

On the Conundrum of the Heat Capacity of Metallic Nanoclusters

V.M. Samsonov^{1*}, Yu.Ya. Gafner², S.L. Gafner², I.S. Zamulin²

¹Tver State University, 170027, Brigadnaya 37, Tver, Russia

²Katanov Khakass State University, 655017, Lenin St., 90, Abakan, Republic of Khakassia

Abstract

The heat capacity of nanoclusters was investigated using thermodynamics of surfaces, taking into account the surface enthalpy introduced by E. Guggenheim. It is shown that the cluster heat capacity C_p should be greater than the heat capacity $C_p^{(b)}$ of the corresponding bulk phase. However, the $(C_p - C_p^{(b)})/C_p^{(b)}$ ratio should not exceed 50% up to very small clusters containing 100 atoms. Theoretical estimations agree with molecular dynamics results. So, experimental data on metallic nanoclusters and nanostructures demonstrating that C_p exceeds $C_p^{(b)}$ in 2-5 times should be incorrect.

Introduction

Current advances in new constructional and functional materials are associated, first of all, with the development of compacted nanomaterials. In particular, the practical application of nanocrystalline metals and their various compounds has been causing intensively studies of their mechanical, thermal, electrical, magnetic and other properties. The heat capacity, being one of the main thermophysical properties of nanomaterials, must be considered in view of preparation and applications of such materials. However, up to the present time, the behavior of the specific heat capacity of nanoparticles (nanoclusters) and nanostructured materials is an important and not solved problem. With enough confidence one can only talk about the case of very low temperatures. Theoretical estimates show that at temperatures $T \rightarrow 0$ K, because of quantum effects, the cluster heat capacity decreases faster than the heat capacity of the corresponding conventional bulk material. As a rule, it is believed that just below Einstein and Debye's characteristic temperatures [1, 2], noticeable quantum effects of the heat capacity reduction will take place. However, these characteristic temperatures, being for most bulk metals in the temperature range

200-300 K, should be rather interpreted as the temperatures for which quantum effects in question only begin to be developed. Indeed, the temperature range in which the lattice vibrations must be considered on the basis of quantum concepts are defined not by Debye's temperature [3], but by the degeneracy temperature of order of 10 K [1, 2]. When temperatures are higher than the degeneracy one, the heat capacity of the cluster begins to exceed the thermal capacity of the bulk material up to Debye's temperature, and effect in question is confirmed experimentally [4-7]. Measurements of the heat capacity of lead nanoparticles of 2.2, 3.7 and 6.6 nm in diameter as well of indium nanoparticles have shown that at low temperatures it is by 25-75% higher than the heat capacity of the same bulk metals [4, 5]. In [6] the results are presented on the specific heat capacity of Pd nanoparticles of 3.0 and 6.6 nm in diameter, obtained by the condensation of vapor. According to this paper, the doubled increasing in the heat capacity of Pd nanoparticles ($D = 3.0$ nm) was observed compared to the bulk palladium at temperatures up to 30 K. Even more significant increase in the heat capacity (3-10 times in comparison with tabulated values) was found in [7] for gold ($D = 4, 6, 18$ nm) and silver ($D = 10$ nm) nanoparticles. However, the most general theoretical considerations (see below) show that the excess specific (and molar) heat capacity of ensembles of free nanoparticles and of compacted nanomaterials

*corresponding author. E-mail: samsonoff@inbox.ru

should be commensurated with the magnitude of the heat capacity of the corresponding bulk sample.

Not better things are with estimations of the specific heat capacity for clusters and nanostructured materials at high temperatures. Thus, according to [8], the heat capacity of coarse-grained copper clusters of about 50 nm in size is higher than the normal heat capacity of the bulk copper in 1.2-2.0 times at temperatures from 200 K to 450 K. In [9] similar results were obtained for nickel nanoparticles of 22 nm in diameter: their heat capacity was twice higher than that of the bulk nickel at temperatures 300-800 K. A study of the heat capacity of nanostructures consisting of nickel clusters with of 10 nm in diameter by the fast neutron scattering method [10] also demonstrates the increase in the heat capacity in 1.5-2.0 times compared to that for conventional materials. However, according to [11], for nanocrystalline palladium ($D = 6$ nm) and copper ($D = 8$ nm) in the temperature range 150-300 K, the heat capacity increasing effect should be much smaller 29-53% and 9-11%, respectively, compared to conventional polycrystalline values for Pd and Cu).

