Temperature- induced structure evolution of Ag nanoparticles

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Abstract. The molecular dynamics method with a modified tight-binding (TB-SMA) potential has been used to study the thermal stability of the initial fcc phase in perfect silver clusters to 2.0 nm in diameter, including the "magical" icosahedral size of N = 55 and 147 atoms. It has been shown that the temperature factor can cause a transition from the initial fcc phase to other structural modifications in small Ag clusters (up to 200 atoms). Thus, the fcc structure of clusters with N > 200 atoms is thermally stable to the melting point. For silver nanoparticles of smaller size, the situation is much more complicated, and numerous cases of thermally induced changes in the cluster structure have been observed, often occurring in different scenarios. Thus, to use such small silver clusters, it is necessary to study in detail the problems of the thermal stability of the cluster structure, apparently taking into account the influence of various "magic" numbers.

1. Introduction

Metal clusters with sizes of several nanometres can be used in future technologies, such as biosensors, in catalysis or in medicine [1]. An ultra-small cluster is a nanoparticle that shows a significant in size, it is a nanoparticle of less than 2.0 nm. The structural, electronic, and optical behavior of the nanoparticles with such dimensions can demonstrate new properties. Novel, ultrafast and instant methods of synthesis facilitate the development of a representative number of applications based on silver nanoparticles and their functionalization and make these applications available to the scientific and technical community. The main quality of some of these applications is based on the morphology of the nanoparticles.

In particular, the properties of silver clusters open up a wide field of applications due to their optical activity and antimicrobial effect [2]. However, the rapid oxidation/sulfidation from the ambient atmosphere dramatically reduces all bonuses of silver and causes complications in terms of practical applications. For example, sensors containing Ag usually require storage in inert gases, and the operating time of such devices in the ambient atmosphere is rather limited. One of the existing solutions is to make a protection layer that can prevent Ag structures from degradation due to reactions with environmental species. However, these treatments are not always applicable or rather difficult to use on an industrial scale [3].

The first type of stabilizers is an inorganic scaffold/substrate. Due to the strong cohesive energy between the metal atoms and between the atoms of a metal and another inorganic material, for example, silicon, the metal clusters on the surfaces must be passivated by organic molecules or separated by an inactive matrix. For silver clusters, molecules with thiol groups are often used to passivate cluster surfaces. A natural alternative is to passivate the bulk surface instead of the cluster [4]. Several types of Ag nanoparticles were experimentally synthesized using various protective
ligands, such as proteins, peptides and dendrimers. However, experiments with thiol groups were the most successful, since it was here that high stability, a small size of Ag clusters, and a narrow distribution of them in size were observed [5, 6].

While the majority of the hosts/scaffolds employed for Ag nanoclusters are liquid, polymer or organics based materials, it has only very recently been discovered that some bulk, oxyfluoride glasses can also host Ag nanoclusters. The obvious advantages of the glassy state, such as the possibility of fiber, film, and arbitrary bulk shape manufacturing, open up a novel application [7].

A possible approach to solve this problem could be the formation of very pure particles with a perfect crystalline structure. They should be more stable against the above-mentioned phenomena of degradation. A very promising approach for preparation of such nanoparticles (NPs) is the aggregation of metal atoms into clusters from very pure sources in a vacuum. These clusters can be collimated into beams, size selected and deposited or implanted on/in different substrates, which provides great opportunities for controlling the structure and properties of materials on the nanoscale [3].

Indeed, in mono-crystalline NPs with fcc structure, only atoms present on the surface would be reactive due to reduced coordination numbers and the presence of dangling bonds. In the case of poly-crystalline particles, there is higher probability that the reactive species can attack silver atoms at the grain boundaries, thus, converting them into compounds in expense of the pure metal. We believe that the use of silver nanoparticles with a size equal to the "magic" numbers of different structures can become another unaccounted opportunity to increase the stability of the structure. This position is confirmed by experimental analysis of the distribution of experimentally obtained particles in terms of size (mass spectrum). It showed that clusters with a certain number of atoms that correspond to "magic" numbers are much more stable than clusters of a different size. At the same time, the degree of defectiveness of the surface of clusters with "magic" numbers of atoms is minimal, while in others it can be very significant.

Due to the new applications of sub-nanometric material, it is important to analyze the structural, electronic, and optical behavior on several units of atoms, as well as to show the stabilization mechanisms of these sub-nanometric materials. Since the different internal structure of metallic nanoparticles means different physico-chemical properties, from the point of view of using silver nanoclusters, it is very important to determine the limits of the thermal and dimensional stability of the initial crystal structure of nanoclusters.

