



Computer Analysis of Some Thermodynamic Properties of Platinum Nanoclusters by Melting-Crystallization Processes

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The processes of melting and crystallization of Pt nanoclusters with a diameter ranging from 1.6 to 10 nm have been investigated using the molecular dynamics simulation. The performed simulation has shown that the melting begins with the surface of the cluster. Another feature of this phase transition is that it occurs in a temperature range where the liquid and solid phases can coexist. However, it is found that, for small platinum clusters, the melting and crystallization temperatures coincide with each other. The behavior of some thermodynamic characteristics of platinum nanoclusters is investigated in the vicinity of the solid–liquid phase transition. Analysis of the data obtained has revealed a number of regularities that are in agreement with the results of analytical calculations. In particular, the melting and crystallization temperatures of platinum nanoparticles are linear functions of $N^{-1/3}$. However, the melting heat ΔH_m and the melting entropy ΔS_m vary in a more complex manner.

Keywords: Molecular-Dynamics Simulations, Tight-Binding, Platinum Nanoclusters, Melting, Crystallization.

1. INTRODUCTION

Rapid progress made in science and engineering already at the end of the last century led to the necessity of using new devices comparable in size to the atomic scale. Before long, it became clear that properties of nanomaterials used for the fabrication of these devices depend, to a large extent, on specific features of their constituent particles. In this respect, small particles (clusters) containing from several tens to several thousands of atoms have been extensively studied in recent years. Investigation of metallic nanoparticles is an especially important problem because of the wide applied possibilities for their use in quite different fields of nanotechnologies from medicine to catalysis and power engineering.^{1,2} However, experimental investigations of nanoclusters involve certain problems that are associated primarily with the small size of particles. Therefore, one of the possible approaches to the investigation of nanoobjects consists in analyzing computer models. In our opinion, the most promising approach to the investigation of thermodynamic properties of metallic clusters is the molecular dynamics method, which allows one

to understand the influence of particular factors on the properties of these particles at the atomic level.

Since platinum clusters are candidates for the use in different electronic nanodevices and especially catalysts,^{3–6} investigation of the properties of these particles is an important problem. With the aim of investigating the thermodynamic properties of metallic nanoparticles, we carried out a number of computer experiments with the use of the molecular dynamics method. The main objective of the molecular dynamics simulation was to determine of some thermodynamic parameters at studying of melting (crystallization) processes in platinum clusters.

2. COMPUTATIONAL METHOD

The forces acting between atoms were calculated using the modified tight-binding potentials⁷ with a fixed cutoff radius corresponding to the fifth coordination shell inclusive. These potentials have been widely used in different types of computer simulation of macroscopic materials and clusters.

The potentials proposed by Cleri and Rosato⁷ have already worked very well in the simulation of systems in the crystalline state and have been thoroughly verified to

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advantage for many parameters.⁷ In particular, the results of the simulation of a number of parameters of structural point defects (vacancies, interstices, and their small complexes), thermodynamic properties of metals (melting temperatures, transition temperatures, heat capacity, thermal expansion coefficient, Grüneisen parameter, etc.), and phonon spectra were compared with experimental data. It should be noted that the calculated phonon spectrum of face-centered cubic copper at $T = 80$ K (in Ref. [7]) differs from the experimental spectrum by no more than 5%.

In the simulation, the temperature of the system was determined from the average kinetic energy of atoms. This energy was calculated using the fast Verlet algorithm⁸ with a time step $h = 2$ fs. During the simulation, the temperature of the system was changed in steps of approximately 50 K and the clusters at each fixed temperature were held for 0.5 ns. In order to reduce the errors in the determination of the thermodynamic properties due to the side effects associated with the thermal noise, the temperature step in the crystallization (melting) range was decreased and the clusters were kept at fixed temperatures for approximately 2 ns.

The melting and crystallization points of clusters were determined from the jumps in the potential energy as a function of the temperature, which resulted in an increase in the heat capacity in a very narrow temperature range around the transition point. This approach has been rather widely used in the computer simulation of melting (crystallization) processes in metallic nanoclusters^{9,10} and makes it possible to rather accurately identify their onset. Moreover, the radial distribution functions $g(r)$, which allow one to analyze the structures of the simulated nanoparticles and to determine the character of phase transitions, were additionally calculated at different temperatures.