Taking into account the mysterious behavior of the specific heat capacity of nanoclusters and nanostructured materials, in [12] we studied the heat capacity of the metal nanoclusters (nickel and copper) using molecular dynamics computer experiment and the tight-binding potential [13] proposed to describe the interatomic interactions in transition metals. In these computer simulations we really observed the increasing of the heat capacity compared to that of corresponding bulk phases, but not so significant as in most of the above mentioned experimental works. Thus, for nickel nanoclusters of 2 nm in diameter the increase in the heat capacity was only 14% compared to the tabulated value for the specific heat capacity of polycrystalline Ni, and increasing the cluster size to 6 nm the effect was reduced to 10%.

In [14] the behavior of the specific heat capacity of metal nanoclusters (gold, copper and aluminum) was investigated on the basis of Monte Carlo, i.e. an alternative method of simulation, and using another many-body potential (Gupta's one). When the nanocluster size was of the order of 1.0 nm, the effect of 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 [14] the temperature range corresponds to a vicinity of the melting point.

A Thermodynamic Approach to the Problem of the Heat Capacity of the Nanocluster Ensemble

First of all we should note that talking about the heat capacity of free clusters we, of course, mean the heat capacity of an ensemble of nanoparticles. As was discussed in [15] an ensemble is always supposed when thermodynamics is applied to small object not only when Hill's ensemble method [16] is used but also when Gibb's method [17] is extended to nanoparticles.

In [12] we put forward a hypothesis that the significant experimentally observed increase in the heat capacity of nanostructured metals (in 1.5-5 times) can be caused by some agglomeration of clusters. To the present time, however, this explanation seems us to be physically inadequate [18]. Indeed, the specific (per atom) isochoric heat capacity of the ideal gas and of the crystal, in the high-temperature approximation, can be written as follows:

$$c_v = \frac{i}{2}k \quad (1)$$

where k is Boltzmann's constant, and i is the effective number of degrees of freedom of atoms. For the monatomic ideal gas $i = 3$ and, respectively, $c_v = (3/2)k$. For the crystal $i = 6$ and $c_v = 3k$ (Dulong and Petit's law), i.e. the heat capacities of the crystal and of the ideal gas differ in about two times. From this point of view the heat capacity of liquids and dispersed systems cannot differ from that of crystalline phase in 2-5 times and more. In other words, there are no physical reasons and mechanisms to increase the heat capacity in several times when the same mass of the same substance is transformed into a dispersed state.

Below a more detailed thermodynamic analysis of the size dependence of the specific heat capacity is presented for the high-temperature region when quantum effects can be neglected. In what follows we consider the isobaric heat capacity C_p of nanoparticles, since the condition of the constant pressure ($p = \text{constant}$) seems to be more adequate to real nanoparticles and nanosystems. However, it should be noted that under low pressures ($\leq 10^5 Pa$) the difference between isochoric and isobaric heat capacities can be also neglected for both nanoparticles and corresponding bulk condensed phases.

That the heat capacity C_p of a body can be found differentiating the enthalpy H with respect to the temperature T [2]:

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \quad (2)$$

Applying (2) to nanoclusters one should take into account that the enthalpy H includes not only the bulk term H_b but also the surface enthalpy H_s first introduced by E. Guggenheim [19]:

$$H = H_b + H_s \quad (3)$$

It is noteworthy that in 30-th as well K. Adam introduced into consideration the concept of the surface heat capacity [20].

