

Role of “Magic” Numbers in Structure Formation in Small Silver Nanoclusters

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Abstract—The molecular dynamics method with the modified tight-binding (TB-SMA) potential has been used to study thermal stability of the initial fcc phase in perfect silver clusters to 2 nm in diameter. Dimensional boundaries of nanoparticles, at which the internal atomic configuration changes upon heating, have been determined using the molecular dynamics simulation. It has been shown that the temperature factor can cause the transition from the initial fcc phase to other structural modifications, including those with pentagonal symmetry, in small Ag clusters. It has been demonstrated that “magic” numbers play an important role in the formation of the internal structure of silver clusters.

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1. INTRODUCTION

The last two decades were marked by heightened interest of researchers in the development and study of different nanostructures. Nanostructures are of practical and scientific significance from the viewpoint of understanding fundamental electrical, magnetic, optical, catalytic, thermal, and mechanical properties of nanoscale materials [1], as well as from the viewpoint of fabrication of new technical devices on their basis [2]. It is already clear that the quantum-mechanical effects implemented in nanostructures, such as the conductance quantization, band gap renormalization, Coulomb blockade, and others, can significantly improve functional characteristics of different electronic devices [3, 4].

The determination of physical and chemical properties of individual elements of nanomaterials, i.e., nanoclusters, is of particular interest due to the possibility of studying the transition from free atoms and molecules to bulk condensed systems. Clusters, being the main unit of such evolution, are unique objects of study and can give a clue to understand the nature of different processes, including nucleation, dissolution, catalysis, adsorption, phase transitions, and others [1].

Furthermore, already in the early 1990s, the first experiments were performed on the development of electronic elements consisting of metal units of in fact nanometer size. Further experiments showed that the circuitry of such electronics can be developed based on metal nanoclusters exhibiting quantum conductance properties at room temperatures [3]. However, free nanoparticles, e.g., of pure fcc metals are typically very reactive and, hence, have short lifetimes. Therefore, the direct use of such particles as functional objects of

nanoelectronics is complicated due to their extremely low stability and susceptibility to aggregation.

This problem can be solved by stabilizing metal nanoparticles by ligands, i.e., by adding atomic groups between cluster atoms and the cluster surface [5]. Nanoparticles required for technical applications can also be produced in liquid media [6], which eliminates contact with air. Such particles are referred to as passivated, since they are coated with a layer of the other material, but the chemical nature of this layer can have a significant effect on nanoparticle properties [2, 7], which is not always positive. The introduction of nanoclusters into an inert matrix (matrix isolation) [8] also makes it possible to stabilize the nanophase, to avoid aggregation, and to protect it from external influences. The interaction of free clusters with this type of external medium is an independent problem and is not considered in the present paper.

One of the main methods for synthesizing metal clusters is condensation from the gas phase in a cooling inert gas atmosphere [8–11]. This approach requires the production of supersaturated vapor from metal atoms followed by deposition of produced particles on the surface. The vapor of atoms or molecules can be produced by different methods, including ion, plasma, or magnetron sputtering, laser ablation, explosive vaporization, and others. Ordinary thermal evaporation of materials is often used to produce high-pressure vapor of metal atoms.

In this synthesis method, clustering is controlled by the gas phase and is already independent of ligands, and the stability and properties depend on “magic” numbers of atoms forming the cluster [12]. This statement is confirmed by an experimental analysis of the size distribution (mass spectrum) of produced parti-

cles, which showed that clusters with a certain number of atoms, corresponding to “magic” numbers are much more stable in comparison with clusters of the other size.

According to [12], structural “magic” numbers exist even for very large clusters. For example, it was found that such numbers in the case of gold particles had an effect to sizes of 10 nm. In this case, the surface defect density of clusters with “magic” numbers of atoms is minimum, while it can be rather significant for others. However, as studies showed, stable clusters with the number of atoms different from structural “magic” numbers are quite often formed during synthesis. Simulation showed that these numbers correspond to clusters with the most stable electronic configuration. Therefore, these numbers were called the electronic “magic” numbers. It is worth noting that the energy configuration with electronic “magic” numbers is most stable for small clusters; as the size increases, the clusters with structural “magic” numbers appear to be more stable. For example, for Na clusters, the first fifteen “magic” numbers with $N = 3, 9, 20, 36, 61, \dots, 1220$ atoms are electronic, and the following numbers, beginning with $N = 1415$ atoms, are structural [8].

Thus, taking into account all above-mentioned, the main objective of this work is to study the possible effect of electronic and structural “magic” numbers on stability of free small silver clusters, since clusters of exactly this metal are currently efficiently synthesized by different physicochemical methods [1, 3, 13]. Furthermore, due to the almost free s -electron in the valence shell, silver has high conductivity, hence, is widely used in electronics.

