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Estimation of the influence of icosahedric „magic“ numbers of thermal stability of small silver nanoclusters

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A comparative analysis of thermally induced structural transitions in silver nanoclusters, the number of atoms of which corresponded to the „magic“ numbers of the icosahedral (Ih) structure with variation of their initial morphology, was carried out by the molecular dynamics method using the modified tight-binding potential TB-SMA. It is shown that, in the case of the initial fcc phase, the formation of the Ih modification, depending on the particle size, occurred either at the stage of preliminary thermal relaxation or during further heating. At the initial amorphous morphology, the nature of the structural transitions underwent significant changes. Thus, even in the case of Ag_{55} clusters, the icosahedral structure was formed only in 50−60% of the experiments performed. Based on the data obtained, it was concluded that to create a stable Ih structure, it is necessary to use the thermal cycling procedure.

Keywords: nanoclusters, silver, computer simulation, „magic“ numbers, structure of nanoclusters.

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1. Introduction

Silver nanoparticles (AgNPs) are now becoming increasingly popular in various technological fields, such as electronics, photonics, and medicine [1]. Let us consider only some of the reasons for the increased attention to AgNPs. Solar panel elements widely used in modern life, touch screens, LCD displays, organic electroluminescent panels, light-emitting diodes (LED and OLED), often use electrodes made of sputtered films of indium oxide and tin oxide (ITO) in their construction [2,3]. However, these films have a number of serious disadvantages, such as high cost, brittleness [4] and toxic composition. To solve these problems, other materials are currently being considered as alternatives, such as graphene, carbon nanotubes, or conductive polymers with the addition of metal nanostructures [5–7]. But only films made of silver nanoparticles are superior to ITO films in light transmittance and electrical conductivity [8]. In this regard, we note that the optical properties of AgNPs in many cases are determined by localized surface plasmon resonance (LSPR), which strongly depends on the shape, size of NPs, and the material of the environment [9].

Another interesting physical phenomenon that uses the plasmon effect is surface-enhanced Raman scattering (SERS), which has extreme sensitivity and high selectivity to the substance under study, which is of great importance for chemical analysis and studying the structure of matter. Among various plasmonic materials, it is silver SERS substrates that provide the strongest Raman amplification and, therefore, are most promising for wide practical applications [10].

The type of metal, size, shape, and degree of particle aggregation determine the energy range (frequency) of light that can excite plasmons (Mie scattering theory). Surface plasmon resonance can be controlled by controlling the shape of AgNPs, which, in turn, regulates electron oscillations. For example, the main absorption wavelength of spherical AgNPs (size 10 nm) is ≈ 400 nm. On the other hand, larger AgNPs and AgNPs of various shapes due to different absorption modes absorb light with a different wavelength [11]. Thus, silver nanoparticles with an average size of 34 ± 14 nm in the form of triangular prisms caused a glow in the blue range of electromagnetic waves, and quasi-spherical AgNPs with an average size of 16 ± 7 nm had the pronounced yellow color [12].

The use of AgNPs in biomedicine accounts for more than a third of their total application, and the influence of the shape and internal structure on the properties of AgNPs was also noted here. When studying the bactericidal activity of spherical AgNPs of various sizes against E-coli, Bacillus subtilis and Staphylococcus aureus, it was concluded that their effectiveness increases with decreasing size, regardless of bacterial strains [11], which may be due to with higher surface areas that promote attachment to cell membranes. On the other hand, studies show that the reactivity and antibacterial activity of AgNPs are stronger in particles with predominant $\{111\}$ faces with a higher atomic density compared to other morphological forms. Thus, the effectiveness of spherical and filamentous AgNPs was tested in relation to their antibacterial activity against various bacteria and it was shown that the mortality rate of Klebsiella pneumoniae was higher when exposed to spherical AgNPs with larger $\{111\}$ faces compared to AgNPs in the form of rods [12].