Since the pressure p does not belong to parameters of Gibbs' non-autonomous surface phase [17], the surface enthalpy H_s is equal to the excess total surface energy:

$$H_s = w\omega \quad (4)$$

where w is the specific per unit area total surface energy, ω is the surface area of the particle. In what follows it is assumed that the particle radius R is interpreted as the radius of the equimolecular dividing surface [17, 21], i.e. the surface for which the excess number of atoms is zero. Taking into account (3) and (4), the equation (2) can be rewritten as:

$$C_p = C_p^{(b)} + C_p^{(s)} = c_p^{(b)} N + \frac{\partial(w\omega)}{\partial T} \quad (5)$$

where $c_p^{(b)}$ is the specific (per atom) heat capacity of the bulk phase. The dividing surface area ω can be expressed in terms of the number of atoms N and the number of atoms density n :

$$\omega = 4\pi R^2 = (4\pi)^{1/3} \left(\frac{3N}{n}\right)^{2/3} \quad (6)$$

Correspondingly, the expression for the surface enthalpy and its temperature derivative can be written as follows:

$$H_s = w(4\pi)^{1/3} 3^{2/3} \left(\frac{N}{n}\right)^{2/3} = (4\pi)^{1/3} 3^{2/3} (N)^{2/3} v^{2/3} w, \quad (7)$$

$$\left(\frac{\partial H_s}{\partial T}\right)_{p,N} = (4\pi)^{1/3} 3^{2/3} (N)^{2/3} \left[v^{2/3} \frac{\partial w}{\partial T} + 23wv^{2/3} v \frac{\partial v}{\partial T} \right] \quad (8)$$

where $v = n^{-1}$ is the specific volume.

The first term in square brackets is negative and the second positive. However, as it is noted in [22], the specific total surface energy slightly decreases with increasing temperature, and a sharp fall occurs only in the vicinity of the critical point, while the specific excess free energy σ coinciding for the equimolecular dividing surface with the surface tension γ decreases with the increasing of the temperature following to the linear law, at least as a first approximation. Respectively, in the first approximation, the term $v^{2/3} \partial w / \partial T$ can be neglected. So, we obtain the next expression for the relative surface heat capacity:

$$\frac{C_p^{(s)}}{C_p^{(b)}} = (4\pi)^{1/3} 3^{2/3} \frac{2}{3} \frac{1}{c_p^{(b)}} \frac{w\alpha_p}{N^{1/3}} v^{2/3}, \quad (9)$$

The final expression for the relative surface (excess) heat capacity of the cluster $\xi^{(s)} = C_p^{(s)} / C_p^{(b)}$ becomes

$$\begin{aligned} \xi^{(s)} &= 2 \left(\frac{4\pi}{3}\right)^{1/3} \frac{w}{c_p^{(b)}} \alpha_p \left(\frac{M}{\rho}\right)^{2/3} \frac{1}{N^{1/3} N_A^{2/3}} = \\ &= 2 \left(\frac{4\pi}{3}\right)^{1/3} \frac{w}{\tilde{c}_p^{(b)}} \alpha_p \left(\frac{M}{\rho}\right)^{2/3} \left(\frac{N_A}{N}\right)^{1/3}, \end{aligned} \quad (10)$$

where $\alpha_p = v^{-1}(\partial v / \partial T)_p$ is the isobaric thermal expansion coefficient, $\tilde{c}_p^{(b)}$ is the molar heat capacity of the bulk phase, M is the molar mass, ρ is the density of the nanoparticle material and N_A is Avogadro's number.

The relative heat capacity of the cluster $\xi = C_p / C_p^{(b)}$ can be written as:

$$\xi = \left(C_p^{(b)} + C_p^{(s)}\right) / C_p^{(b)} = 1 + \xi^{(s)}$$

The results of evaluations of the relative heat capacity of nickel nanoclusters (temperature $T = 200$ K) are presented in Table 1. The coefficient of the thermal expansion α_p was evaluated using usual formula $\alpha_p = 3\alpha_p^{(l)}$ that is exactly fulfilled for isotropic materials ($\alpha_p^{(l)}$ is the linear coefficient of the thermal expansion). Parameters ρ and $\alpha_p^{(l)}$, necessary for evaluations, were taken from [23, 24]. The values of the specific total surface energy w were recalculated using tabulated values of the specific surface free energy (surface tension) σ and its temperature derivative $d\sigma/dT$ using the thermodynamic Gibbs-Helmholtz equation $\sigma = w = T d\sigma/dT$.