In this study, particular attention was paid to the internal nanoparticle structure stability, since a change in the atomic configuration of the cluster can have an effect on many other properties [3, 14], in particular on its electronic structure. It is well known that clusters with different sizes and internal structures have different distances between energy levels [15], which cannot but attract interest from the technical point of view. For example, density functional calculations showed that the binding energy per atom in the Al_{13} icosahedral cluster (2.77 eV) is significantly lower than that in the bulk fcc crystal (3.39 eV) [7]. The Al_{13} cluster has one unpaired electron in the valence shell; an additional electron completes the shell, which causes an appreciable increase in the binding energy in the Al_{13} ion (3.10 eV), thus changing its physicochemical properties. Similar results for the dependence of the binding energy of Ag_{20} clusters on their geometrical structure are given in [16].

2. NUMERICAL MODEL

It is difficult to imagine modern science without numerical simulation. The replacement of an initial

object with its mathematical model makes it possible to relatively rapidly determine its characteristics and properties with minimum effort. In contrast to the purely theoretical approach, numerical simulation makes it possible to study objects in their characteristic state, which, before the advent of numerical models, was one of the main advantages of only the experimental approach.

In solid state physics, instead of expensive experiments, a model replacing a real object can be studied using modern computers. To date, many methods have been developed for simulating the nanocluster behavior, first of all, the molecular dynamics (MD) method [17]. Furthermore, atomic-level studies are performed using the classical Monte Carlo method [18, 19], methods based on the quantum theory and including integration over trajectories [20], modified Monte Carlo methods, and MD in combination with the electron density functional theory [21, 22]. Discrete approaches, e.g., cellular automata and the lattice Boltzmann equation method, are also used.

In spite of such a variety of possible methods for studying clusters and nanoparticles, in our opinion, the molecular dynamics method is nevertheless most promising for studying fcc metal nanostructures. This approach makes it possible to simulate a detailed pattern of the internal mobility of cluster atoms and to comprehensively study the effect of external factors on the lattice order.

The MD method is based on the calculation of classical (Newtonian) trajectories of object motion in the phase space of coordinates and momenta of its atoms [23]. In the simplest version of this method, classical trajectories of atomic motion in the force field of the empirical atom–atom potential, i.e., a detailed microscopic pattern of the internal thermal mobility is simulated in nanosecond time intervals.

MD simulation of nanostructures is completely based on a detailed description of particles composing them. In MD, the classical viewpoint is most often used, according to which atoms or molecules are represented as point masses interacting via forces depending on the distance between these objects. In the numerical analysis, such forces are calculated using different interatomic interaction potentials, and the confidence level of the results obtained is directly dictated by the used potential choice. Therefore, after analyzing different representations of the potential energy, Ag nanoclusters were simulated using well-established tight-binding (TB-SMA) potentials [24] with fixed cutoff radius corresponding to the fifth coordination shell inclusive.

These potentials based on the approximation of the second moments of the tight-binding Hamiltonian were developed by Cleri and Rosato [24]. The modified tight-binding method proposed by them was successfully used in a number of cluster studies. The method is based on the fact that a large group of prop-

erties of transition metals can be fully defined using the density of states of outer d -electrons. The second moment of the density of state is μ_2 ; it was experimentally found that the cohesion energy of metals is proportional to the width of the density of states, which, in the approximation of the second moments, is simply $\sqrt{\mu_2}$. If only $dd\sigma$ -, $dd\pi$ -, and $dd\delta$ -orbitals are taken into consideration, then, according to this model, the band energy of atom i can be written as

$$E_B^i = -\left(\sum_j \xi_{\alpha\beta}^2 e^{-2q_{\alpha\beta}(r_{ij}/r_0^{\alpha\beta}-1)}\right)^{1/2}. \quad (1)$$

It depends only on the distance between atoms i and j , i.e., r_{ij} , and is formally the same as the embedding function in the embedded atom method. Furthermore, the model includes a term accounting for the repulsive interaction in the form of the sum of Born–Meyer ion pair potentials,

$$E_R^i = \sum_j A_{\alpha\beta} e^{-p_{\alpha\beta}(r_{ij}/r_0^{\alpha\beta}-1)}, \quad (2)$$

where α and β are different types of atoms. Thus, the total energy of the system is written as

$$E_c = \sum_i (E_R^i + E_B^i). \quad (3)$$

The quantities $\xi_{\alpha\beta}$, $p_{\alpha\beta}$, $A_{\alpha\beta}$, $q_{\alpha\beta}$, $r_0^{\alpha\beta}$, and the potential cutoff radius r_c define the parameters of system elements. The values of $\xi_{\alpha\beta}$, $p_{\alpha\beta}$, $A_{\alpha\beta}$, and $q_{\alpha\beta}$, are determined by fitting the cohesion energy, lattice parameter, bulk modulus B , and elastic constants C_{44} and C' to experimental values. Despite the simple functional form, the tight-binding model quite adequately describes elastic properties, defect characteristics, and melting for a wide range of fcc and hcp metals. In our opinion, it is one of the most appropriate schemes for numerical analysis of small metal particles consisting of a few hundred atoms.