Thus, it was found that it is the $\{111\}$ facets that are to a greater extent responsible for the antibacterial activity of AgNPs, which raises the question of creating AgNPs with a spherical (quasi-spherical), decahedral, or octahedral structure that is stable at room temperatures.

Therefore, from the point of view of the use of silver nanoclusters in plasmonic and other applications, it seems very important to determine the boundaries of thermal and dimensional stability of the crystal structure and shape of Ag nanoparticles. To do this, we will consider possible configurational changes in silver clusters during heating to the melting temperature and an attempt is made to identify the size boundaries of nanoparticles in which the structural transition can occur.

2. Computer model

It is well known that it is the structure and mutual arrangement of atoms that largely determine the properties of nanoparticles. Description of the mechanisms for formation and the dynamics of changes in internal morphology can help in predicting their structure. The study of these processes by experimental methods is associated with a number of significant difficulties due to the small sizes of nanoparticles, and therefore computer simulation methods may turn out to be more effective in this case. In our opinion, it is this method that is the most promising in the study of structural transformations, the mechanisms of formation and growth of nanoparticles, the determination of equilibrium configurations, thermodynamic properties and the kinetics of ongoing processes, the dynamics of their change under the influence of external conditions: temperature, pressure, etc.

In the present work, computer simulation of silver nanoclusters was carried out by the molecular dynamics method using the modified tight binding potential TB-SMA [13] which is based on the assumption that a large group of properties of transition metals can be completely determined from the density of states of external d-electrons. It is this method, in which the ion-ion interaction is described taking into account the band nature of the bond and the short-range repulsive pair potential, in our opinion, that is able to correctly describe some of the characteristic features of small metal nanosystems. Therefore, the simulation of silver nanoparticles was carried out using just such an interatomic interaction potential.

Computer analysis of all the processes occurring in Ag-clusters was carried out in the canonical NVT-ensemble. The temperature of the system was determined by means of the average kinetic energy of atoms, calculated using the speed Verlet algorithm with a time step 1 fs. Initial spherical clusters were obtained by cutting out from an ideal FCC lattice followed by thermal relaxation at 20 K. At this stage, the first ensemble of particles under study was formed. Then the AgNPs were heated stepwise to completely destroy the long-range order in them and abruptly cooled with a high rate of thermal energy removal to a temperature of 20 K. From the resulting array of nanoparticles, those that had an amorphous structure were isolated. Thus, the second ensemble of AgNPs was formed. Next, AgNPs of various initial morphologies were heated stepwise to a temperature of 1000 K with a step of 20 K, and in the region of structural transitions — with a step of 5 K. At each fixed value, the particles were kept for 1 ns.

The simulation was carried out using the MDNTP software developed by Dr. Ralf Meyer, University Duisburg Germany. The presence of structural transitions was determined from the dependence of the potential energy of nanoclusters on temperature, the OVITO visualization program, and the radial distribution function.

3. Results and discussions

Based on the fact that variations in the structural properties of silver nanostructures are most pronounced precisely in small-sized clusters, when performing a computer analysis of the thermal stability of the structure of AgNPs, particles with a diameter of up to 2.0 nm were selected. In our opinion, the reason for this phenomenon is that, at this small diameters, AgNPs are close in their physicochemical properties to molecular rather than space structure, since their linear values are comparable to the electron Fermi wavelength (~ 0.5 nm for Ag), for which quantum effects begin to prevail here. Another important consequence of quantum features is that in small nanoparticles, the so-called „magic“ numbers of various nature can play a significant role in the stability of the structure.

In our earlier works on this topic [14,15] we have already analyzed the thermal stability of the structure of silver nanoclusters with a diameter of up to 2.0 nm under the condition of their initial FCC structure. It was shown that this form of Ag clusters is thermally stable for nanoparticles with a diameter of $D > 1.8$ nm (170−180 atoms). However, at smaller sizes, the scenarios for the thermal evolution of the internal structure of silver nanoclusters became much more complicated, and in some cases, the formation of the maximum possible spherical shape in AgNPs, often with an icosahedral or decahedral arrangement of atoms, was observed. The octohedral faceting of silver nanoparticles of such sizes was not fixed even during heating to high temperatures.