In the computer simulation, spherical clusters of face-centered cubic platinum produced by cutting a sphere from a perfect face-centered cubic lattice were used as initial objects. In order to accurately investigate the influence of a particular parameter on the thermodynamic properties, it is necessary first of all to minimize the interaction between the particle and the environment. In this respect, we considered the so-called “free” or isolated clusters that were placed in a thermal reservoir filled with virtual particles (a Nose thermostat¹¹ or an Andersen thermostat¹²) and did not interact with the substrate.

The processes of melting and crystallization of platinum nanoclusters were analyzed with the MDNTP program developed by Dr. Ralf Meyer (Universität Duisburg, Germany).

3. SURFACE MELTING IN PLATINUM CLUSTERS

The mechanical (hardness, plasticity) and magnetic properties, reactivity, polarizability, and some other parameters

of bulk materials differ substantially from those of nanoparticles.¹³ Moreover, the changeover from massive crystals to nanoclusters is accompanied by the change in their melting (crystallization) temperature. Investigations have revealed that the specific feature of small particles not only is a decrease in their melting temperature but also is that their melting can begin with the surface of the cluster. In particular, this was confirmed by the results of the computer simulation of melting of particles consisting of several hundreds of gold atoms.¹⁴

In experiments, the surface melting was observed rather frequently. As a clear example, this can be demonstrated using the results obtained by Kofman et al.¹⁵ who studied the surface melting of Sn particles on the SiO_2 substrate (Fig. 1). As the temperature increases, the thickness of the surface layer in the molten state (shown in white) increases and, at a limiting value, the entire cluster spontaneously transforms into the liquid state.

Our simulation also showed that the phase transition from the solid state to the liquid state begins with the surface of the platinum nanoparticle, where atoms randomly move and their distribution in the surface layer leads to the formation of an amorphous structure. The inverse process of crystallization is accompanied predominantly by the formation of primary nuclei of a new phase. These nuclei grow with a decrease in the temperature, and atoms in the majority of cases have managed to be rearranged with the formation of a specific crystalline modification.

As an example of the established regularities, we consider configuration changes in platinum clusters upon the transition between two aggregate states. The process was investigated using a spherical cluster of face-centered cubic platinum with $N = 7635$ atoms. For this purpose, the simulated system (with the averaging over a canonical ensemble) was gradually heated to the temperature $T = 2000$ K, which is considerably higher than its melting temperature ($T_m = 1500$ K), and then was cooled to room temperature. The character of atomic motion during heating