Clusters were simulated within the canonical ensemble using a Nose thermostat [25]. 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 simulation was determined from the average kinetic energy of atoms, which was calculated based on the velocity Verlet algorithm with time step $h = 1$ fs. The simulation was performed with the MDNTP program developed by Dr. Ralf Meyer (Universitat Duisburg, Germany).

3. RESULTS AND DISCUSSION

In general, the nanoparticle crystal structure is the same as that of a bulk material. However, in some cases, small particles can have the other internal structure. The experimental determination of the atomic

configuration of small metal particles is very difficult and such data are small in number [7]; therefore, numerical simulation can be used as an alternative method. To determine thermal stability limits of different isomeric modifications of small silver nanoclusters, the effect of the size and temperature on the formation of this or that crystalline modification was studied. To this end, the molecular dynamics method based on the modified tight-binding TB-SMA potential [24] was used to study a group of clusters with an initial structure corresponding to the perfect fcc lattice with a diameter to 2 nm. Structural transitions were determined using visual analyzers and the radial distribution function depending on the potential energy on temperature.

All clusters at $T = 20$ K were subjected to an obligatory procedure of thermal relaxation to optimize the internal structure and shape. Then, the simulated systems were gradually heated from 20 to 800 K using the Nose thermostat. Temperature limits were set on grounds of expediency. The lower temperature limit of 20 K is set not to miss the point of the change in the cluster structure, which can be observed below 100 K. The upper limit of 800 K is sufficient to melt simulated particles, since the melting temperature for Ag clusters is significantly lowered with decreasing particle size in comparison 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, clusters were kept for 1 ns.

The first experiment on the study of thermal stability of the fcc phase was performed for silver clusters with sizes equal to “magic” numbers of the fcc structure ($N = 79, 135, 201$ atoms). In this case, the situation was ambiguous. An analysis of the simulation data clearly shows that the heating of Ag_{79} and Ag_{201} caused only a gradual increase in their potential energy followed by a sharp step at the melting temperature. When considering the structural changes in clusters, it was found that the initial fcc structure was retained to the melting temperature, being gradually destructed beginning with the cluster surface. Thus, it was shown that the structural transition is not typical of such sizes of silver nanoparticles, and the initial fcc phase is thermally stable in this case.

However, for the cluster with $N = 135$ atoms ($D = 1.59$ nm), an abrupt decrease in the potential energy, accompanied by a change in the crystal structure from the fcc to icosahedral modification was observed (Fig. 1). Upon further heating, the icosahedral structure was retained until the melting process start. We can see in Fig. 1 that an increase in the cluster temperature from 20 to 401 K leads to only a slight change in atomic positions in the particle while retaining the fcc configuration. A distinct structural transition occurs