This result is not surprising, since in the case of small clusters, the surface energy begins to dominate, and the octahedral structure is much inferior in this indicator to icosahedral (Ih) or decahedral (Dh) structures, which have a much smaller surface area. Therefore, this article is devoted to the consideration of the issues of obtaining the thermally stable icosahedral (decahedral) structure of silver nanoclusters with a diameter of up to 2.0 nm, in which FCC or an amorphous configuration was taken as the initial phase, which makes it possible to trace the influence of the initial Ag morphology nanoparticles on the nature of possible structural transitions in order to better understand their nature.

The characteristic feature of silver atoms is their relatively high reactivity, as a result of which, in order to preserve chemically pure AgNPs, it is necessary to use various stabilizers, in particular, ligands. Another possible approach to solving the problem of oxidation/sulfiding of silver nanoclusters can be the formation of very pure particles with an ideal crystal structure [16], which should be more resistant to the above phenomena.

We believe that the use of silver nanoparticles with the size equal to the „magic" numbers of various structures can become another unaccounted opportunity for improvement in the stability of the composition and shape of AgNPs. This assumption is confirmed by experimental analysis of the size distribution of the synthesized particles (mass spectrum), which showed that clusters with a certain number of atoms corresponding to „magic" numbers are much more stable compared to clusters of a different size. In this case, the degree of defectiveness of the surface of clusters with „magic" numbers of atoms is minimal, while for the rest it can be quite significant.

In the works [14,15], we analyzed the influence of some „magic" numbers on the stability of the internal structure of small AgNPs, including those with different initial arrangements of atoms [17]. It was shown that the nature of thermally induced structural transitions in the studied groups of nanoclusters differs sharply, but the complete stabilization of the icosahedral (decahedral) phase was still not recorded in the course of computer experiments.

Therefore, in the present work, we will focus on studying the influence of geometric „magic" numbers corresponding to icosahedral symmetry, for which we consider silver nanoclusters with the number of atoms exactly corresponding to the geometric „magic" Ih-numbers (Ag_{55} and Ag_{147}). The results of the simulation showed that, under the condition of the initial FCC structure, the smallest cluster had the FCC → Ih polytype transition already at the preliminary stage of thermal relaxation and an ideal icosahedral structure was formed. No pre-melting effects were observed here, the dependence of the potential energy of the now icosahedral Ag_{55} cluster on temperature had a strictly linear character up to the melting temperature, after which the long-range order was destroyed.

In the case of the second ensemble of particles (with the initial amorphous state), the process of thermal evolution of the structure underwent significant changes. The main ones were already two variants of thermal evolution, realized in approximately equal proportions: the first — Ag_{55} particles retained their initial amorphous structure; the second — there was a structural transition to the Ih-modification (Fig. 1). It can also be seen from the obtained data that the potential energy of the Ag_{55} nanocluster with an ideal icosahedral structure (the first ensemble of particles) at $T = 40$ K was -2.5761 eV/atom, and in the case of the second ensemble of particles, while maintaining the amorphous substructure and passing to the Ih-structure, it increased by $\Delta E = 0.0272$ eV/atom and $\Delta E = 0.0279$ eV/atom, respectively. Thus, the increase in the specific potential energy of Ag_{55} particles of initial amorphous morphology, obtained under conditions of extremely fast cooling, by only 0.7 meV/atom turned out to be able to significantly affect the nature of the further thermal evolution of the cluster.

