



Evaluation of the Heat Capacity of Compactified and Nanostructured Metals Exemplified on Palladium Nanoclusters

Yu. Ya. Gafner^{1,*}, S. L. Gafner¹, L. V. Redel¹, I. S. Zamulin¹, and V. M. Samsonov²

¹Katanov Khakas State University, Abakan, 655017, Russia

²Tver State University, Tver, 170002, Russia

Using molecular dynamics method and several different tight-binding potentials, the heat capacity of fcc palladium clusters of 6 nm in diameter has been investigated in the temperature range from 150 to 300 K. We have concluded from the results of our computer simulations that the heat capacity in the case of isolated free clusters can exceed that of a bulk material. At 150 K the values obtained for palladium nanoparticles exceed those of the corresponding bulk material by 12–16%. It was also found that the difference in question becomes less noticeable under growing the temperature. So, at 300 K the isobaric heat capacity of nanocrystalline palladium was only by 4–5% higher in comparison with the bulk phase. Consequently, the large heat capacities of palladium nanostructures observed in some real experiments cannot be related to the characteristics of free clusters. We hypothesize that these properties of a nanomaterial depend on the degree of agglomeration of its constituent particles, i.e., the surfaces and interphase boundaries of interconnected nanoclusters can have a strong effect. To test this hypothesis, we took metallic clusters of various sizes produced through the simulation of condensation from the gas phase. At high temperatures, we failed to adequately assess the role of the interphase boundaries in calculating the heat capacity of nanoparticles. The reason was the mass diffusion of atoms to impart an energetically more favorable shape and structure to the synthesized clusters. To explain the disagreement of our results with the available experimental data on compactified palladium, additional investigations were carried out on palladium sample with the density corresponding to 80% of the bulk value. The possible role of hydrogen in the increase of the heat capacity observed for compacted palladium has been estimated. The conclusion, that the results, which are in satisfactory agreement with the experimental data, were obtained only when the concentration of hydrogen atoms accounted for approximately 50% of the concentration of palladium atoms has been drawn. In all probability, the nature of so significant overestimation of the heat capacity of compactified nanomaterials relates both to their disordered state and, to some extent, to noticeable content of different dopes, mainly of hydrogen.

Keywords: Molecular-Dynamics Simulations, Tight-Binding, Platinum Nanoclusters, Heat Capacity.

1. INTRODUCTION

Current, advances in new constructional and functional materials are associated, first of all, with the development of the production of compactified nanomaterials. In particular, practical applications of nanocrystalline metals and their various compounds have been stimulating intensive studies of their mechanical, thermal, electrical, magnetic and other properties. For theoretical interpretation of experimental data obtained on compactified

nanomaterials, it is, first of all, necessary to separate surface effects and those relating to small volume of particles the nanomaterial consists of Ref. [1]. The problem is far of its solution as studying compactified nanomaterials is yet at its prior stage of the result collection.

It is well-known that just the developed surface of separate nanoparticles gives high contributions into their physical-chemical properties and, as a consequence, into size effects on thermodynamic quantities. At low temperatures the main mechanism of the changing of thermodynamic characteristics of nanoparticles in comparison with

* Author to whom correspondence should be addressed.

the bulk phase is a variation in the form of the phonon spectrum. Thus, in the phonon spectrum of nanoparticles the lower-frequency modes arise not observed in corresponding spectra of crystalline bodies.² As a result, specific features of the vibrational spectrum of nanoparticles will be reflected, first of all, in their heat capacity.

The heat capacity, being one of the main thermodynamic properties of nanomaterials, must be investigated in view of the production and application of such materials. However, up to the present time, the behaviour of the specific heat capacity of nanoparticles (nanoclusters) and nanostructured materials is an important and not solved yet problem. With enough confidence, one can only talk about the case of very low temperatures. Thus, theoretical estimations show that at temperatures $T \rightarrow 0$ K the cluster heat capacity decreases faster than that of the corresponding bulk material because of quantum effects. The temperature interval in which the lattice vibrations may be treated on the basis of quantum considerations is determined by the degeneracy temperature of order of 10 K.³