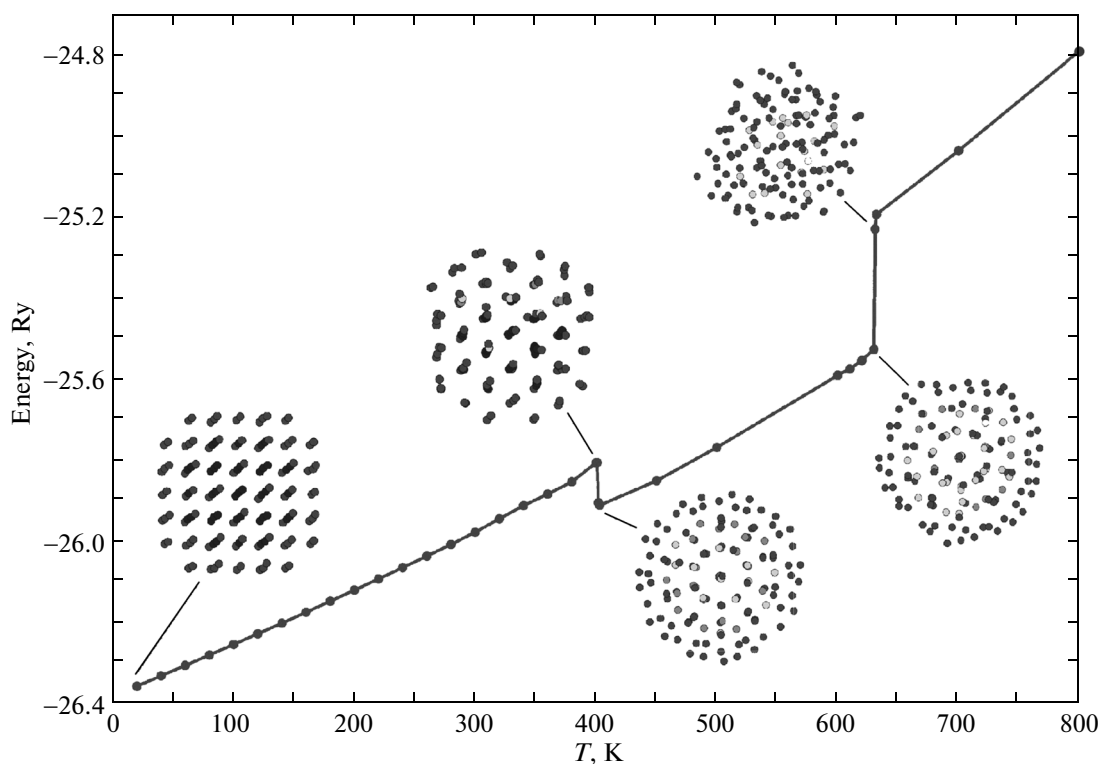


Fig. 1. Dependence of the potential energy of the fcc Ag cluster ($N = 135$ atoms) on the absolute temperature T and structural changes in the nanoparticle.

only at a temperature of ~ 402 K. Further heat transfer to the simulated system causes gradual increase in its energy and partial deformation of the icosahedral structure. Total destruction of the cluster crystalline structure was observed at $T_m = 631$ K.

Hence, it can be concluded that the structure formed upon thermal exposure for a silver nanocluster of size $N = 135$ atoms is determined not only by the “magic” fcc number, but also other factors which have yet to be studied. In particular, the authors of [26] studied the structure of small aluminum clusters with 25–84 atoms using the SIESTA numerical code come to the conclusion that the cluster stability can be simultaneously affected by both structural and electronic effects. Furthermore, the ratio of energies of different cluster configurations also depends on temperature [27].

In this context, it may be noted that, in the case of sodium which is similar to silver in the outer electron shell structure, the cluster of $N = 138$ atoms exhibits a pronounced mass spectrum maximum which indicates increased stability of such clusters. Nanoclusters with such a “magic” number of atoms have higher binding energies, ionization potentials, and others, which was taken as the basis of cluster electronic structure concepts, since it is well known that those systems among atoms appear to be the most stable, in which certain energy levels are populated. Physical grounds

for using the shell model are considered in detail in [28].

It was experimentally demonstrated that intensity maxima of mass spectra of alkali and rare-earth metal clusters arise due to the formation of closed electron shells. For clusters with complete energy levels, exactly the electronic “magic” numbers have the strongest effect on the internal structure formation. Hence, the equilibrium state of such metal clusters can be associated with the complete electron shell [29], rather than with the regular geometrical atomic arrangement.

In our opinion, the “magic” numbers in small clusters of transition metals, including silver, are determined by both structural and electronic aspects. This is evidenced by the fact that the surface contraction occurred in the Ag_{135} nanoparticle with increasing temperature, which is controlled by the structural “magic” numbers. The structural “magic” numbers are called so since they arise when minimizing the volume with a maximum possible density of the nanoparticle with close to spherical shape. It is clear that the maximum volume minimization is determined by the formation of the so-called Mackey icosahedron formed as follows: the smallest Mackey icosahedron consists of 13 atoms, one of which is at the cluster center and is surrounded by a shell 12 other atoms. The surface of this icosahedron consists of 20 equilateral triangles. Larger Mackey icosahedra are formed by