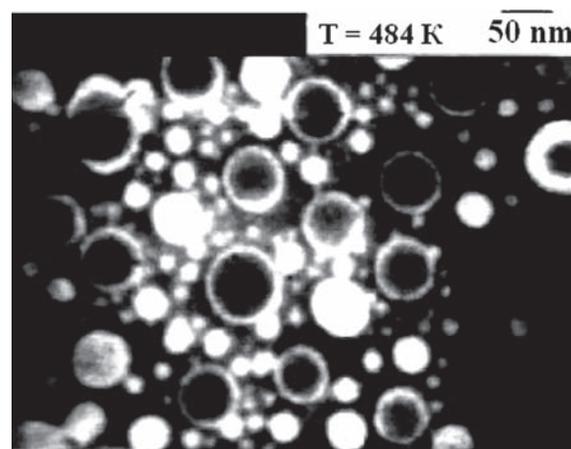


Fig. 1. Electron microscope image of tin clusters on the SiO_2 substrate.¹⁵

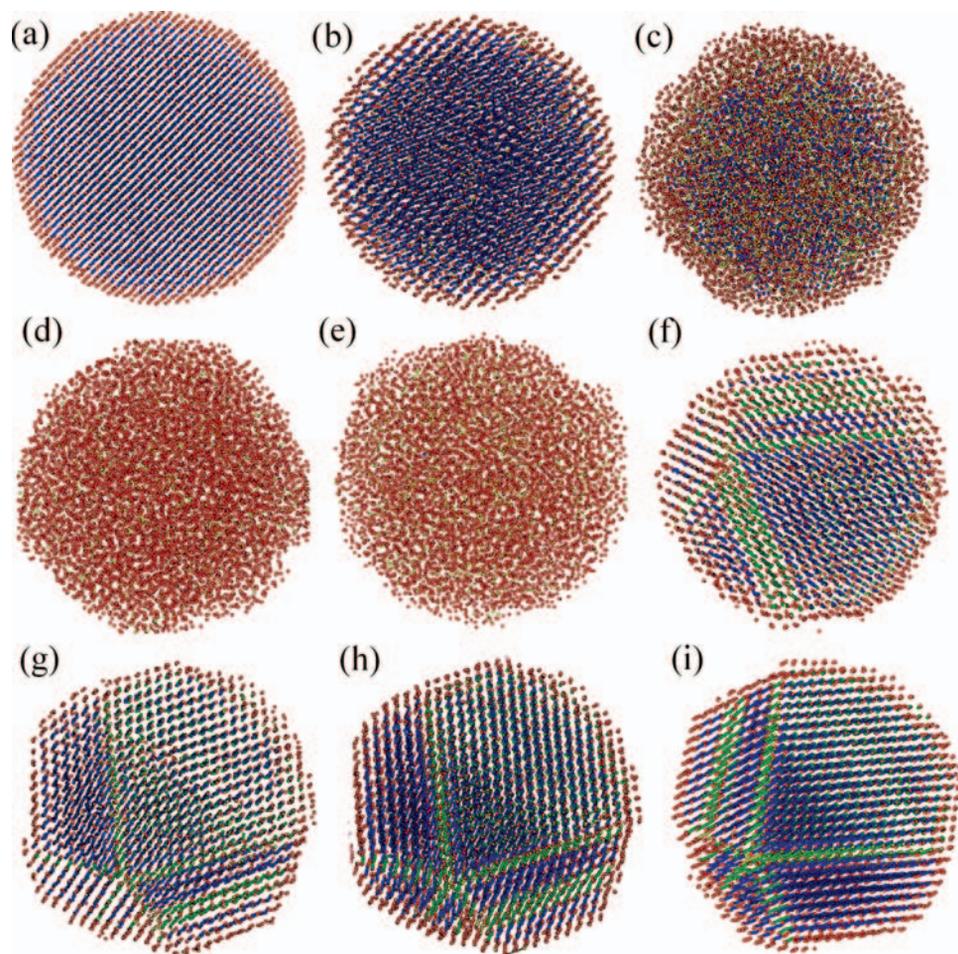


Fig. 2. Dynamics of the process of heating and cooling of the platinum nanocluster ($N = 7635$) to temperatures $T =$ (a) 300, (b) 900, (c) 1490, (d) 1500, (e) 1099, (f) 1098, (g) 900, (h) 600, and (i) 300 K.

and cooling of the platinum nanocluster with the given size (which was studied using the standard CNA analysis¹⁶) is illustrated in Figure 2. The colors of the atoms denote the result of a CNA analysis as follows: atoms drawn in blue (green) have a local crystalline fcc (hcp) environment; yellow atoms have no identified structure, however their coordination number is $Z = 12$. Atoms with coordination numbers $Z \neq 12$ are drawn in red.

The chaotic distribution of atoms in the surface of the cluster upon heating indicates that the melting of the nanocluster begins with the surface (Figs. 2(b), (c)). The isolated cluster in the vicinity of the phase transition is not a thermodynamically equilibrium system. Correspondingly beginning with a specific temperature, which is referred to as the melting temperature of a particle, the liquid state becomes thermodynamically stable and a phase transition from the solid state to the liquid state occurs (Fig. 2(d)).

The analysis of the dynamics of cooling of the platinum cluster containing 7635 atoms allows us to make the inference that the structure of this nanoparticle is formed very rapidly. A large crystalline nucleus with a spherical shape

is formed immediately below the crystallization temperature $T_c = 1098$ K (Fig. 2(f)). In this case, the formation of primary crystallization centers is not revealed. As the temperature decreases, the cluster structure takes an energetically more favorable regular shape. During cooling of the nanoparticle to room temperature, the distribution of atoms in inner layers changes insignificantly and they only execute vibrations with respect to lattice sites, whereas atoms in the surface layer are redistributed, tend to equilibrium positions, and form a rather regular decahedral structure (Fig. 2(i)).