When the temperature is higher than that of the degeneracy, the heat capacity of the cluster begins to exceed the thermal capacity of the corresponding bulk material and the effect in question has been confirmed experimentally. Thus, measurements of the heat capacity of lead nanoparticles of 2.2, 3.7 and 6.6 nm in diameter D as well as of indium ones have shown that at low temperatures it is by 25–75% higher than that of the same bulk metals.^{4,5} Cosma et al.⁶ presented results on the specific heat capacity of palladium nanoparticles of 3.0 and 6.6 nm in diameter, obtained by the condensation of vapour. According to their paper, the doubled increase in the heat capacity of Pd nanoparticles ($D = 3.0$ nm) was observed compared to the bulk Pd at temperatures up to 30 K. Even greater increase in the heat capacity (3–10 times as compared to the tabulated value) was found for gold ($D = 4, 6$ and 18 nm) and silver ($D = 10$ nm) nanoparticles.⁷

However, most experimental studies of the heat capacity were carried out using not separate (free) clusters but some compactified nanomaterials prepared by one of the available technologies. Probably, just because of different ways of the sample processing and specific features of its structure, the available experiments give significantly differing values of the heat capacity. At the same time, all the works show some excess in the heat capacity for nanostructured materials as compared to the bulk bodies, but the values of such an increase vary greatly enough.

Not better things are with estimations of the specific heat capacity for clusters and nanostructured materials at high temperatures. Thus, the heat capacity of coarse-grained copper clusters of about 50 nm in size has been found to be 1.2–2.0 times higher than the normal heat capacity of the bulk copper in the temperature range from 200 to 450 K.⁸ Similar results were obtained for nickel nanoparticles of 22 nm in diameter: their heat capacity

was twice higher than that of the bulk Ni at temperatures 300–800 K.⁹ A study of the heat capacity of nanostructures consisting of Ni clusters of 10 nm in diameter by the fast neutron scattering method also demonstrated that their heat capacity was 1.5–2.0 times as high as that of the conventional material.¹⁰ However, for nanocrystalline Pd ($D = 6$ nm) and Cu ($D = 8$ nm) in the temperature range 150–300 K, the heat capacity increasing effect was much smaller: 29–53% and 9–11%, respectively, compared to the conventional values for the same polycrystalline metals.¹¹

To sum up, obvious discrepancies take place in experimental data on the heat capacity of the compactified metallic nanomaterials. And it is noteworthy that all the cases in question relate just to the high-temperature region where quantum effects should not be developed.

2. COMPUTER SIMULATIONS

Taking into account the mentioned above significant scatter in values of the heat capacity of nanoclusters and nanostructured materials, the heat capacity of ideal separate Ni and Cu nanoparticles was investigated in our former works^{12–15} in the temperature range 200–800 K. It was found that at $T = 200$ K the increase in the heat capacity of Cu nanocluster ($D = 6$ nm) was only 10%, and 13% for Ni nanoclusters of the same diameter. The results in question were obtained using molecular dynamics method and a modified tight-binding potential (TB-SMA) proposed by Cleri and Rosato.¹⁶

The behaviour of the specific heat capacity of metallic nanoclusters (gold, copper and aluminium) was also investigated¹⁷ on the basis of Monte Carlo, i.e., an alternative method of simulation, using another multiparticle potential (Gupta's one). When the nanocluster size was of the order of 1.0 nm, the effect on the specific heat capacity increasing was 30–40% that is in a qualitative agreement with the results of our molecular dynamics experiments.¹² It should be, however, noted that in the above Monte-Carlo experiments the temperature range corresponded to a vicinity of the melting point that, no doubt, affected the estimated values of the heat capacity.

We supposed^{14,15} that experimentally observed significant overestimations of the heat capacity of nanostructured materials can be associated with the degree of agglomeration of its constituent particles, i.e., of interfacial boundaries, and the increase in the root mean square displacements of atoms on the common surface of the interconnected nanoclusters can induce a strong effect. Thus, the increase in the heat capacity of nanostructures can be significantly affected by low frequency atomic vibrations appearing with increasing amplitudes attributable to the increased surface of the agglomerated clusters and to the interfacial boundaries in nanostructures. To test the above hypothesis, we took Ni and Cu clusters of various sizes (4000–7200 atoms) produced in the

course of the simulation of their synthesis. We chose the method of condensation from the gas phase because this way plays an important role in the industrial production of metallic nanomaterials, and, in particular, of superfine grained materials.