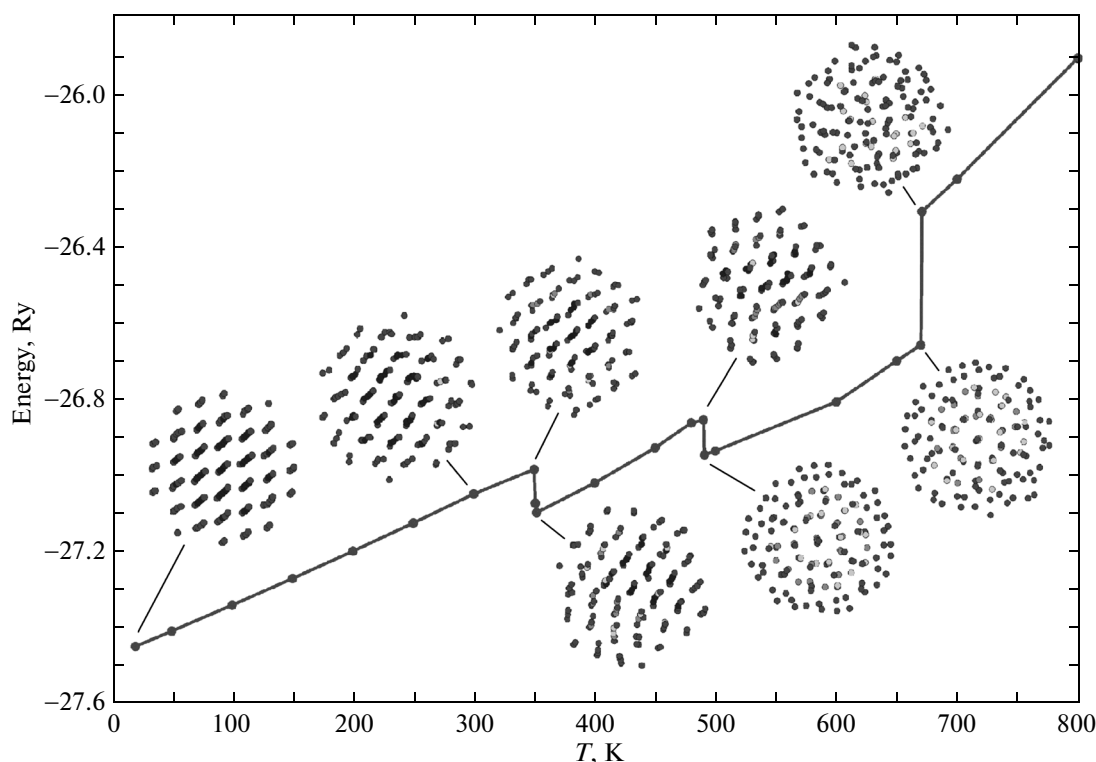


Fig. 2. Temperature dependence of the potential energy of the fcc Ag cluster ($N = 141$ atoms) and structural changes in the nanoparticle.

adding further shells, which does cause cluster surface area minimization and a corresponding gain advantage in the surface energy.

However, in the case of Ag_{79} and Ag_{201} clusters, a similar transition to the icosahedral structure did not occur. In our opinion, the major cause of this was that the "magic" icosahedral numbers ($N = 13, 55, 147, 309, \dots$) closest to these ideal fcc sizes were too far, i.e., farther than for the Ag_{135} cluster.

In latter case, the very close electronic "magic" number $N = 138$ could also provoke the transition from one structure to another. The point is that the energy barrier between fcc and icosahedral structures is typically low [30, 31]; therefore, the effect of side factors such as the structural defects, temperature, and electronic "magic" numbers, can become decisive.

Since silver clusters with defect-free structure were simulated, and the temperature increased identically in all clusters proceeded, the first two factors can be excluded, and a preliminary conclusion can be made that not only the geometrical atomic arrangement, but also electronic configurations are responsible for the Ag_{135} particle structure stability.

To confirm this assumption, the cluster structures of silver nanoparticles with a size slightly larger than the electronic "magic" numbers $N = 138$ were then studied. To this end, an Ag_{141} cluster array ($D = 1.6$ nm) was taken. In most cases, the systematic fea-

tures obtained for the Ag_{135} cluster were still observed, but already with a number of unusual features. Having analyzed the change in the internal structure of Ag_{141} nanoclusters upon heating, we distinguished three possible scenarios of their evolution. For example, in the first case ($\sim 10\%$ of experiments), the situation similar to the above case of Ag_{135} was observed, i.e., the particle potential energy almost linearly increased as the cluster temperature increased to 400 K while retaining the fcc structure. At $T = 401$ K, the Ag_{141} cluster potential energy abruptly decreased, and the well-defined icosahedral modification was formed. Such a five-particle structure was totally destroyed only at $T_m = 658$ K, when the cluster transformed to a liquid state.

The second more complex behavior scenario is shown in Fig. 2. We can see that the particle potential energy twice sharply drops with changes in its structure during Ag_{141} nanocluster heating. Thus, a rather rare double structural transition in the cluster is observed. A similar situation was observed in 50% of performed numerical experiments.

Let us consider this case in more detail. A comparison of structures formed in such an 141-atomic silver cluster showed that the initial perfect fcc particle modification was retained to ~ 300 K. A temperature increase to 350 K resulted in a partial displacement of silver atoms in the cluster with the formation of several

