SURFACE, ELECTRON AND ION EMISSION

Melting Temperature of Nanoparticles and the Energy of Vacancy Formation in Them

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Received March 20, 2010

Abstract—The results of studying the size dependence of the vacancy concentration in nanoparticles are presented. An analysis demonstrates that an increase in the vacancy concentration with decreasing nanoparticle size is the most grounded conclusion with allowance for the relationship between the melting temperature, the binding energy, and the energy of vacancy formation.

INTRODUCTION

Theoretical and experimental investigations demonstrate that melting temperature of nanoparticles T_r decreases with decreasing particle size as compared to this temperature for macroscopic samples T_s.

As for the size dependence of the energy of vacancy formation E_r and, correspondingly, the vacancy concentration in nanoparticles, conflicting opinions exist in the literature: both a decrease and an increase in these characteristics with decreasing particle size were noted. This discrepancy is likely to be related to the absence of direct unambiguous measurements of the size dependence of the vacancy concentration in nanoparticles. Indirect data, e.g., data on diffusion processes and a change in the lattice parameter in nanoparticles, indicate a decrease in the energy of vacancy formation in them. Experimental observations of a decrease in the diffusion activity in nanoparticles or related materials are unavailable.

Since the size dependence of the energy of vacancy formation is important to explain many processes occurring in nanoparticles and nanomaterials, it seems reasonable to consider the existing concepts of and experimental data on the relationship between the melting temperature of nanoparticles and the energy of vacancy formation in them. This consideration is most strongly grounded, since we can expect that the sign of a change in melting temperature T_s and energy of vacancy formation E_V with the nanoparticle size for solids should be the same due to a natural relationship between them. This expectation follows from the fact that, according to modern concepts, the size dependence of the melting temperature of nanoparticles or the energy of vacancy formation depends mainly on the surface energy of nanoparticles [1, 2].

DATA AND DISCUSSION OF THE VACANCY CONCENTRATION IN NANOPARTICLES

In [3] (which was published a 100 years ago and was the first work in which the melting temperature of nanoparticles was considered), Pawlov showed that the melting temperature decreases with decreasing particle size due to an increase in the effect of the surface energy, namely, due to an increase in its contribution to the free energy, since the surface energy of a liquid phase at the boundary with its vapor is lower than the surface energy of the solid phase. In this case, the melting temperature of nanoparticles is taken to be the temperature at which crystalline and liquid particles of the same mass are in equilibrium with their vapors.

Frenkel [1], who introduced the notion of a vacancy—interstitial pair in the solid-state physics, showed that the vacancy concentration in a crystal in thermal equilibrium is determined by the equation that describes the vapor concentration, with the only difference that the energy of vacancy formation plays the role of the heat of sublimation. This was also noted in [2]; moreover, it was mentioned in that work that the energy of vacancy formation is lower than the heat of sublimation for most solids, which is caused by lattice restructuring around a vacancy to stabilize this defect (i.e., its energy decreases). Therefore, the vacancy concentration should be higher than the equilibrium vapor concentration [1, 2].

The authors of [4] were the first to substantiate an increase in the vacancy concentration with decreasing vacancy size. Their arguments are as follows.

A decrease in the melting temperature of nanoparticles by ΔT can be related to a change in the effective pressure ΔP without considering the mechanism of this change. In this case, ΔT and ΔP are connected by the obvious relation

$$\Delta P = \frac{dP}{dT}\Delta T, \qquad (1)$$

where $\frac{dP}{dT}$ is determined by the Clausius–Clapeyron equation

$$\frac{dP}{dT} = \frac{\lambda}{T_s \Delta V}, \qquad (2)$$

where λ is the heat of melting and ΔV is the difference in the specific volumes of the liquid and crystalline phases.

As follows from Eqs. (1) and (2), a decrease in the melting temperature corresponds to the change in the effective pressure

$$\Delta P = \frac{\Delta T}{T_s}\frac{\lambda}{\Delta V} \qquad (3)$$

and the corresponding decrease in the energy of vacancy formation

$$\Delta E_r = \Delta P V_V = \frac{\Delta T}{T_s}\frac{\lambda}{\Delta V}V_V, \qquad (4)$$

since $\Delta T = T_r - T_s < 0$, $\lambda > 0$, and $\Delta V > 0$. Hence, the passage from macroscopic samples to nanoparticles is accompanied by an increase in the vacancy concentration; that is, a vacancy size effect takes place [4].

An increase in the vacancy concentration in small particles was used as a possible explanation of an increase in the solubility [5] and a change in the lattice parameter [6] in them.