But, in our molecular dynamics experiments at high temperatures using TB-SMA potential, we failed to properly explain the role of the interfacial boundaries in the heat capacity of nanoparticles. The problem was in the mass diffusion of Ni and Cu atoms to provide some energetically more favourable shape and structure of the cluster. At low temperatures, the heat capacity of real clusters exceeded that of clusters with the ideal shape and structure by 3.2–10.6%. In this case, such a difference in the heat capacity could not be associated with the difference in the numbers of surface atoms and atoms belonging to the interfacial boundaries. The assumption that the cluster with the greatest difference in the heat capacity relative to the ideal nanoparticle should simultaneously be most extended spatially appears to be more plausible. Probably, the large linear size of the cluster allows the low frequency part of its phononic spectrum to manifest itself by reducing the mean vibration frequency which can lead to an increase in the cluster heat capacity.

The analysis of available publications makes it possible to conclude that experimental studies of the heat capacity of compactified nanomaterials are limited by a few works in the form of short communications which do not elucidate the nature of the observed phenomenon. Most striking seem to be experimental evaluations of the heat capacity of nanocrystalline Cu ($D = 8$ nm) and Pd ($D = 6$ nm) in the temperature range 150–300 K.¹¹ According to these authors, the heat capacity of nanosamples is by 29–53% higher than that of the usual polycrystalline Pd. At the same time, under similar experimental conditions, the heat capacity of the nanocrystalline Cu exceeded that of the polycrystalline metal by 9–11% only. However, from general and reasonable theoretical considerations, one can expect that excesses in the heat capacity of separate nanoparticles should be commensurable for all the metals, i.e., should not differ by almost 5 times! Rupp and Birringer¹¹ suggested that the more noticeable size effect (in comparison with that for Cu nanoparticles) is due to an agglomeration, i.e., to a peculiar structure of interfaces between individual nanoparticles. However, up to the present time, this explanation seems us to be improbable as it is already established that the structure of grain boundaries in compactified nanomaterials slightly enough differs from that of corresponding crystallites.¹

Available data of other authors demonstrate even higher increasing the heat capacity of compactified nanomaterials relative to polycrystalline samples without any explanation of such an effect. A proposition was only made that the excess in the heat capacity can be explained by some impurities, first of all by hydrogen. Thus, studying

the heat capacity of nanocrystalline Pd, a conclusion was made that at temperatures comparable with the room ones the main term of the excess heat capacity of compactified nanomaterials may be caused by an excitation of hydrogen atoms which often dope nanomaterials obtained by condensation of nanoclusters in noble gases with the following compactification.¹

In accordance with mentioned above, to prove earlier experimental evaluations by Rupp and Birringer,¹¹ a detailed analysis of the heat capacity of Pd nanoclusters was carried out. The choice of Pd may be justified by the fact that our computer simulation results obtained for Cu nanoparticles ($D = 8$ nm) at $T = 200$ – 300 K coincide with experimental values obtained by Rupp and Birringer¹¹ within the error of 2–3%. The main goal of the present work was both to evaluate the maximally possible increasing of the cluster heat capacity relative to the bulk sample and to reveal the role of some specific features of real experiments on compactified nanocrystalline Pd. Besides, possible nature of so significant difference between the heat capacities of Cu and Pd nanoclusters found in the same experimental work was also of interest.

At computer molecular dynamics simulations, we used the MDNTP computer code developed by Dr. Ralf Meyer (Universität Duisburg, Germany). The computations were performed on a SunFire 4150 server based on two 4-core 64-bit Intel Xeon processor with the clock frequency 3.2 GHz (the operating medium was Linux SuSE version 11.2).

3. APPROBATION OF THE MULTIPARTICLE POTENTIAL

As the simulations were carried out using an interatomic interaction potential, the results directly depend on the choice of the potential. After analysis of different forms of the functional presentation of the potential energy, we have chosen the modified tight-binding potential TB-SMA¹⁶ with the fixed cut-off radius corresponding to the 5-th coordination sphere, inclusively, for following calculations of interatomic forces.

The potentials proposed by Cleri and Rosato¹⁶ have demonstrated the advantage in simulating polycrystalline systems and passed through comprehensive tests in many parameters. In particular, the simulation results were compared to the experimentally determined parameters of point defects, some thermodynamic properties of bulk metals, and their phononic spectra. However, despite the fact that the potentials of Cleri and Rosato¹⁶ are often used to simulate nanoclusters of various metals, their applicability is not indisputable. Therefore, we first analysed the ability of the potentials in question to describe single nanoparticles qualitatively and quantitatively.