Experimental values of σ and $d\sigma/dT$ for metals in the solid state, including nickel at 1070 K were taken from [25] and [26]. It is also necessary to note that the experimental data on the surface tension of solids, including metals in the solid state, are scanty enough. It is also noteworthy that in the both last sources the same value 1820 mJ/m² of the surface tension σ for macroscopic flat surface of solid Ni is given whereas the values of the temperature derivative $d\sigma/dT$ figuring in [25] and [26] are significantly different: -0.5 mJ/m² K and -1.1 mJ/m² K, respectively. For this reason, a range of ξ values is presented in the table, and the boundaries of this interval correspond to the above two values of the temperature derivative of the surface tension. We be-

lieve, however, that the value -1.1 mJ/m² K given in [26] is more reliable, since for the nickel melt, i.e. the system which is much more convenient for measurements than the solid phase, $d\sigma/dT = 0,98$ mJ/m² K. In the same table the values of ξ are presented calculated from the results of our molecular dynamics experiments [12]. As one can see, thermodynamic estimations are in a good agreement with molecular dynamics results. The table also presents values of the reduced radius $R^* = R/d$ of the cluster where d is the effective atomic diameter. It was assumed that the parameter d can be found as the doubled Ni atomic radius equal to 0.124 nm [27].

Table 1

Evaluation of the relative excess heat capacity of Ni nanoclusters

N	R, nm	R*	$\xi = C_p/C_p^{(b)}, \%$	
			Theory	Molecular dynamics [12]
100	0.7	2.8	9-12	17
256	1.0	3.9	6-9	14
1000	1.6	6.3	4-5	13

When $N < 100$ the application of formula (10) becomes incorrect because of the size dependence of the surface energy. However, according to our theoretical estimations [28, 29] and molecular dynamics results [30], a sharp decrease in the specific surface free energy σ should be at $R^* < 2,5$ i.e. $N < 100$.

Computer experiments

In our previous paper [12] the heat capacity behavior of free nickel and copper nanoparticles of different diameters (or rather, as was mentioned above, of corresponding ensembles of nanoparticles) was investigated in the temperature range from 200 to 800 K using isothermal molecular dynamics and the tight-binding many-body potential [13]. This potential was proposed just to describe interatomic interactions in transition metals. As can be seen from the table and Fig. 1, at $T = 200$ K the excess specific heat capacity of nickel nanoclusters of $D = 1,6$ nm in diameter is 17% relative to the bulk nickel phase, and 13% for nickel clusters of 6 nm in diameter. The results obtained using molecular dynamics are in a fairly good agreement with theoretical estimations presented in the same table. For copper nanoclusters ($D = 6$ nm) the excess in the heat capacity is only 10% that also agrees with experimental data [11].

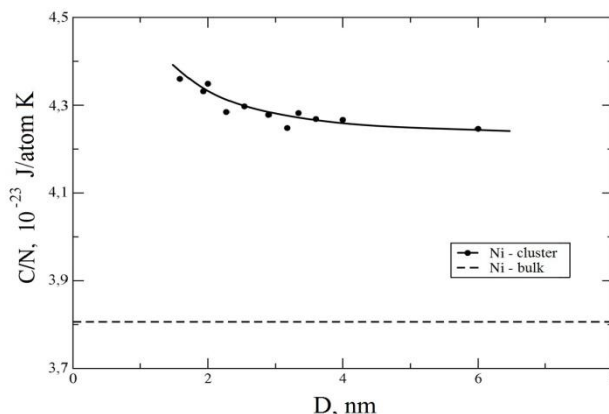


Fig. 1. Size dependence of the heat capacity (per atom) for an ensemble of Ni nanoclusters at $T = 200$ K obtained using results of our molecular dynamics experiments. Dashed line corresponds to the bulk phase of Ni [21].