2. The computer model

Many various methods have been developed to imitate the behavior of nanoclusters. First of all, we should mention the molecular dynamics method (MD). It is most appropriate for determining the structures of metal clusters of a certain diameter, which are stable in a wide temperature range. The initial objects by computer simulations were spherical fcc silver clusters obtained by cutting a sphere from a perfect fcc lattice with a size of up to 2.0 nm. The choice of clusters of such small size is due to the fact that it is in these sizes that the so-called "magic" numbers play the most important role in the stability of the structure [8-10].

Clusters were simulated within a canonical ensemble using a Nose thermostat. In this case, the number of particles N, volume V, and temperature T remain unchanged (NVT ensemble), and the total momentum p of the system is zero. The temperature during the simulation was determined from the average kinetic energy of the atoms, which was calculated based on the Verlet velocity algorithm with a time step h = 1 fs. The simulation was performed with the MDNTP program developed by Dr. Ralf Meyer (University of Duisburg, Germany). After analyzing various representations of potential energy, Ag nanoclusters were simulated using well-established tight-binding (TB-SMA) potentials [11] with a fixed cutoff radius corresponding to the fifth coordination shell inclusive. Structural transitions were determined using visualizers and from the graphs of the radial distribution function and the temperature dependence of the potential energy.

All clusters at T = 50 K were subjected to the obligatory procedure of thermal relaxation to optimize the internal structure and shape. Then the simulated systems were gradually heated from 50
to 1000 K using the Nóse thermostat. The lower temperature limit of 50 K is set so as not to miss the point of the change in the cluster structure, which can be observed below 100 K. The upper limit of 1000 K is sufficient to melt the simulated particles, since the melting temperature for Ag clusters decreases significantly with decreasing particle size compared with the case of a bulk material (\(T_m = 1235.1\) K). To determine the most stable cluster structure, an array of equally sized nanoparticles was taken. During heating, the temperature was changed with a step of 20 K; in the region of structural transitions, the step was 1 K; at each fixed temperature, the clusters were held for 1 ns.

3. Results and discussion

As the most interesting examples, let us consider the Ag\(_{55}\) and Ag\(_{147}\) silver nanoclusters, i.e. clusters with the number of atoms exactly corresponding to geometric "magic" icosahedral numbers. The simulation results showed that the smallest of the simulated clusters behaved quite predictably under heating. Already at the preliminary stage of thermal relaxation, a polytype transition of the fcc \(\rightarrow\) Ih occurred and an ideal icosahedral structure was formed. That is, as expected, with such a small cluster size and the number of atoms equal to two complete Ih shells, the gain in surface energy and the absence of structural defects immediately lead to the formation of an extremely stable icosahedral modification, which is fixed by many authors for a variety of metals. No pre-melting effects were observed here, the dependence of the potential energy of the Ag\(_{55}\) cluster on the temperature had a strictly linear character up to the melting point, after which a very rapid destruction of the long-range order occurred in the cluster (figure 1).

The second considered cluster of the group of ideal icosahedral ones under consideration was already completely filled with the third Ih shell. In this case, the number of atoms becomes much larger (\(N = 147\)) than in the Ag\(_{55}\) cluster, which can be decisive for such small subnanometer clusters. A typical dependence of the potential energy of the cluster Ag\(_{147}\) on the temperature is shown in figure 2. In this figure we will dwell in more detail, but first we give some preliminary arguments.

As already mentioned, in the bulk state, silver has a face-centered cubic lattice, but the competition between the bulk and surface energies in the nanometer range can lead to the formation of several different isomers, the stability boundaries of which have not yet been determined. Many theoretical studies were mainly focused on searching for the total energy of a cluster at very low temperatures in various structural modifications as a measure of their relative stability, and the data obtained were directly affected by the chosen potential. Apparently, we must recognize that even insignificant defects in silver, especially at small sizes, can play a very important role in determining the equilibrium structure of a particle.
Another cause of such serious discrepancies consists in very close energies calculated for different structural modifications. For example, the MD simulation of gold clusters close to silver in the processes of structuring performed in [12] with the Gupta potential at \( N = 38 \) atoms gives the following free cluster energies in its ground state: \(-3.4405\) eV/atom in the amorphous state, \(-3.44\) eV/atom in the fcc state, and \(-3.431\) eV/atom in the icosahedral (Ih) state. Such small differences between these three isomers were retained up to room temperature. At \( T > 250\) K, thermal energy is sufficient to overcome potential barriers between these structures; as a result, all three isomers begin to appear randomly. Such significant changes are believed to be mainly caused by the fact that, with such cluster sizes, almost all atoms lie on the cluster surface, and an insignificant change in their arrangement induced by thermal diffusion is sufficient for a spontaneous formation of another structural modification. This conclusion was supported experimentally: the cluster structure and shape fluctuations were clearly visible in gold clusters with a diameter of 2.0 nm in using an electron microscope. The larger size of the fluctuating particles is due to the fact that the cluster structure and shape changes were induced by both thermal processes and electron irradiation.

