of electronic states DOS total and projected on d-band states where energy degeneracy of states with j=3/2 and 5/2 is removed by the spin-orbit interactions (See Fig.2). In Fig. 2 showed the spatial behavior of the DOS is significant depended on "shells" of the icosahedral clusters. In 55-clusters DOS on Fermi energy is provided mostly by $d_{5/2}$ states belonging to surface atoms (where is the extra-charge observed, according the Bader analysis). So one can suggest that 55-clusters of about 1 nm size can manifest conductive properties mostly due to $d_{5/2}$ states, which is principally in agreement with the experimental data for clusters 1-1.5 nm [1]. As the size of the clusters increases (comparing the investigated one) the spin-orbit energy splitting $d_{3/2}$-$d_{5/2}$ decreases. In the one given cluster splitting $d_{3/2}$-$d_{5/2}$ increases from center to surface.



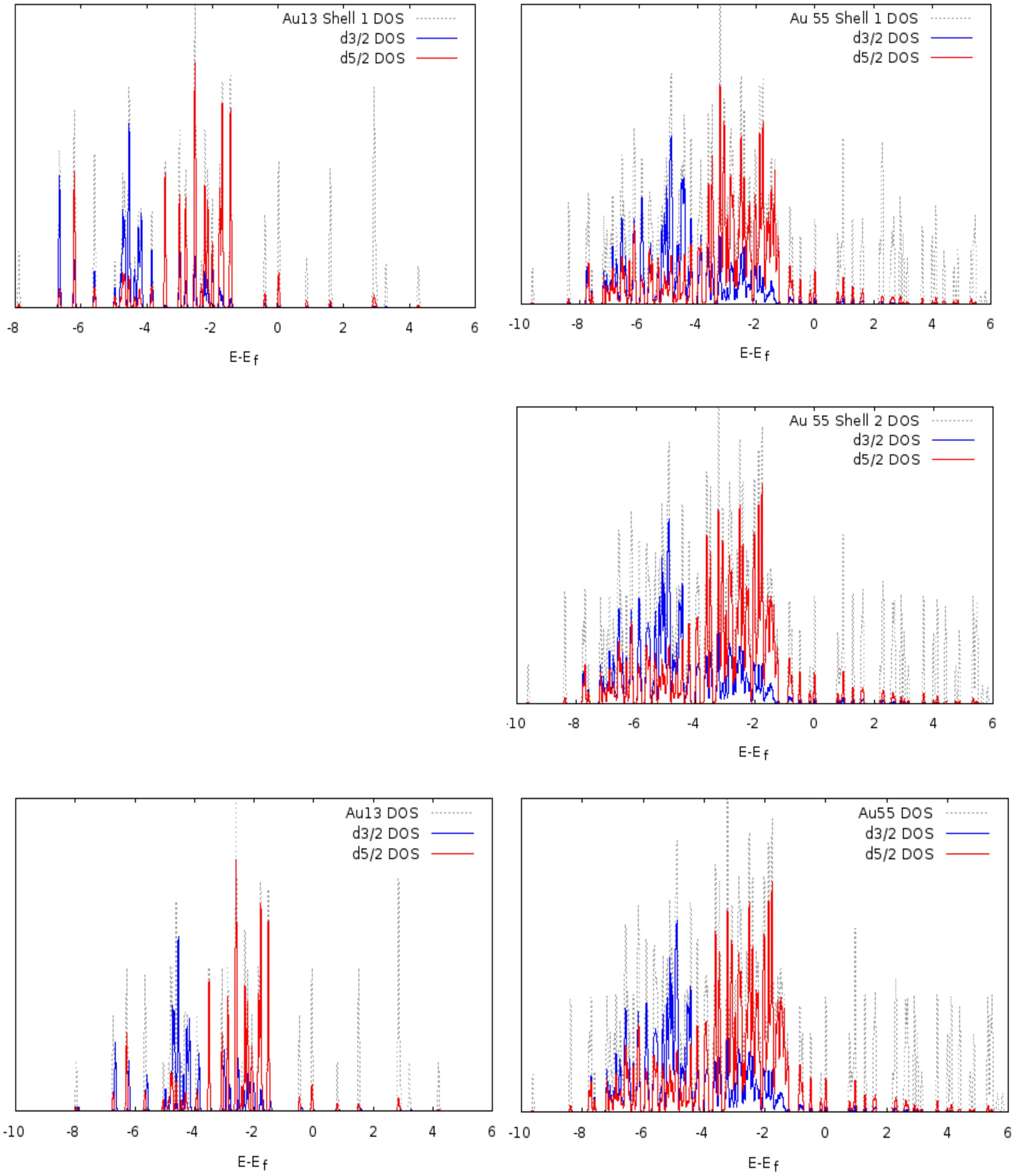


Fig. 2. Density of electronic states DOS projected on (l, j) and spatial atomic shells for Au_{13} and Au_{55} nanoclusters. Au_{13}: center, shell 1 - 12 icosahedral vertexes. Au_{55}: center, shell 1 - 12 icosahedral vertexes, shell 2 - surface atoms. Blue lines shows the DOS projected on $d_{3/2}$ states (l=2, j=1.5), red – $d_{5/2}$ states (l=2, j=2.5)

The structure and electronic properties of small Au nanoclusters was studied using density functional theory with pseudopotential in relativistic approximation. It was found that the spatial behavior of the electronic states density of the icosahedral clusters, is significant dependent on the "shell", in both cases the extra electronic density on surface was founded. Projected density on (l,j) states manifests the momentum anisotropy for the different “shells”. 1nm clusters can manifest conductive properties, caused by the $d_{5/2}$ surface states localized near the Fermi energy. Summarizing this dependences, we can suggest that nanoclusters with a large proportion of the surface (in relate to volume) can be interesting for further investigation of their electronic properties thermoelectric properties of the materials formed from them. Although a larger surface-to-volume ratio usually means a smaller nanocluster size, or high roughness, in the first case one can also optimize the size with conductive properties and melting temperature. Knowledge about the evolution of DOS, interconnects the dimensional, geometry and relativistic effects, can provide to find the most effective way to combine small structures into macroscopic structures like porous nanoclustered films with high tunable properties.

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