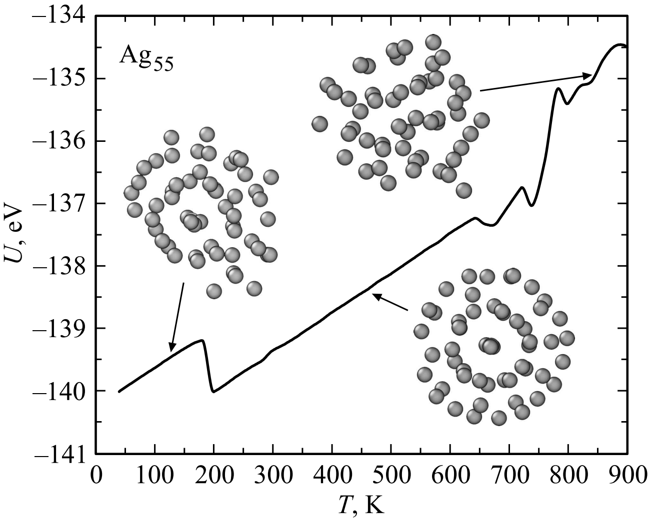

Figure 1. Dependence of the potential energy of an Ag cluster ($N = 55$ atoms) with an initial amorphous state on temperature in the case of a structural transition. The most probable variant of thermal evolution is shown.

Let's try to explain the result. In the state by volume, silver has the face-centered cubic lattice, but in the nanometer range, the competition between bulk and surface energies can lead to the formation of several different isomers due to very close energies of different structures. Thus, MD-simulation of gold clusters, carried out in [18] using the Gupta potential, at $N = 38$ of atoms gives the following values of the free energy of the cluster in its ground state: amorphous (-3.4405 eV/atom), FCC (-3.44 eV/atom), icosahedral (-3.431 eV/atom). Moreover, such a slight difference for all three isomers persisted up to room temperature. At $T > 250$ K, the thermal energy is already sufficient to overcome the potential barrier between different structures, as a result of which all three isomers begin to occur randomly. In [19], also MD-simulation made similar estimates for larger gold clusters. Thus, the difference in binding energy at $N = 55$ was 9.4 meV/atom between the amorphous and Ih-structures, and at $N = 75$ the five-particle Dh-modification turned out to be only 5.7 meV/atom is more stable than the amorphous one. That is, due to the proximity of the energies of different structural types, even a small change in it can really significantly change the direction of cluster evolution.

The interesting feature of the FCC → Ih structural transition observed by us was its two-step character (Fig. 1). That is, during the preliminary thermal relaxation of the Ag_{55} amorphous cluster, in about half of the cases, the process of rearrangement of the internal arrangement of atoms towards the creation of five-particle symmetry began, which resulted in the formation of the clearly fixed icosahedral nucleating seed. However, unlike the first group of Ag_{55} clusters (the initial FCC phase), the icosahedral structure is still not completely formed here and only with increasing thermal energy ($T \approx 200\,K$) there was the final transition to such a structure type.

Another unexpected moment was the complete absence of a structural transition in a sufficiently large number of experiments for the Ag_{55} amorphous cluster. We believe that the main reason was the fact that the amorphous structure is characterized by the lower average coordination number compared to the FCC arrangement of atoms, which is why, in this case, atoms have the higher probability movements to form the most energetically favorable position. For the considered clusters of such a small size, this can lead to the minimum possible value of the surface energy due to the formation of the spherical shape, which we observe in computer experiments. However, the FCC cluster cannot have such a value of surface energy due to the peculiarities of its structure (presence of large flat faces). Therefore, if during the initial thermal relaxation, as a result of stochastic diffusion processes, an amorphous cluster enters the state of a local energy minimum, then a situation may arise when a disordered structure can become energetically even more favorable than FCC. This also explains the two-step character of the FCC → Ih transition, which we fix in other cases.