In [11] the results for the nanocrystalline palladium ($D = 6$ nm) are presented in the temperature range 150-300 K. These results show that the specific heat capacity is by 29-53% higher than the conventional value for the polycrystalline Pd. The authors of [11] suggested that the more noticeable size-effect (compared to that for copper nanoparticles) is due to an agglomeration effect, i.e. to a peculiar structure of the interface between individual nanoparticles. Up to the present time, this explanation seems us improbable as it is already estab-

lished that the structure of grain boundaries in compacted nanomaterials slightly enough differs from that of corresponding crystallites.

In view of mentioned above, the size dependence of the specific heat capacity of palladium nanoclusters was investigated using computer molecular dynamics experiments. For this purpose we used the program MDNTP developed by R. Meyer (Universität Duisburg, Germany). The calculations were performed on the 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). Simulation results for palladium nanoclusters of $D = 6$ nm in diameter are shown in Fig. 2. As one can see from Fig. 2, the values of the heat capacity of ensembles of free palladium nanoclusters investigated in our molecular dynamics experiments, really exceed the usual heat capacity, i.e. that of the coarse-grained Pd, but not more than by 11% and this result is entirely consistent with the above theoretical treatment based on thermodynamic analysis of the problem under investigation.

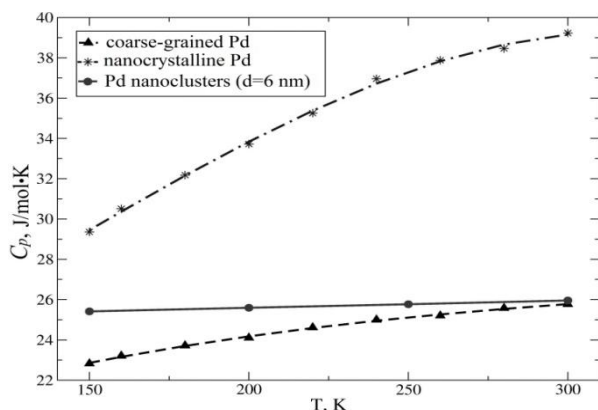


Fig. 2. Comparison of our molecular dynamics results for the temperature dependence of the heat capacity of Pd nanoclusters ($D = 6$ nm) with experimental data for coarse-grained Pd.

Discussion

Earlier [12] in our computer experiments on Ni and Cu nanoclusters we have established that their heat capacity cannot exceed corresponding bulk values in several times. In this paper our former conclusion was confirmed by molecular dynamics results on Pd nanoclusters. The difference between experimental data for nanocrystalline and coarse-grained Pd, presented in Fig. 2, reaches 53%. We believe that even such an increase in the heat capacity compared to its ordinary value is inadequately large.

In what follows two important aspects of our work will be also discussed concerning the possibility of its further development and refinement. The first of them corresponds to taking into account the size dependence of surface characteristics, i.e. the dependence of σ and w on the particle radius R . For very small radii R A.I. Rusanov [21] proposed the linear formula

$$\sigma = KR \quad (11)$$

where K is the proportionality coefficient depending on the temperature and pressure. In our previous studies, formula (11) was confirmed by theoretical analysis [28, 29] and on the basis of computer simulations [30, 31]. However, one should take into account that the surface tension σ and the specific total excess energy w are characterized by different values of the proportionality coefficient K . In addition, there are very scanty experimental data on the K parameter. We know only one experimental work [32] on this topic. Besides, clusters of the same metal can have different structures and, respectively, different values of the coefficient K . In [33] we showed that Ni clusters containing $N < 300$ atoms can have both fcc and icosahedral («onion like») structure. Thus, the estimation of the K parameter is not a trivial problem. However, the last structure is much less probable and can be observed in a vicinity of the melting point only. At the same time, as was shown in [28-31], we can use the macroscopic value of σ , at least as a first approximation, for clusters containing $N \geq 100$ atoms.