Unfortunately, in the available literature there are no data on thermodynamic characteristics of Pd nanoclusters.

For this reason, the calculating scheme was tested, first of all, on nanoclusters of Ni, Cu and Au. To our mind, the analysis of thermodynamic properties of clusters of these metals can help to value appropriateness of the potentials usage¹⁶ and in case of palladium, as according to error estimates¹⁶ in the determination of physical characteristics of palladium do not exceed such for Ni, Cu and Au.

One of the most important characteristics of the cluster is its specific potential energy, i.e., the potential energy per atom E_p/N (N is the number of atoms the cluster consists of). Our computer experiments demonstrated that E_p/N decreases significantly with increasing the number of atoms in the nanoparticle and the effect was most pronounced in small clusters. Such behaviour agrees qualitatively with the available experimental and theoretical data.^{18–20} For a qualitative comparison, we present here the data on Ni obtained by molecular dynamics simulation using a modified EAM potential.²⁰ The difference in the parameter in question does not exceed 5.4%. But as the cluster size increases, this difference decreases. In particular at $N = 201$ the difference is 5.38%, and 3.13% at $N = 1505$. Even better agreement with the results of simulation based on other multiparticle potentials^{21,22} was achieved for gold nanoclusters. The difference from the results of these works was only about 3% for sufficiently small clusters ($N = 555$).

The second parameter, chosen to test the potential under consideration, is the melting temperature. To determine this cluster characteristics, the simulation was carried out in frames of the canonical ensemble (Nose's thermostat) that made it possible to provide exactly enough control of the temperature of Ni particles of 1.38–6.0 nm in diameter. An analogous MD simulation of size dependences of the melting and crystallization temperature of Ni nanoclusters was carried out by Qi et al.²³ To calculate the interatomic potential they used the multiparticle Satten-Chen force field. Comparing our data and the results by Qi et al.,²³ one can conclude that the divergence in measurements of the melting temperatures of Ni nanoparticles using two different force fields is about 7%.

In the course of computer experiments, it was revealed that, as could be expected, the melting temperature of copper clusters decreased substantially as compared to the melting point of the macroscopic sample (Fig. 1). It should be also noted that a very large decrease (up to several hundred K) in the melting temperature was also observed by Morokhov et al.²⁴ and Goldstein et al.²⁵ for Sn, Ga, and Hg clusters as well as for colloidal CdS nanoparticles with the diameter ranging from 2 to 8 nm.

Experimental data for the melting temperature obtained in this work were also analysed in the framework of some theoretical models. The formulas that describe a decrease in the melting temperature of small particles with the decrease in their size are available in literature.^{25–27} Some of these relationships derived by different authors

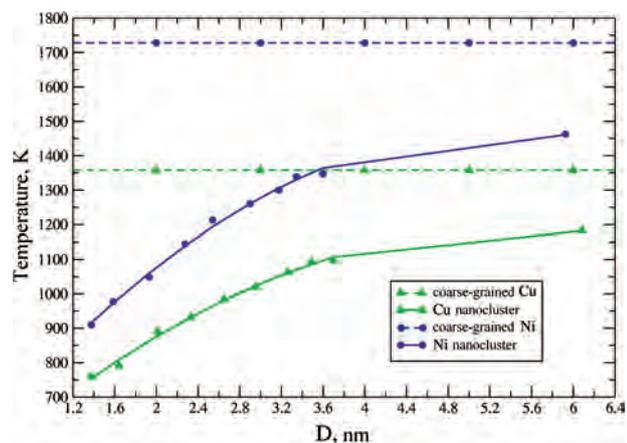


Fig. 1. Dependence of the melting temperature of Cu and Ni nanoclusters on their diameter.

to describe the size effect of the melting temperature of nanocrystalline particles, can be represented in the form Ref. [3]

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

where T_{mb} is the melting temperature of the bulk solid material, r is the particle radius, and α is a constant depending on the density, the melting heat of the material and its surface energy.