Thus, the presence of the initial FCC morphology of the Ag_{55} cluster completely guarantees its transition to the maximum possible quasi-spherical facet form (Ih-structure), while with the initial amorphous structure such a form formed only in 50–60% of the conducted experiments. In other cases, the appearance of Ag_{55} clusters was also close to the sphere (without the presence of facets) at relatively low temperatures, but such a loosely packed arrangement of atoms still cannot preserve the spherical shape of the cluster at higher temperatures as opposed to Ih-structure. Therefore, for the case of the Ag_{55} cluster, the initial FCC morphology may be preferable from the point of view of the antibacterial action of AgNPs.

The second cluster under consideration (Ag_{147}) already had a completely filled third Ih-shell, which can be of decisive importance for such small particles. All this can be clearly seen in the case of our analysis of the thermal behavior of an Ag_{147} cluster with an initial FCC phase (Fig. 2). Here, in contrast to Ag_{55}, no FCC → Ih complete structural transition was observed at the preliminary stage of thermal relaxation, which indicates a small gain in surface energy at that sort of a size, for which a greater value of thermal energy kT is required to overcome the energy barrier between polytype modifications. In this case, the Ag_{147} cluster becomes an analogue of the amorphous Ag_{55} cluster with the Ih-transformation, and it also undergoes the two-step transition to five-particle structures. At the first stage, up to temperatures approximately of 100–120 K, the Ih-nucleating seed is observed, displaced relative to the center of the particle, with the clearly incomplete outer shell of the cluster. The obtained result is also confirmed by the work [20], where it was shown that the energy stability of the Ag_{147} cluster decreases by about 30–35% compared to Ag_{55}, becoming almost the same as the decahedral cluster Ag_{146}. The reason for this phenomenon is that in the case of Ag_{55} approximately 76% of the atoms lie on the cluster surface, while in the Ag_{147} cluster there are only 62%. It is clear that because of the smaller coordination number and, consequently, the lower value of the binding energy, it is easier for surface atoms to move around the cluster, forming an energetically more favorable arrangement. That is why the FCC cluster Ag_{147} initially retained its distorted Ih-structure up to temperatures of the order of 120 K.

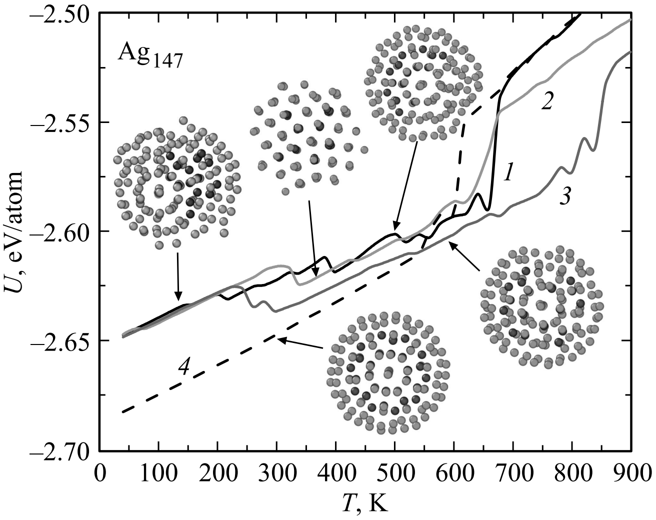

Figure 2. Dependence of the potential energy of the Ag cluster ($N = 55$ atoms) on temperature. The most probable variants of thermal evolution are shown: *1* — initial FCC structure, *2* — initial amorphous structure with structural transition to Dh-modification, *3* — initial amorphous structure with structural transition to Ih-modification; *4* — when the cluster is cooled from the melt. For convenience in assessing the relative stability of the structure, the energy is given in eV/atom.

Then the expected structure rearrangement occurred, as a result of which multiple stepwise changes in the potential energy of the nanoparticle were observed, due to shape optimization and the formation of the Ih-cluster with the already completed outer shell (70% of experiments) or, in some cases (30% of experiments) decahedron (Dh). Complete destruction of the crystal structure of the Ag_{147} nanoclusters occurred at different temperatures, depending on the scenario of thermal evolution. Thus, despite the fact that the FCC cluster Ag_{147} strictly corresponded to the geometric „magic“ icosahedral number; during heating, both icosahedral and decahedral modifications could be formed, which indicates close energy values of these five-particle structures [20].