Therefore, the results of our experiments with platinum clusters allow us to argue that the melting of nanoparticles begins with the surface, where atoms randomly move and their redistribution in the surface layer results in the formation of an amorphous structure. The cooling of the cluster from the molten state to room temperature can lead to two scenarios of the structural organization: the formation of small new-phase nuclei growing with a decrease in the temperature and the formation of a large spherical crystalline nucleus with the size increasing upon subsequent cooling of the cluster.

4. INFLUENCE OF THE SIZE ON THE SOME THERMODYNAMIC

4.1. Characteristics of the Simulated System

When the particle size becomes so small that the surface-to-volume ratio cannot be ignored, it can be expected that the influence of the surface should affect the temperature dependences of the thermodynamic functions and will lead to the effects associated with the nanoparticle size. Let us investigate more thoroughly a number of these size effects.

At the first stage, the simulation of the melting and crystallization processes is carried out within the canonical ensemble based on the interaction of the system with the Nose thermostat. Experimentally, this can be provided by placing the cluster in a chamber filled by helium or another inert gas with metal walls maintained at a specified temperature.^{17,18} Owing to the collisions of helium atoms with the walls and the cluster, the cluster temperature becomes equal to the wall temperature.¹⁹

In order to completely destroy the long-range order in the platinum clusters of different diameter ($D = 1.6 - 10$ nm), they were smoothly heated to the temperature $T = 2000$ K. Then, the clusters were gradually cooled to the temperature $T = 300$ K. The typical thermal cycle curve is depicted in Figure 3, which shows the temperature dependence of the potential energy of the platinum cluster. In the course of the computer experiment, it was revealed that, as could be expected, the melting temperature of the platinum clusters decreases substantially as compared to the melting point of a macroscopic sample. The decrease in the melting temperature is maximum (1116 K) for the cluster with $N = 141$ atoms and minimum (492 K) for the cluster with $N = 34881$ atoms. It should be noted that a very large decrease (up to several hundred degrees) in the melting temperature was also observed for Sn, Ga, and Hg clusters and CdS colloidal nanoparticles with a diameter

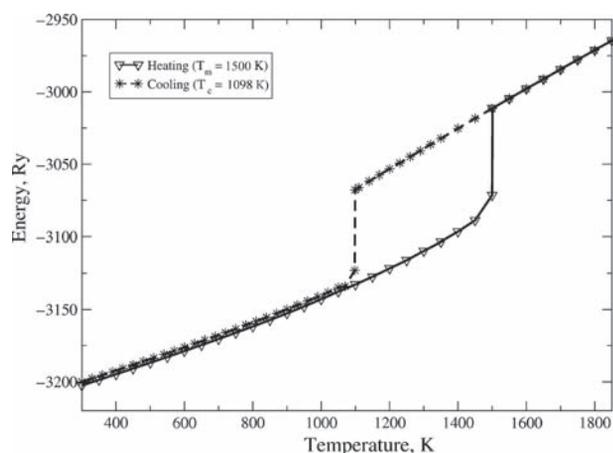


Fig. 3. Dependences of the potential energy E_p of the platinum nano-cluster on the absolute temperature in the process of melting and crystallization in terms of the NVT ensemble with $N = 7635$ atoms ($1 \text{ Ry} = 13.6054 \text{ eV}$): (∇) heating ($T_m = 1500 \text{ K}$) and ($*$) cooling ($T_c = 1098 \text{ K}$).

ranging from 2 to 8 nm in Ref. [20]; nickel nanoparticles in Ref. [9]; gold nanoclusters in Ref. [21]; and a number of other works.

It should also be noted that the size effect of the melting temperature of small particles is not only of pure scientific interest but also of practical significance. For example, in the course of soldering or sintering of powders, their particles are heated to the onset of coalescence. Finely dispersed powders require a lower soldering or sintering temperature. Moreover, a decrease in the melting temperature is important for microelectronics and nanoelectronics using miniature operating components. Therefore, the melting temperature determines the range of normal operation and stability of the corresponding components.

The experimental data obtained in this work were analyzed in the framework of some theoretical models. The formulas that describe a decrease in the melting temperature of small particles with a decrease in their size are available in the literature (see, for example, Refs. [22, 23]). These relationships, which are derived by different authors for the description of the size effect of the melting temperature $T_m(r)$ for nanocrystalline particles, can be represented in the form²²

$$T_m(r) = T_{\text{bm}} \left(1 - \frac{\alpha}{r} \right) \quad (1)$$

where T_{bm} is the melting temperature of the massive solid material, r is the radius of a small particle, and α is the constant dependent on the density and the melting heat of the material and its surface energy.