The performed molecular dynamics simulations of the melting processes in Ni, Cu and Au nanoclusters with radii larger than 0.7 nm revealed that the calculated data on the melting temperature deviated from the $T_m(r) \sim 1/r$ dependence corresponding to formula (1). The linear dependence $T_m(r^{-1})$ obtained earlier^{26,27} is comparable to our data for Ni, Cu and Au clusters only for particle radii larger than 1 nm; in this case, the difference between the melting temperatures is about 10–15 K.

The dependence $T_m(r)$ obtained for Sn particles of 4–40 nm in radius from the electron diffraction data²⁶ also indicated that the experimental and calculated results differed significantly. The discrepancies in question were attributed by the majority of authors to the error in the determination of the melting temperature of clusters. Assuming that the melting of nanoparticles begins on the surface, the equation that most adequately describes the experimental size dependence of the melting temperature $T_m(r)$ should be more complex to account for the presence of the liquid shell.

On the whole, when analysing the results of various authors, we conclude that the Cleri-Rosato¹⁶ potentials satisfactorily describe the behaviour of a number of thermodynamic quantities of metallic fcc clusters on both qualitative and quantitative levels. The differences between the simulation results and the data obtained by other multiparticle potentials do not exceed 3–5%.^{28,29}

4. SIMULATION RESULTS

To carry out computer simulation of the heat capacity, a spherical Pd cluster of 6 nm in diameter with the ideal fcc structure was chosen as the initial configuration. To avoid possible error caused by an inadequate presentation of the potential energy of interatomic interaction, three different potentials were approximated^{16,30,31} belonging, however, to the same group of TB potentials with different cut-off radii: from 2-nd to 5-th coordination spheres, inclusively. The obtained averaged results are presented in Figure 2 in comparison with experimental data.¹¹ Figure 2 demonstrates a significant divergence between the evaluations by Rupp and Birringer¹¹ and our simulation results. Thus, at $T = 150$ K in spite on using different potentials, our calculations of the excess in the heat capacity of Pd nanoclusters give only 10–16% whereas of estimations by Rupp and Birringer¹¹ gave the quantify of 29%.

While the temperature is growing up to 200 K, the divergence under consideration becomes more significant. However, practically 40% growth of the heat capacity, proclaimed by Rupp and Birringer¹¹ just for this temperature, disagrees with the 6–8% growth found via MD simulations, and such a trend keeps up to $T = 300$ K: Then, 53% increase in the nanocrystalline Pd heat capacity was fixed by Rupp and Birringer¹¹ whereas our estimations give only 4–5%. The above a discrepancy with our simulation results looks rather curious as our analogous analysis of the heat capacity of Cu nanoclusters of 8 nm in diameter¹² gave practically the same results as those by Rupp and Birringer.¹¹

Let us try to reveal the nature of so significant disagreement. In this connection, it is worth to mention that the sample of the compactified Pd prepared for experiments had much lower density than the corresponding pore-less polycrystalline metal. Really, for Pd samples the density

was 80% of the theoretical one whereas the density of the nanocrystalline Cu was much higher, i.e., of order of 90–95% in comparison with the conventional polycrystalline material.

It is well known that the density of nanocrystalline materials, obtained by different methods of the powder compactification, was found to be from 70–80% to 90–95% of the theoretical density. In the simplest case, the nanocrystalline materials, including compactified material, consist of one sort of atoms, containing, at the same time, two components differing by the structure, i.e., the crystalline nanograins and the grain boundaries which are from 0.4 to 1.0 nm in width.¹ The X-ray and neutron diffraction analyses of compactified Pd showed that the density of the grain boundaries is by 20–40% lower than that of the ordinary Pd because of vacancies and vacancy agglomerates.

Besides, the time period after compactifying the sample is also of principle. It was shown³² that in Pd samples investigated later than in 10 days after the compactification, 8–14% of all atoms did not locate in the lattice points, and the degree of the short-range translational order was very low. In other words, just after production of the compactified sample, the grain boundaries in nanocrystalline Pd are in a non-equilibrium state with the low short-range order. Such a state is unstable, and for several months the sample undergoes the transition into a more ordered state with a different heat capacity.