The second problem, related to the first one too, is an unusual behavior of some "bulk" properties of nanoclusters. Thus, an anomalous behavior of the thermal expansion coefficient α_p is reported in some papers. On the one hand, according to [34] this coefficient can significantly exceed the value typical for the corresponding bulk material. On the other hand, the negativity of the coefficient in question was also reported [35, 36]. In accordance with the derivation of formula (10), α_p should be interpreted just as the value attributed to the cluster itself rather than to the corresponding bulk phase. So, at the first sight, in the case of the anomalous behavior of α_p one should only substitute its value into formula (10). But in fact, that cannot be done without a special justification. Indeed, the anomaly in question should be caused by an anomaly in the nanocluster structure. The structure, in turn, can affect the value of the surface energy. In [15] we noted that the extension of Gibbs' surface phases

method to nanoparticles is associated with the choice of the phase of comparison, i.e. of the bulk phase, the excess surface energy and the other excesses to be determined just relative to it. If the conventional bulk phase is chosen as the comparison phase and the cluster has some principally different structure, the using of tabulated experimental values of the surface tension σ will be incorrect. When a virtual comparison phase is chosen corresponding to a peculiar asymptotic structure of the cluster (at high values of its radius, i.e. at $R \rightarrow \infty$), one should first describe the properties of such a virtual bulk phase. It is quite possible, that for the phase in question the surface tension will noticeably differ from the conventional tabulated value for the flat interface.

However, at least for single component metallic nanoclusters an anomalous behavior of α_p was not reported. At the same time, the usual, i.e. the most probable structure of metallic nanoclusters investigated in mentioned above direct and computer experiments corresponds to the fcc-lattice, i.e. to the structure typical for the same bulk metals. Besides, a further development of this work in the above directions (accounting for size effects of the surface energy and of the thermal expansion coefficient) is certainly of interest, but should not give some unexpected and interesting results for the size dependence of the heat capacity, principally differing from those obtained in the present paper. Really, the above simple considerations demonstrated that an atom in any dispersed matter cannot have much more degrees of freedom than in any bulk phases of the same substance.

Conclusions

So our main result is that the specific heat capacity of clusters cannot exceed the corresponding bulk value in several times. This result seems to be quite reasonable and hardly can be confuted by any further theoretical and experimental investigations. The transfer from the specific heat capacity of free nanoclusters to the heat capacity of nanostructured materials must obviously be based on some percolation model that should also give intermediate values between the heat capacities of an ensemble of free nanoparticles and of the corresponding bulk phase. From this point of view, the results of experimental studies [8-10] predicting a manifold increase in the heat capacity for nanoclusters and nanostructured materials, should be revised.

The work was performed under financial support of Ministry for Education and Science of Russian Federation, program "Scientific and pedagogical staff of the innovation Russia" (2009-2013), as well as under support of Russian Foundation for Basic Research (grants No. 11-02-98003-r_sibir_a and 13-02-98006-r_sibir_a).