The performed molecular dynamics simulation of the melting processes in the platinum nanoclusters with radii larger than 0.8 nm revealed that the calculated data on the melting temperature deviate from a dependence $T_m(r) \propto 1/r$ following from expression (1). The linear dependence $T_m(r)$ obtained in Refs. [22, 23] is comparable to our data for the platinum clusters only with particle radii larger than 1 nm; in this case, the difference between the melting temperatures is of the order of 10–15 K.

The dependence $T_m(r)$ obtained for tin particles 4–40 nm in radius from electron diffraction data also indicates that the experimental and calculated results differ significantly. The available discrepancies were attributed by the majority of authors to the error in the determination of the melting temperature of clusters. By assuming that the melting of nanoparticles begins with the surface, the equation that most adequately describes the experimental size dependence of the melting temperature $T_m(r)$ should be more complex and account for the presence of the liquid shell.

By using the computer simulation, it is also possible to determine the jumps in the melting heat and the entropy at the melting temperature of the cluster. In order to determine the melting heat ΔH_m , we approximated the potential energy curves for the liquid and crystalline

phases and calculated their difference at the melting temperature T_m .⁹ The change in the entropy upon this transition was calculated from the relationship

$$\Delta S_m = \frac{\Delta H_m}{\hat{O}_m} \quad (2)$$

It was established that these quantities are also characterized by a similar size dependence: a decrease in the number of atoms N in the platinum nanoclusters results in a smooth decrease in the quantities under investigation.

Qi et al.⁹ attempted to justify theoretically the monotonic decrease (observed in the computer experiment) in the thermodynamic characteristics of nickel clusters with a decrease in their size. It was demonstrated that, for some characteristics, a power dependence on $N^{-1/3}$ can be a good approximation. With the aim of confirming these assumptions, we studied the behavior of the melting temperature, the melting heat, and the change in the entropy for the platinum nanoparticles as a function of $N^{-1/3}$ (Fig. 4(a)). The analysis of the dependence plotted in Figure 4(a) shows that the approach proposed in Ref. [9] leads to correct theoretical estimates of the melting temperature of small platinum particles. However, the corresponding power dependences of the quantities ΔH_m and ΔS_m on $N^{-1/3}$ are observed only for clusters with large diameters. This discrepancy between the theoretical and experimental data cannot be explained in terms of the model developed in Ref. [9].

One more important characteristic of the evolution of the properties of clusters to the properties of the bulk material is the potential energy of the nanocluster per atom E_p/N . The analysis of this quantity was carried out at room temperature, and the performed computer experiment demonstrated that the ratio E_p/N decreases considerably with an increase in the number of atoms in the nanoparticle; in this case, the effect most clearly manifests itself in the range of small clusters. Our data obtained for the form of the dependence of the potential energy per atom

E_p/N in the platinum clusters on the number of atoms in clusters with a close packing are comparable to those of other authors.^{24,25}

As is known, small metallic particles grow as a result of the attachment of new atomic shells or spheres,¹³ which leads to a smooth decrease in the potential energy per atom E_p/N . The potential energy per atom for the face-centered cubic platinum nanoparticle is maximum for the cluster with $N = 141$ atoms ($E_p/N = -0.3962$ Ry/atom) and minimum for the cluster with $N = 34881$ atoms ($E_p/N = -0.4231$ Ry/atom). An increase in the cluster surface results in an increase in the number of atoms in the shells; as a consequence, the function $E_p/N = f(N)$ becomes smoother.

The behavior of the ratio E_p/N as a function of $N^{-1/3}$ (Fig. 4(b)) was examined in the same manner as for the above quantities. It can be clearly seen from Figure 4(b) that the potential energy per atom for platinum clusters that have a face-centered cubic structure and contain several hundreds or several thousands of atoms is approximated accurate to within a few percent by the dependence on $N^{-1/3}$. A similar result was obtained by Erkoc,²⁶ who studied the dependences $E_p/N = f(N)$.