To reproduce the effect of the lower density of the compactified sample, the heat capacity was studied of Pd nanoclusters containing by 20% atoms less than those in the prior experiments on nanoparticles of the same size ($D = 6$ nm). In other words, each 5-th Pd atom was randomly replaced by the vacancy (Fig. 3(a)), and the obtained system was heated up in the temperature range 150–300 K. However, similar to our former work,^{14,15} we could not adequately estimate the effect of the lower density of the sample on its heat capacity. The origin of such a failure was the mass diffusion of Pd atoms provoking the cluster to acquire an energetically more favourable structure. Such a rearrangement of the internal atomic configuration was observed even at $T = 150$ K with a peak at 300 K (Fig. 3(b)). As a result, at $T = 150$ K the maximal increase in the heat capacity of the simulated sample over the heat capacity of the macroscopic Pd was only 10%.

No doubt, these vacancies in nanoclusters appear to be unstable from thermodynamic point of view, beginning to be displaced towards the surface. On the one hand, such a vacancy migration takes significant energy expenditure that affects the value of the heat capacity. On the other hand, the reduced density of the sample releases the rearrangement of the internal structure of the particle in the direction of the energy reduction that, in turn, can in some cases result in the formation of a structure with the pentagonal symmetry not observed in macroscopic bodies. These processes are also associated with expenditures

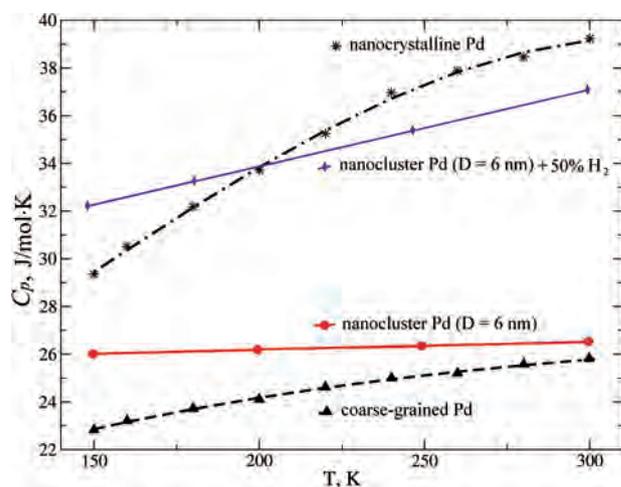


Fig. 2. Comparison of the averaged data of the molecular dynamics simulation of the temperature dependence of the heat capacity of Pd nanoclusters ($D = 6$ nm) with the experimental data for coarse-grained and nanocrystalline Pd samples.¹⁰

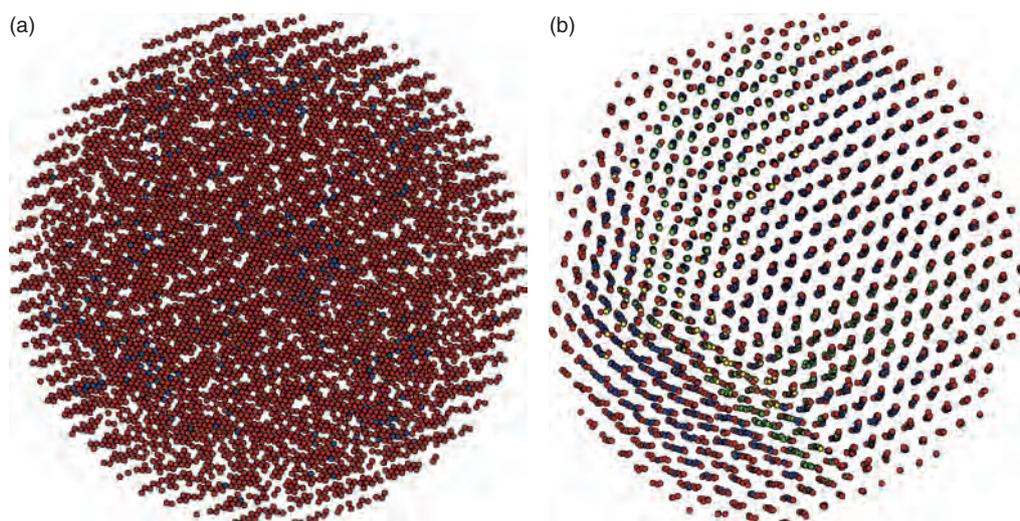


Fig. 3. Pd cluster ($D = 6$ nm): (a) the initial fcc configuration with 20% of vacancies (b) Pd cluster ($D = 6$ nm): the cluster at $T = 300$ K.

of the energy and, as a consequence, can affect the heat capacity.