To estimate the size dependence of the vacancy concentration, the authors of [7] used the proportionality between the energy of vacancy formation and the melting temperature [2]. Naturally, when the latter decreases by ΔT (e.g., when passing from macroscopic samples to nanoparticles), the energy of vacancy formation decreases correspondingly by

$$\Delta E_r = \Delta E_V \frac{\Delta T}{T_s}. \qquad (5)$$

It was shown [7] that the size dependences of the vacancy concentration calculated with allowance for Eqs. (4) and (5) coincide. To obtain an expression for a numerical estimation of vacancies in nanoparticles, the authors of [7] took into account the analogy between evaporation [1] and vacancy formation. Since a particle of radius r has the surface energy $4\pi r^2\sigma$ (where σ is the specific surface energy) before evaporation, the energy of vacancy formation in it and the energy of evaporation are decreased by $\frac{3\sigma}{r}\Omega$ (where Ω is the atomic volume) to a first approximation. The Laplace pressure increases the energy of vacancy formation by $\frac{2\sigma}{r}V_V$ (where V_V is the vacancy volume). With allowance for both factors, the vacancy concentration in a particle was written as [7]

$$C_r = C_\infty \exp\left[\frac{\sigma}{r}\left(3\frac{\Omega}{V_V} - 2\right)\frac{V_V}{kT}\right], \qquad (6)$$

where C_∞ is the vacancy concentration in a bulk sample and k is the Boltzmann constant.

It was shown that the vacancy concentrations calculated for golden particles with $\sigma = 1600$ erg/cm^2 at 300 K are close to those calculated by Eqs. (4) and (5) for a decrease in the energy of vacancy formation if $V_V = 0.3\ \Omega$.

Almost simultaneously with [7], the authors of [9] noted that the difficulties of a theoretical study of the vacancy size effect are caused by the fact that the excess (Laplace) pressure "rejects" vacancies from small particles and the excess (surface) energy simultaneously decreases the energy of vacancy formation. As a result, the vacancy concentration should increase. The magnitudes of both effects are of the same order of magnitude. This follows from the following expression for the dependence of the vacancy concentration on the particle size [9]:

$$C_r = C_\infty \exp\left[-\frac{2\sigma}{rkT}\left(V_V - \frac{1}{2}\Omega\right)\right]. \qquad (7)$$

It was derived in the quasi-chemical approximation and takes into account both the rejecting effect of the Laplace pressure (first term in the parentheses in the right-hand side) and the effect of the excess surface energy (second term). For example, if $V_V > 0.5\ \Omega$, the vacancy concentration decreases with decreasing particle size; otherwise, it increases.

However, based on experimental data on a decrease in the lattice parameter of nanoparticles and their surface energy, the authors of [6, 10] cast doubt on the concept of the Laplace pressure.

The concept of the Laplace pressure for solids was theoretically analyzed in detail in [11–15]. The Laplace pressure was shown to be a formal quantity that makes it possible to express the chemical potential of a sample of finite sizes through the chemical potential of the corresponding infinite sample. However, the size shift of a chemical potential is also observed in bodies with a shape at which the Laplace pressure is zero, e.g., planar films. Thus, it was concluded that the Laplace pressure is a purely mathematical concept and cannot cause compression of bodies.

With allowance for these conclusions, the energy of vacancy formation in [16–21] was estimated using the molecular-kinetic concepts in [1, 2] with allowance for the analogy between evaporation and vacancy formation.

As noted above, the presence of a particle surface decreases the energy of evaporation per atom by $\frac{3\sigma}{r}\Omega$ [1]; therefore, to a first approximation, the energy of vacancy formation in a particle decreases by

$$\Delta E_r = \frac{3\sigma}{r}\Omega. \qquad (8)$$

The figure shows the dependences of E_r/E_V on the golden-particle size calculated by Eqs. (4), (5), and (8) in [17–21]; they are seen to agree well with each other. For the calculations, we used the data on the size dependence of the melting temperature of golden particles [8] and the following parameters: $\sigma = 1500$ erg/cm^2, $\Omega = 17.96 \times 10^{-24}$ cm^{-3}, $\lambda = 12.372$ kJ/mol, $E_V = 1.0$ eV, and $\delta = 5.1 \times 10^{-2}$. The relative vacancy volume was taken to be $\frac{V_V}{\Omega} = 0.43$. In [16], we derived relationships using the relation

$$\frac{V_V}{\Omega} = \frac{E_V}{\lambda}\delta \qquad (9)$$

which follows from the equality of Eqs. (4) and (5).

These calculated and plotted data indicate that the contribution of the surface energy is a key factor in the decrease in the energy of vacancy formation.