5. HYSTERESIS RANGE OF THE MELTING AND CRYSTALLIZATION TEMPERATURES

One of the purposes of the performed simulation was to determine the hysteresis ranges of the melting and crystallization temperatures of clusters. In macroscopic systems, the transition from a liquid state to a solid state and vice versa occurs at a temperature that is strictly specific for a particular compound if amorphous materials are disregarded. This temperature is referred to as the melting temperature or the crystallization temperature depending on whether the heating or cooling of the system occurs.

In the case of nanoparticles, a similar behavior is observed upon melting (crystallization), except that a step

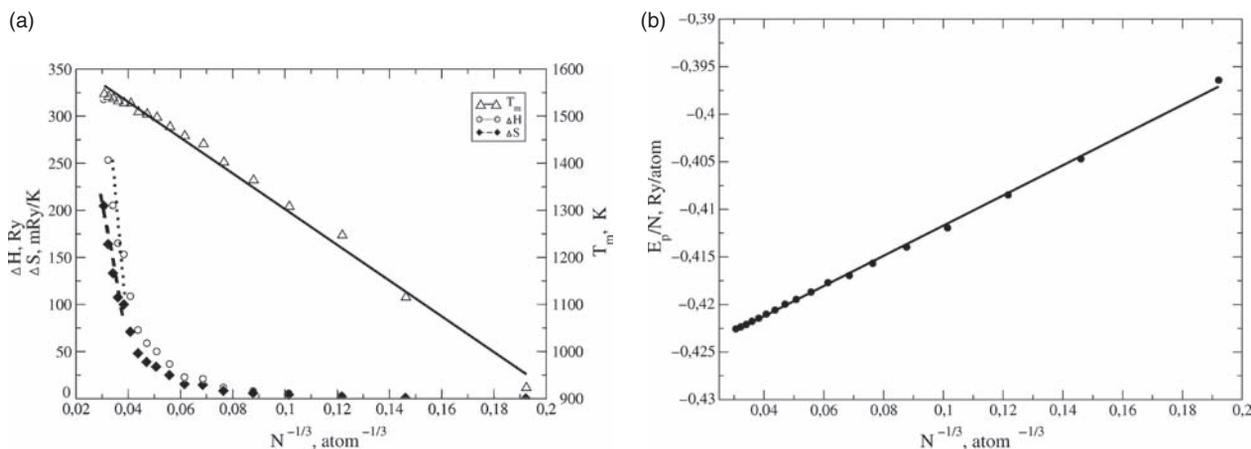


Fig. 4. (a) Dependences of (Δ) the melting temperature, (\circ) the melting heat, (\blacklozenge) the change in entropy on $N^{-1/3}$ for platinum clusters. (b) Dependences of the potential energy per atom E_p/N on $N^{-1/3}$ for platinum clusters.