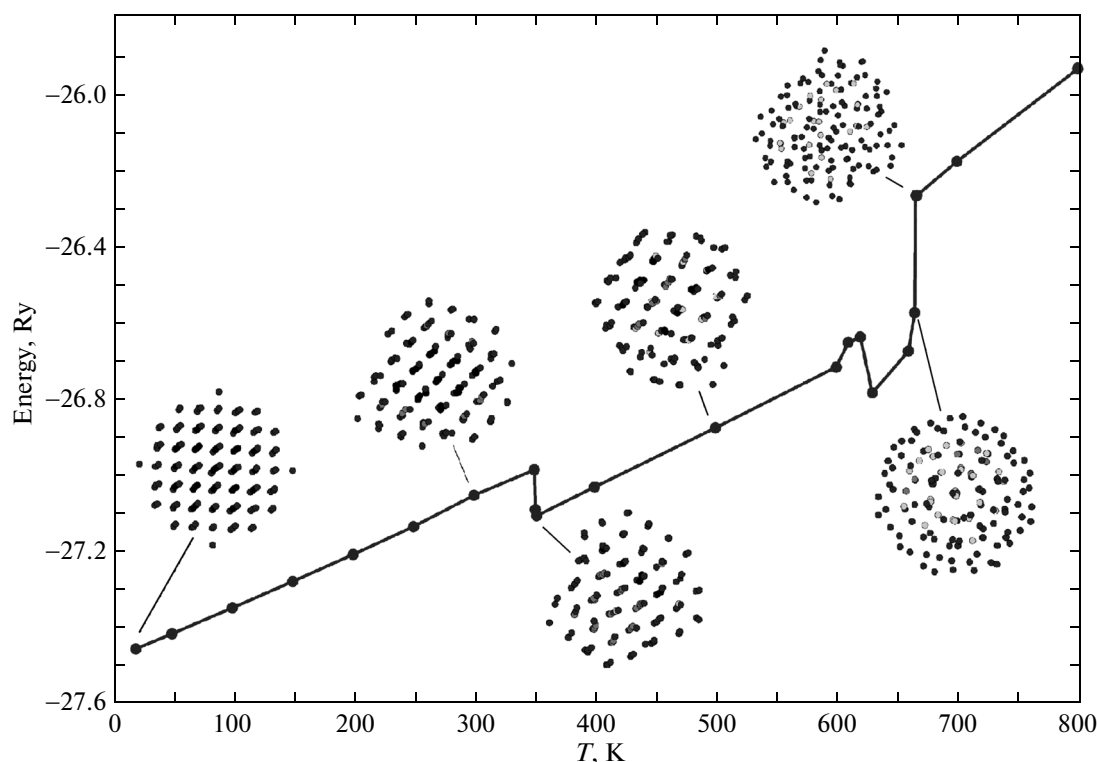


Fig. 3. Temperature dependence of the potential energy of the Ag cluster ($N = 141$ atoms) during the third evolution version (see text).

hcp planes. We note that a similar local rearrangement of atoms was observed before the structural transition of the 135-atomic particle as well. At $T = 351$ K, the potential energy abruptly decreases, which indicates the formation of an energetically more stable cluster structure. We can see in Fig. 2 that the structure obtained is very similar to the twin fcc + hcp configuration. However, some atomic planes of the cluster are slightly twisted, which indicates the possible appearance of the icosahedron- (Ih) or decahedron-type (Dh) structure nucleus. It is possible that the thermal energy in this temperature range is still insufficient to form the complete five-particle atomic structure in the nanoparticle.

We note that equilibrium clusters can have even a multiple twin structure knowingly nonequilibrium for bulk samples. As the icosahedral structure, it arises due to the trend to decreasing the particle surface energy; however, this is achieved not by a total change in the crystallographic structure, but by its certain deformation. Energy expenditures for this deformation should be compensated by a gain in the surface energy. For example, (111) faces in fcc lattices, as a rule, have the least energy; however, the Wulff polyhedron for such lattices, in addition to (111) faces, contain also high-energy faces. They can be eliminated via the following construction. An icosahedron consisting of 20 equivalent tetrahedra whose all faces are (111) triangular is constructed.

If these tetrahedra are not deformed, gaps increasing the surface energy will exist between them. But if their solid angles are increased, these tetrahedra appear to be close-packed, which will lower this energy. Such multiply twin structures are also often experimentally observed [31, 32].

Upon further Ag_{141} heating, only a small change in the cluster structure was observed; however, a spontaneous transition to the icosahedral phase occurred at $T = 491$ K; this phase was retained with further temperature increase. Figure 2 shows that the second structural transition is also accompanied by an abrupt decrease in the cluster potential energy, i.e., the eventual transition to the closest-packed structure with minimum possible surface energy occurs.

The third type of the thermodynamic curve obtained during heating of Ag_{141} nanoparticles is shown in Fig. 3. This dependence type was indicated in 40% of performed experiments. At the initial stage, the thermal evolution occurs similarly to the second scenario, i.e., the initial fcc structure is as a whole retained to temperatures of ~ 300 K. In the range of 300–350 K, this structure is slightly distorted with hcp component inclusion. However, such a structure appears to be unstable, and the cluster potential energy abruptly decreases at the same temperature $T = 351$ K, and the cluster takes an energetically more favorable shape. However, in contrast to the second thermal evolution type, the cluster structure transformation

does not lead to fcc(hcp) phase twinning, and a more stable structure with a decahedron nucleus is formed. Thus, due to a deeper potential energy drop than in the case of the second scenario, this structure intermediate between fcc and icosahedron appears to be quite stable; in this case, the second structural transition shifts almost to the cluster melting temperature. In this premelting region, the cluster is in a very unstable state, and its potential energy exhibits strong variations. Analyzing the change in the Ag_{141} internal structure in this region, we confirmed the existence of the expected transition to the icosahedral modification.