Curve *2* in Fig. 2 corresponds to the case of an Ag_{147} cluster with an initial amorphous structure, when a transition to the Dh-modification (20% of all experiments) at a temperature of 370 K followed by its destruction at $T \approx 720$ K. But the most interesting is the curve *3* observed for particles of the second ensemble in the vast majority (80%) of experiments. Here, the Ag_{147} cluster with initial amorphous morphology forms an Ih-structure in the temperature range from 300 to 400 K. In this case, the outer shell has a complete shape and AgNPs remain stable up to the melting point, which is about 840 K. It should be noted that the values of the specific potential energy Ag_{147} at $T = 40$ K in all considered cases are actually equal to each other, and the greatest energy gain at $T > 300$ K is given only by transition from the amorphous state to the icosahedral one.

That is, by analyzing the energy component of the stability of the structure of Ag_{147} nanoparticles with different initial structures (Fig. 2), we can draw a fairly clear conclusion that it is this transition that provides the greatest stability of the quasi-spherical facet shape in the room temperature range. The formation of a decahedral structure (curve *2*) expectedly leads to the slightly lower stability, comparable to the stability of the icosahedral structure obtained by heating primary FCC clusters Ag_{147}.

Finally, the first three variants of thermal evolution were compared with the case of slow cooling of Ag_{147} from the melt (curve *4*). It is clearly seen that it is with this technique that the particle forms the most ideal Ih-structure at a temperature of 600 K. Such internal structure corresponds to the most stable crystal configuration of the Ag_{147} nanoparticle at $T < 550$ K, and at $T = 40$ K the Ag_{147} cluster has the energy $E = -7.1587$ eV/atom, which is $\Delta E = 83$ meV/atom less than the cases of curves *1–3*.

Therefore, based on the computer analysis of the processes of heating-crystallization (thermocycling) of silver nanoparticles with the number of atoms corresponding to icosahedral „magic“ numbers (Ag_{55} and Ag_{147}) and different initial structures (FCC and amorphous), as well as the results obtained earlier [14,15,17], we can conclude that in order to form a stable quasi-spherical structure with a large number of facets, it is desirable to use Ag-clusters with „magic“ Ih-size. In addition, for the Ag_{55} case, the best results are obtained under the condition of the initial FCC structure, and for the Ag_{147} cluster, the most stable required form can be obtained with process of slow cooling from the melt. If you do not resort to this procedure, then, regardless of the initial structure in the region of room temperatures, the formation of an icosahedral or decahedral structure still occurs, but not quite ideal.

4. Conclusion

In the present work, with the help of computer simulation by the method of molecular dynamics, the issues of thermal stability of the internal structure of small silver nanoparticles corresponding to the geometric „magic“ numbers of the icosahedral structure with different initial morphology were studied. It was shown that the presence of the initial FCC structure of the Ag_{55} cluster completely guarantees its transition to the maximum possible quasi-spherical facet form, while in the case of the initial amorphous structure such a form was formed only in 50–60% of experiments done. In the case of larger clusters, the required structure was obtained at any initial morphology of silver nanoparticles; however, in the case of the initial amorphous structure, the required structural transition occurred in the range above room temperature, which is not very convenient from the point of view of practical application. Thus, the type of the initial configuration of the nanoparticle determines the nature of subsequent thermally induced structural transitions and, in some cases, affects the stability of the formed crystalline modifications at high temperatures. Therefore, it was concluded that in order to obtain the most stable facet structure of AgNPs, it is necessary to use the thermal cycling procedure at the preliminary stage.

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Conflict of interest

The authors declare that they have no conflict of interest.

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