References

1. Girifalco L.A. Statistical Mechanics of Solids, Oxford University Press, London, Oxford, 2000.
2. Kittel Ch. and Kroemer H. Thermal Physics, Freeman and Company, New-York, 1980.
3. Nonnenmacher Th.F. Phys. Lett. 51A:213 (1975).
4. Novotny V., Meincke P.P.M., Watson J.H.P. Phys. Rev. Lett. 28:901 (1972).
5. Novotny V., Meincke P.P.M. Phys. Rev. B. 8: 4186 (1973).
6. Comsa G.H., Heitkamp D., Rade H.S. Solid State Commun. 24:547 (1977).
7. Goll G., Lohneyen H. Nanostruct. Matter. 6:559(1995).
8. Chen Y.Y., Yao Y.D., Lin B.T. et al. Nanostruct. Matter. 6:597 (1995).
9. Yao Y.D., Chen Y.Y., Hsu C.M. et al. Nanostruct. Matter. 6:933 (1995).
10. Trampenau J., Bauszur K., Petry W., Herr U. Nanostruct. Matter. 6:551 (1995).
11. Rupp J., Birringer R. Phys. Rev. B. 36:7888 (1987).
12. Gafner S.L., Redel L.V., Gafner Yu.Ya., Samsonov V.M. J. Nanoparticle Research. 13:6419 (2011).
13. Cleri F., Rosato V. Phys. Rev.B. 48:22 (1993).
14. Sdobnyakov N.Yu., Sokolov D.N., Samsonov V.M. and Komarov P.V. Russian Metallurgy (Metally). 3:209 (2012).
15. Samsonov V.M. Russian Journal of Physical Chemistry A. 76:1863 (2002).
16. Hill T. Thermodynamics of small systems. Part. 1. W.A. Benjumin, inc., publishers., New-York – Amsterdam, 1963.
17. Gibbs J.W. The collected Works of J. Willard Gibbs V. 1. Longmans, Green and Co., New-York – London – Toronto, 1928.
18. Gafner S.L., Redel L.V., and Gafner Yu.Ya. Journal of Experimental and Theoretical Physics 114:428 (2012).

19. Guggenheim, E.A. Modern thermodynamics by the methods of Willard Gibbs. Methuen & Co. Ltd., London, 1933.
20. Adam N.K. The physics and chemistry of surfaces. Oxford university press, London, Oxford, 1941.
21. Rusanov A.I. Phasengleichgewichte und Oberflächeneigenschaften. Akademie-Verlag, Berlin, 1978.
22. Adamson A.W., Gast A.P. Physical chemistry of surfaces. A Wiley-Interscience Publication John Wiley & Sons, Inc., New-York - Chichester - Weinheim - Brisbane - Singapore - Toronto, 1997.
23. Kittel Ch. Introduction to solid state Physics. A Wiley-Interscience Publication John Wiley & Sons, Inc., New-York - Chichester - Weinheim - Brisbane - Singapore - Toronto, 2004.
24. R. Hultgren, R.D. Decali, D.T. Hawkins, M. Gleiser, K.K. Kelley, D.D. Wagman. Selected values of the thermodynamic properties of the elements. Metals Park. Amer. Soc. for Metals, Ohio, 1973.
25. Alchagirov A.B., Alchagirov B.B., Taova T.M., Khokonov Kh.B. Transactions of Joining and Valding Research Institute. Special Issue. 30:287 (2001).
26. Wilson R.D., Metallurg. Rev. 10:381 (1965).
27. Gordon A.J., Ford R.A. The chemist's companion. A Handbook of practical data, techniques, and references. A Wiley-Interscience Publication John Wiley & Sons, Inc., New-York - Chichester - Weinheim - Brisbane - Singapore - Toronto, 1972.
28. Samsonov V.M., Bazulev A.N., Sdobnyakov N.Yu., Central European Journal of Physics. 1:474 (2003).
29. Samsonov V.M., Sdobnyakov N.Yu., Bazulev A.N., Colloids and Surfaces. 239:113 (2004).
30. Samsonov V.M., Khashin V.A., Dronnikov V.V. Colloid Journal. 70:763 (2008).
31. Sdobnyakov N.Yu., Komarov P.V., Sokolov D.N., and Samsonov V.M. The Physics of Metals and Metallography. 111:13 (2011).
32. Vitol E.N., Kolloidn. Zhurn. 54:21 (1992) (in Russian).
33. Gafner S.L., Redel' L.V., Goloven'ko Zh.V., Gafner Yu.Ya., Samsonov V.M. and Kharechkin S.S. JETP Letters. 89:364 (2009).
34. Nikolaev V.I., Shipilin A.M. Physics of the Solid State. 42:112 (2000).
35. Zheng X.G., Kubozono H., Yamada H., et al. Nature Nanotechnology. 3:724 (2008).
36. Li W.H., Wu S.Y., Yang C.C., et al., Phys. Rev. Lett

Received 24 October 2012