In our sight, one of the main reasons of the discrepancy of our simulation results and evaluations of the heat capacity by Rupp and Birringer¹¹ may be in different methods of its definition. Really, in computer analysis, the heat capacity is found as a derivative of the cluster internal energy with respect to the temperature,²³ that gives information just on the thermal behaviour of the cluster, whereas in the course of the experimental research the relation is calculated between the heat absorbed by the compactified sample and the change in its temperature. The experimental unit used by Rupp and Birringer¹¹ was tested on polycrystalline samples of Cu for which both approaches gave identical results because of the high density of the compactified sample that makes it practically impossible to rearrange the internal structure of the nanoparticle in the chosen temperature interval.

However, in the case of Pd the things were much more complicated. Really, the Pd sample was much less consolidated, and the absorbed heat was expended, in accordance with the first law of thermodynamics, not only to increase its internal energy but also to rearrange the internal structure. In view of this fact, the heat absorption resulted in a small enough increase in the temperature. Rupp and Birringer¹¹ interpreted observed temperature increment as a significant growth of the heat capacity. If our hypothesis was assumed, it becomes clear why, according to these authors, the excess heat capacity of the nanocrystalline Cu did not practically depend on the temperature whereas for Pd the significant growth from 29 to 53% was found under the temperature increasing in the range from 150 to 300 K.

In accordance with our simulation results, the rearrangement of the internal structure of Pd nanocluster occurs in the whole mentioned above temperature interval being most intensive just at $T = 300$ K that explains so significant growth of the heat capacity observed by Rupp and

Birringer.¹¹ Thus, it is apparently that just decreasing the density of the nanostructured Pd causes significant increasing the heat capacity relative to the polycrystalline Pd. In all probability, the high excess in the heat capacity over that of bulk samples found in many experimental works is totally unclear from theoretical point of view, being in many cases a direct consequence of intensive processes of thermal atomic motion in the samples under investigation.

On the basis of our simulation results and the available experimental data, a final conclusion can be made that the growth of the heat capacity of compactified nanomaterial is not defined by the higher heat capacity of separate structural units, i.e., clusters the material consists of. In turn, the heat capacity of separate metallic nanoclusters may exceed that of the bulk phase but the excess in question cannot be higher than 16–20% even in the case of very small clusters. Presumably, the nature of much higher values of the heat capacity for compactified nanomaterials may be in both their disordered state and, to a greater or lesser extent, significant content of different dopes, first of all, hydrogen. Really, higher solubility of hydrogen in grain boundaries of the nanostructured Pd was mentioned earlier.^{33,34} According to Eastmen et al.³⁵ hydrogen dissolves, first of all, not in grain boundaries but directly in Pd grains. In spite on some divergence between the above results, Mutschele and Kirchheim,³³ Stuhr et al.³⁴ as well as Eastmen et al.³⁵ agree that a significant amount of hydrogen can be present in the compactified Pd.

Our point of view is confirmed by a known experimental fact practically not noticed before in literature: it was shown³⁵ that after prior annealing a compactified Pd sample up to 750 K, its heat capacity demonstrated only 5% growth at $T = 300$ K instead of the initial excesses of 40% at the first stage of the experiment in question. And 5% growth does completely agree with our estimation (6–8% in dependence on the used potential). So, the nature of the sharp fall of the heat capacity may relate

to a final rearrangement of the internal structure of the nanocrystalline sample at high temperatures as well as to the evolution of hydrogen from it.

Let us evaluate the possible role of hydrogen in the increase of the heat capacity observed for compacted palladium in Ref. [11]. The evaluation was carried out using theoretical data on the heat capacity of molecular hydrogen with allowance made for the increase of its value in the temperature range from $1.5R$ to $2.5R$ (where $R = 8.31$ J/mol K is the molar gas constant). Even under the condition that all the hydrogen dissolved in compacted palladium passed into the molecular form, the results, which are in satisfactory agreement with the data reported in Ref. [11], were obtained only when the concentration of hydrogen atoms accounted for approximately 50% of the concentration of palladium atoms (Fig. 2). Such a high concentration of hydrogen in the palladium sample obtained by compaction is, in principle, possible. In particular, it was found in Ref. [35] that the concentration of hydrogen atoms in the palladium nanosample was approximately equal to 52.4%. The density of this sample also accounted for approximately 80% of the theoretical density of the bulk metal. However, in order to achieve such a high hydrogen concentration, the sample was preliminarily prepared in a special way, namely, it was kept for a day in a pure hydrogen atmosphere at room temperature under a gas pressure of 6–10 kPa.