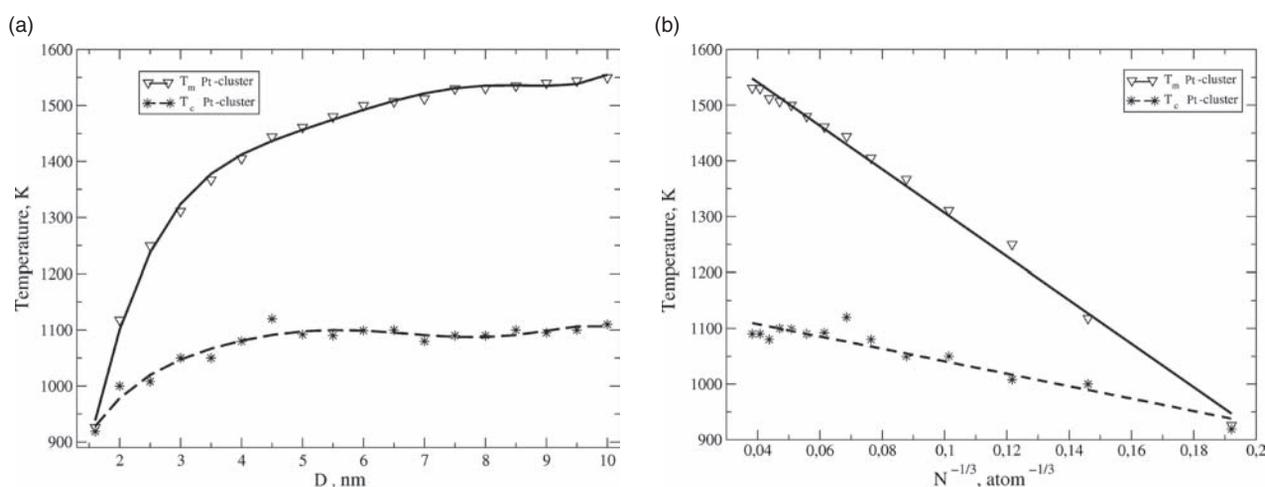


Fig. 5. (a) Dependences of (∇) the melting temperature and ($*$) the crystallization temperature on the diameter D for platinum nanoclusters. (b) Dependences of (∇) the melting temperature and ($*$) the crystallization temperature on $N^{-1/3}$ for platinum nanoclusters.

change in physical characteristics at one strictly fixed temperature is absent. The transition from the liquid state to the solid state and vice versa proceeds in a certain temperature range with a finite nonzero width (Fig. 3). This range is termed the hysteresis range. The hysteresis range is bounded by two temperatures, which are also called the melting and crystallization temperatures; however, these temperatures for clusters are not equal to each other.

One of the important observations that can result from analyzing this range is that, owing to the surface melting, the cluster can be partially in both the solid and liquid states. It should be noted that the transition from the liquid state to the solid state in a finite temperature range was observed in direct experiments with free clusters by Bertsch²⁷ and Schmidt et al.^{17,18} in the studies of sodium clusters consisting of 139 atoms. Furthermore, similar results were obtained by Lai et al.²⁸ in calorimetric investigations of zinc nanoparticles located on substrates.

It is evident that the width of the temperature hysteresis range should depend on the number of atoms in the nanoparticle. As the cluster size N increases, the thermodynamic behavior of the cluster approaches the behavior of macroscopic systems. Therefore, the hysteresis range should become progressively narrower, and the potential energy should increase more steeply, so that the behavior characteristic of macroscopic systems should be observed in the limiting case at $N \rightarrow \infty$.

The analysis of the results of the simulation of the melting and crystallization processes in the platinum nanoclusters indicates that the situation is not so unambiguous. Indeed, with an increase in the particle size, the jump in the potential energy upon the phase transition in the cluster becomes progressively steeper, but the width of the hysteresis range varies in a more complex manner. The dependences of the melting and crystallization temperatures on the diameter of the platinum cluster are plotted in Figure 5(a). It can be clearly seen from this figure that the

melting and crystallization temperatures of the simulated clusters differ from each other and that the width of the hysteresis range smoothly increases with an increase in the cluster diameter up to at least 10 nm.

The available experimental data on the width of the hysteresis range $\Delta T = T_m - T_c$ for the clusters should be compared with the aforementioned models; i.e., it is necessary to evaluate the dependence of the quantity ΔT on $N^{-1/3}$ (Fig. 5(b)). It can be seen from Figure 5(b) that, like the melting temperature of the clusters, the crystallization temperature also satisfies the corresponding dependence. The performed evaluation contradicts the results obtained by Davis et al.²⁹ who showed that an increase in the number of atoms in clusters should lead to a decrease in the temperature hysteresis range. However, Skripov and Koverda³⁰ theoretically predicted that the melting and crystallization lines should converge at one point for spherical metallic particles with a radius $R \approx 0.8\text{--}1.0$ nm. An increase in the particle size should lead to an increase in the width of the hysteresis of the transition from the liquid phase to the crystalline phase. However, the hysteresis width should sharply decrease as the thermodynamic limit is approached

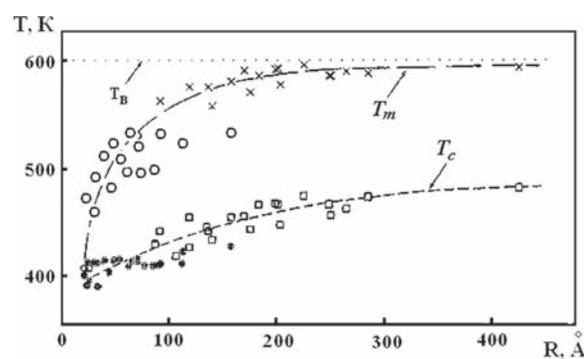


Fig. 6. Dependences of the melting temperature T_m and the crystallization temperature T_c on the radius of lead clusters.¹⁵