Let us try to determine why the Ag_{141} cluster showed much more complex behavior during the thermal evolution than Ag_{135} . The electronic “magic” number $N = 138$ atoms is strictly between sizes of these clusters, hence, should have equal effects on both clusters. It remains to estimate the possible role of structural “magic” numbers. The closest number ($N = 147$ atoms) corresponds to the perfect icosahedron and, by implication, should only facilitate the direct development of the corresponding structure in the Ag_{141} cluster (without an intermediate atomic rearrangement at $T = 351$ K). The next “magic” number at $N = 153$ atoms yields a perfect hcp structure of cluster atoms. It is possible that this factor has a certain effect, and for the Ag_{141} cluster it appears to be stronger than for the Ag_{135} cluster.

In our opinion, a main cause of such a complex behavior of the Ag_{141} cluster is the role of the “magic” number of a distorted octahedron implemented at $N = 140$ atoms. In general, such a structure is not attributed to those mostly observed in clusters, since it has a higher energy than decahedral or icosahedral structures; however, the octahedron distortion along any atomic plane makes it possible to shorten the energy gap between structures. By the example of the Ag_{141} cluster, it is easily seen that exactly the distortion of the primary fcc structure, rather than its transition to the icosahedron, makes it possible to achieve an energy gain in the first stage of the cluster transformation, and only further heat supply which weakens the interaction between atoms makes allows the transition to an energetically more favorable structure, i.e., the icosahedron.

We note that such a complex behavior at the metal cluster size of 141 atom is not characteristic of only silver. For example, aluminum clusters of this size upon heating also showed different scenarios of the behavior. In 60% of cases at $T = 134$ K, the icosahedral cluster structure was formed, which is quite stably retained to the melting temperature. In 40% of cases, the cluster energy increased, but the primary fcc structure, despite a certain violation in the atomic layer packing order with the formation of icosahedral fragments, was retained to $T = 370$ K, and only further heating resulted in the icosahedral structure formation [30]. Thus, the systematic features we noticed in studying

the Ag_{141} cluster can be of significant importance, and are probably characteristic of a variety of fcc metals, at least metals with rather weak interactions between atoms (Al, Au, Ag, Pb).

In the next simulation stage, the structure formation in Ag clusters consisting of 177 atoms (diameter $D = 1.8$ nm) was studied. The typical thermal cycle curve is shown in Fig. 4. We can see that the structural transition with an abrupt decrease in the potential energy is not typical of silver clusters of this size. As the temperature increases from 20 to ~ 400 K, the simulated system retains the initial fcc structure. Upon further heating, the cluster lattice is slightly deformed, and atoms with hcp localization appear. Near the crystalline solid–liquid phase transition, classical surface melting of the cluster is observed; complete melting of the nanoparticle under study occurs at the temperature $T_m = 651$ K.

Such behavior of Ag_{177} clusters during heating was traced in 60% of experiments; in other 40% of numerical experiments, only weak variations in the potential energy near the melting point were observed, which nevertheless resulted in the cluster structure transformation. Having analyzed the change in the atomic arrangement of the Ag_{177} nanocluster in this region, we showed the existence of the structural transition from the fcc phase to the decahedral modification. We note that the size $N = 177$ atoms lies rather far from different structural and electronic “magic” numbers. In our opinion, exactly this circumstance controls the thermal evolution of the Ag_{177} cluster. In most cases, its initial fcc structure was retained to one extent or another almost to the melting temperature similarly to the Ag_{79} and Ag_{201} clusters. However, the fcc structure of clusters of these sizes was stable to its destruction due to melting; the major role in such behavior was played by the structure stabilization due to the fcc structural “magic” number. But if the cluster size does not correspond to such a number ($N = 177$ atoms), the structure stabilization will be incomplete. The interatomic bond weakening observed near the melting temperature allows the appearance of the other atomic structure type with five-particle symmetry, which is confirmed experimentally for this silver nanoparticle size [8].

As the last characteristic example, we consider configuration changes in Ag clusters consisting of 89 atoms, which corresponds to the hcp structural “magic” number. An analysis of the simulation showed that heating sharply decreases the potential energy of the Ag_{89} cluster even at $T = 73$ K, and the nanoparticle attempts to transit from the fcc phase to the mixture of fcc and hcp structures. This mixed structure was further observed to the melting temperature. Sometimes, an icosahedral structure nucleus was formed in it, which never developed into a valuable phase.