The authors of [12] applied MD simulation with the Gupta potential to perform similar estimates for larger gold clusters. The binding-energy difference between the amorphous and Ih structures was found to be \(9.4\) meV/atom at \( N = 55\), and the five-particle Dh modification at \( N = 57\) turned out to be more stable than the amorphous structure by only \(5.7\) meV/atom. To verify this result, the authors of [12] performed an additional ab-initio study of the relative stability of gold clusters with crystalline and amorphous structures. The binding energy difference per atom between the most stable amorphous and crystalline modifications for clusters of the sizes given above was found to be smaller than \(0.01\) eV/atom. The only specific feature found was the distribution of the electron charge density: it was slightly broader in amorphous clusters. All this can be seen well from the analysis of figure 2. Here, unlike the \(\text{Ag}_{55}\) cluster, the structural transition fcc \(\rightarrow\) Ih was not observed in the preliminary stage of thermal relaxation of \(\text{Ag}_{147}\). This fact indicates that the gain in surface energy at such a size is no longer so significant, and to overcome the energy barrier between polytypic modifications, a larger value of thermal energy \(kT\) is required. This result is confirmed by the work [10], where it was shown that the energy stability of the \(\text{Ag}_{147}\) cluster decreases by approximately 30-35% compared to \(\text{Ag}_{55}\), becoming practically identical with the decahedral (Dh) cluster \(\text{Ag}_{146}\). The reason for this phenomenon is that in the case of \(\text{Ag}_{55}\), about 76% of the atoms lie on the cluster surface, whereas in the \(\text{Ag}_{147}\) cluster it is only 62%. It is clear that due to the smaller coordination number and, consequently, a lower value of the binding energy, surface atoms more easily move around the cluster, forming an energetically more advantageous structure.

In full accordance with our theoretical considerations, the cluster \(\text{Ag}_{147}\) retained its original fcc structure to temperatures of the order of 280 K. Further, the structure was rearranged and the cluster...
acquired a decahedral or icosahedral structure, which gradually disintegrated during further heating. The complete destruction of the crystal structure of \( \text{Ag}_{147} \) nanoclusters is observed at temperatures above 620 K. Thus, in spite of the fact that the \( \text{Ag}_{147} \) cluster strictly corresponded to the geometric "magical" icosahedral number, during heating approximately the same proportion of both icosahedral and decahedral modifications could be formed, which indicates close values of the energies of these five-particle structures [10].

4. Conclusions
When studying nanoclusters at the end of the 20th century, the fact seemed unusual that their properties were significantly different from the properties of bulk compounds of the same composition. This was not surprising for the smallest clusters, whose electronic and atomic structure was fundamentally different from the structure of the bulk body. However, even fairly large clusters with internal structures similar to the bulk body may have properties different from those characteristic of it.

When a metal particle decreases in size to several hundred atoms, the density of states in its conduction band drastically changes. The continuous density of states of the bulk body is replaced by a set of discrete levels, the intervals between which can be greater than the thermal energy \( k_B T \), which results in the formation of gaps. Clusters of different sizes and internal structures have different electronic structures, hence, different distances between the levels, which can be used in the design of nanomaterials and the development of various technical devices. For example, light-induced transitions between energy levels control the color of a material. The ability to interact with other materials also depends on the size and structure of the cluster.

It was previously believed that small-sized metal clusters should mostly have a structure with five-particle symmetry, since it is these structures that provide surface energy growth. Hence, the main goal was to determine the size boundary at which the metal cluster changes the structure from the icosahedral one to the structure corresponding to the bulk material. However, as shown in this study, this concept is too simplified; at least for some metals, the problems of thermal stability of the cluster structure should be studied in more detail, taking into account the effect of different “magic” numbers.

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