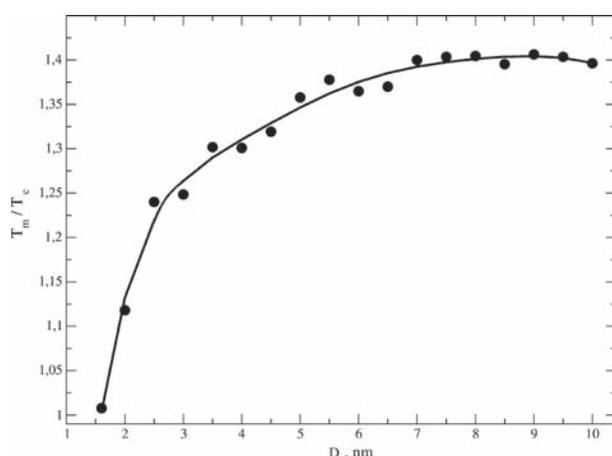


Fig. 7. Dependence of the ratio T_m/T_c on the diameter D of platinum nanoparticles.

and, eventually, the hysteresis range should transform into a point. This theoretical conclusion is confirmed by the experimental dependence shown in Figure 6. It can be seen from this figure that our results and the theoretical predictions by Skripov and Koverda are supported by the direct experimental data.

It is also of interest to analyze the dependence of the ratio T_m/T_c on the number of atoms N in the nanoparticle. It is clear that the ratio $T_m/T_c = 1$ should hold for a macroscopic system with an infinite number of atoms. Figure 7 shows the dependence of the ratio T_m/T_c on the size of the platinum nanoclusters. As can be seen from Figure 7, there is a tendency toward a decrease in the rate of increase in the ratio T_m/T_c with an increase in the cluster radius. It can also be seen that the ratio T_m/T_c reaches a maximum at a particular number of atoms in the nanoparticle and then decreases smoothly. Thus, the analysis of the thermodynamic quantities upon the phase transition provides a deeper insight into the nature of the phenomenon.

6. CONCLUSIONS

The investigation of the physical properties of metallic nanoparticles with characteristic nanometer sizes is an important problem from both fundamental and applied viewpoints due to the wide prospects for their practical applications. However, the main problem of the introduction of nanotechnologies into the industry is associated not with the preparation of new materials but with the influence of thermal effects and force (radiation, deformation, etc.) fields during the operation of nanomaterials, which necessarily leads to recrystallization, relaxation, segregation, and homogenization processes, as well as to decomposition phenomena, phase transformations, sintering and closing of nanopores (nanocapillaries), amorphization, and crystallization. All these factors should affect physicochemical, physicomachanical, and other properties and, hence, the performance characteristics of nanomaterials.

The analysis performed in the present work with due regard for the established experimental facts makes it possible to generalize the aforementioned inferences and to describe in detail the melting (crystallization) process in platinum nanoclusters.

APPENDIX

Influence of the diameter of platinum nanoclusters on the melting and crystallization temperature and some thermodynamic properties.

Diameter d (nm)	Number of atoms	Melting temperature T_m (K)	Crystallization		ΔH (Ry)	ΔS (mRy/K)
			temperature T_c (K)	ΔT (K)		
1.6	141	926	919	7	0.331	0.357
2.0	321	1118	1000	118	1.075	0.961
2.5	555	1250	1008	242	2.843	2.274
3.0	959	1311	1050	261	5.686	4.337
3.5	1481	1367	1057	310	8.129	5.946
4.0	2243	1405	1080	325	12.009	8.548
4.5	3103	1444	1120	324	21.109	14.618
5.0	4321	1461	1092	369	22.575	15.452
5.5	5775	1480	1090	390	36.809	24.871
6.0	7635	1500	1098	402	50.044	33.363
6.5	9597	1507	1100	407	58.809	39.024
7.0	11993	1512	1080	432	73.012	48.289
7.5	14771	1530	1090	440	108.841	71.138
8.0	17861	1531	1090	441	153.350	100.163
8.5	21457	1535	1100	435	165.143	107.590
9.0	25267	1540	1095	445	205.377	133.361
9.5	29797	1544	1100	444	253.550	164.222
10.0	34881	1550	1110	440	317.578	204.891

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