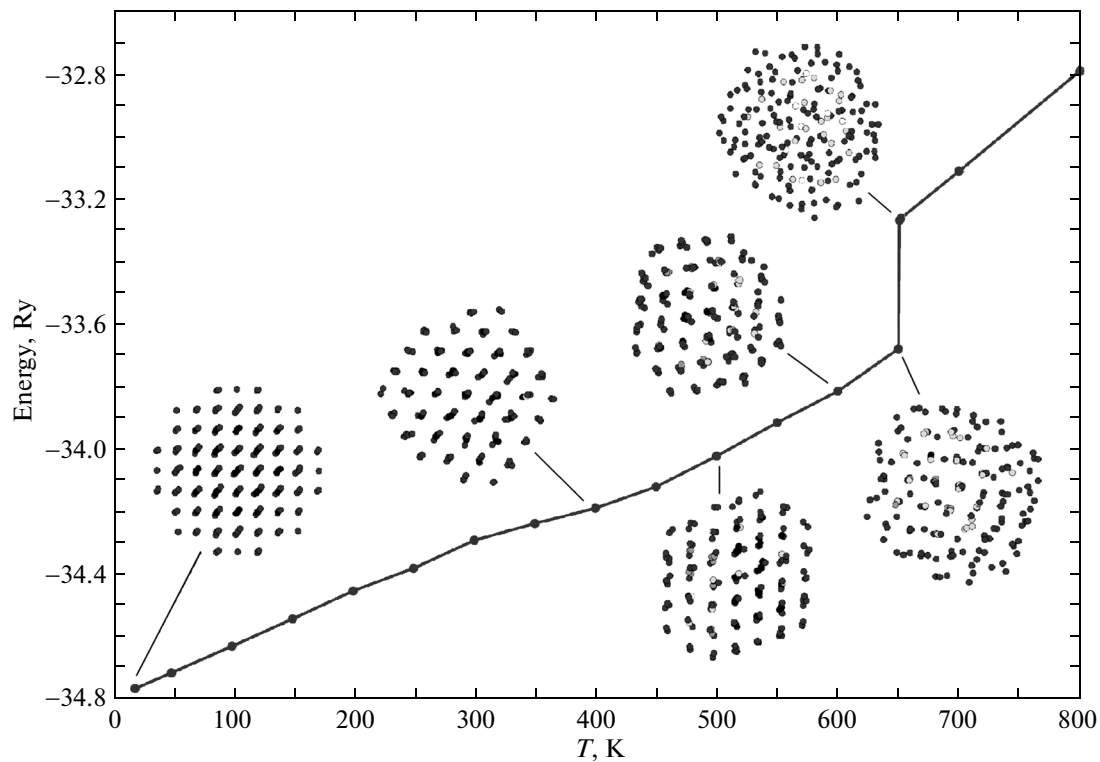


Fig. 4. Temperature dependence of the potential energy of the fcc Ag cluster ($N = 177$ atoms) and structural changes in the nanoparticle.

Thus, during the numerical experiment performed by the MD method, heating of fcc silver clusters to 2 nm in size were studied. A comparison of the obtained cluster structures showed that, in the general case, the obvious role in their transformation is played by “magic” numbers of different types. Furthermore, the appearance of the configuration transition can be associated with the difference between the cluster elastic deformation energy and its surface energy which depend on the number of atoms composing a nanoparticle.

4. CONCLUSIONS

During the study of nanoclusters as early as in the late 20th century, the fact seemed unusual that their properties significantly differ from properties of bulk compounds of the same composition. This is not surprising for the smallest clusters whose electronic and atomic structure fundamentally differed from the bulk matter structure. However, even large enough clusters with internal structures similar to bulk matter could have properties different from those characteristic of it. Another unexpected fact was the detection of that far from all clusters are identically stable, and an important distinctive feature of nanosystems is the manifestation of size quantization effects in them.

The major role in this circumstance is played by structural “magic” numbers responsible for the nano-

particle volume (surface) contraction, and the trend toward a decrease in the surface energy of a small particle can be implemented by changing its crystal structure in comparison with the bulk sample structure.

During the study, it also became clear that structural “magic” numbers are unrelated to the electronic structure of atoms composing the nanoparticle. However, the interaction of valence electrons is sometimes the factor determining the small nanoparticle energy minimum. Configurations of atomic clusters in which such electrons form complete shells are especially stable and generate electronic “magic” numbers which can also affect the formation of the internal structure of metal nanoparticles.

When the metal particle decreases in size to a few 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, intervals between which can be larger than the thermal energy $k_B T$, which results in the gap formation. Clusters of different sizes and internal structures have different electronic structures, hence, different distances between levels, which can be used in designing nanomaterials [33] and developing different technical devices.

For example, light-induced transitions between energy levels determine the material color [6]. The

capability of interacting with other materials also depends on the cluster size and structure.

It was previously thought that small-sized metal clusters should mostly have a structure with five-particle symmetry, since exactly such structures provide a gain in the surface energy. Hence, the main objective was to determine the size boundary at which the metal cluster changes from the icosahedral structure to the structure corresponding to a bulk material [34]. However, as shown in the present study, such a 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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