As follows from the data presented in Ref. [11], it is unlikely that the nanocrystalline palladium sample used in determining the heat capacity was subjected to a similar procedure. Because of the specific features in the processes of synthesis and interaction with the environment, this sample can actually contain a particular amount of hydrogen, but this amount of the gas impurity cannot increase the heat capacity of nanocrystalline palladium to the value of 39 J/mol K.

In our opinion, the ordering of the material, which occurs during annealing, can play the key role in the explanation of the anomalously high values of the heat capacity experimentally observed in compacted nanomaterials. Thus, Rupp and Birringer¹¹ investigated not only nanostructures of Cu and Pd but also of the alloy $\text{Pd}_{72}\text{Si}_{18}\text{Fe}_{10}$ in the glassy state. Its heat capacity in the temperature range 150–300 K exceeded that of the bulk Pd by about 8%. After annealing at $T = 750$ K during 30 min, the alloy had transformed into the crystalline state and the heat capacity was remeasured. In the last case the difference was only 4%, i.e., a half of the prior excess was defined by the disordered state of the alloy, and the second half by some specific features of its chemical composition.

Then, as an additional confirmation of our hypothesis, let us discuss experimental data on Se. Studies of the temperature dependence of the heat capacity of amorphous nanocrystalline and polycrystalline Se in the temperature range 220–500 K³⁶ demonstrated a very small

increase in the heat capacity of the nanocrystalline Se in comparison with the bulk phase, i.e., their heat capacities did practically coincide within the error of measuring. It is also worth to mention here that the compactified nanocrystalline Se was produced via crystallization of the amorphous material that eliminated the effect of the disturbed structure as well as of gaseous and other impurities on the heat capacity.

So, high differences in the heat capacity, in comparison with the polycrystalline state, were observed not only for samples obtained compactifying nanopowders. However, if samples we produced by the crystallization from the amorphous state, the differences in question were small. So, one can assume that the main term into the excess heat capacity of compactified nanomaterial is defined by high surface area, structural disturbances, dopes of different types and some other reasons not relating to higher heat capacity of separate metallic nanoparticles.

5. CONCLUSION

The development of contemporary science has resulted in the necessity to use new devices comparable in size with the atomic scale.³⁷ Then, up to the present time, it becomes clear that properties of nanomaterials, the devices in question consist of, do significantly depend on specific features of their constituents. In this connection, intensive studies have been beginning of small particles (clusters) in the size range from 10 to several thousand atoms. However, experimental studies of nanoclusters face definite difficulties relating, first of all, to their small sizes. For this reason, one of possible approaches to study nanosized objects may be the treatment of their computer models.^{38–40} Most promising for studying physical-chemical properties of metallic clusters is, in our sight, molecular dynamics method which makes it possible to understand effects of different factors on properties of particles at the atomic level.

When nanotechnologies are introduced into industry,⁴¹ the main up-to-date problem is rather not the production of new materials itself but the investigation of thermal effects and force fields (radiation, deformational and others) in the course the usage of nanomaterials. All the above factors should affect physical-chemical properties and, as a consequence, maintenance resources of nanomaterials.⁴² Taking into account mentioned above, the heat capacity of Pd nanoclusters has been determined in our computer simulations and compared with the available experimental data.

In accordance with the results obtained in the present paper as well as in our former works,^{12–15} a conclusion can be made that the heat capacity of nanometer-size objects should not be several times higher than that of the corresponding bulk phase as it was found in some experiments. The origin of such a significant divergence may be in both the disordered state of the experimentally produced nanomaterials and, in lesser degree, significant content of

different dopes, particularly, of hydrogen. From this point of view, the results of experimental works,^{9–11} predicting many-fold growth of the heat capacity of nanoclusters and nanostructured materials, are obviously inadequate.

Acknowledgments: The paper was prepared under the financial support of Russian Foundation for Basic Research (grants No. 13-02-98-006-r_Siberia_a and No. 13-03-00119).

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Received: 6 February 2014. Accepted: 1 March 2014.