The authors of recent works [22–26] make different conclusions regarding the size dependence of the energy of vacancy formation. The authors of [22–25] use the approach that was applied in [1] to prove the equality between the binding energy, which was taken to be the heat of evaporation [1], and the energy of vacancy formation. According to the scheme used in [22] to find the binding energy for small particles and, hence, the energy of vacancy formation in them, a particle is assumed to have a cubic shape and to consist of the same number of cubic cells along three axes. Each cell corresponds to one atom. For simplicity, the calculations only take into account the interaction between the nearest atoms. The calculations in [22] were performed for the simple cubic lattice, since the particle volume changes weakly when the simple cubic lattice transforms into the body-centered cubic (bcc) or face-centered cubic (fcc) lattice. Under these conditions, the expression

$$E_r = E_V\left(1 - 3\frac{d}{D}\right) \qquad (10)$$

was obtained for the energy of vacancy formation in a particle with cube edge length D and atom edge length d (atom is considered to be a cube in this model).

For the calculations in [22], the particle radius ($D = 2R$) was chosen as a variable, and the atomic diameter of gold was taken to be 0.288 nm. The calculated values are plotted in the figure as a dashed line. They are seen to agree well with the data calculated by Eqs. (4) and (5), which are based on the measured decrease in the melting temperature of golden particles [8], and the data obtained using molecular-kinetic concepts and Eq. (8).

In [26], this model was used to calculate the dependence of the energy of vacancy formation on the surface energy at a fixed particle size. It was shown that
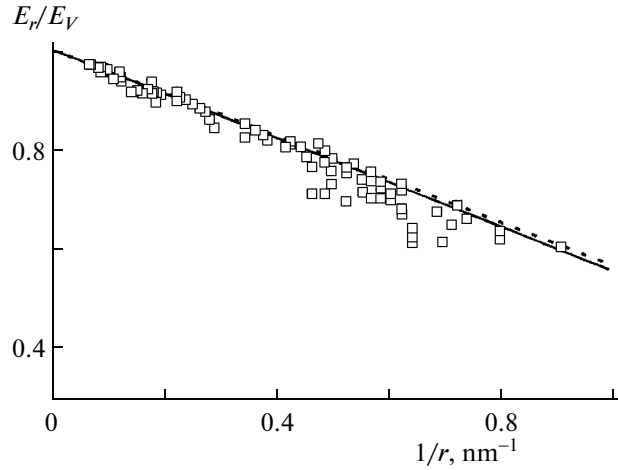
Size dependence of the energy of vacancy formation for small golden particles: (□) calculations with Eqs. (4) and (5) from a decrease in the melting temperature [8], (solid line) calculation by Eq. (8), and (dashed line) calculation by Eq. (10) [22].

the energy of vacancy formation remains almost the same when the surface energy changes by 20%. Therefore, these results indicate that Eq. (8) may be used without regard for the size dependence of σ.

Allowing for the contribution of the surface energy and the surface tension to the energy of vacancy formation, Müller and Albe [25] obtained the following relationship for the vacancy concentration in nanoparticles:

$$C_r = C_\infty\exp\left[-\frac{2(\sigma\Omega + f\Delta V_V)}{rkT}\right], \qquad (11)$$

where f is the scalar approximating the surface tension tensor and $\Delta V_V = V_V - \Omega$ is the change in the volume induced by vacancy formation.

In general, as noted in [25], Eq. (11) can result in both an increase and a decrease in the vacancy concentration with decreasing particle size depending on the surface energy and the surface tension. It was also mentioned that, since the average vacancy relaxation volume for most fcc metals is $\Delta V_V = -0.25\,\Omega$, f should be four times higher than σ to compensate for the contribution of the surface energy and to cause an increase in the vacancy concentration. Since the f/σ ratio calculated for many metals is rarely higher than two, the authors of [25] concluded that the number of vacancies decreases significantly with decreasing nanoparticle size. It should be noted that the vacancy concentration can both be independent of the nanoparticle size and increase with decreasing nanoparticle size, according to the modern data on ΔV_V ($\Delta V_V = -(0.75–0.50)\,\Omega$) for fcc and bcc metals and to the fact that the f/σ ratio is rarely higher than two [25].

When discussing the conclusions of [9, 25] regarding an increase in the energy of vacancy formation in nanoparticles, we pay attention to the related contra-

dictions that do not agree with the well-known existing concepts. For example, the authors of [25] note that Eq. (11) is analogous to the result for the size dependence of the saturated vapor pressure of a component dissolved in nanoparticles; that is, it can both increase and decrease. However, to the best of our knowledge, there are no observations corresponding to a decrease in the pressure. There are also no data on a decrease in the saturated vapor pressure over nanoparticles made of pure substances as compared to the corresponding macroscopic substances. Moreover, as noted in [1], the saturated vapor pressure also increases over films.

Similar comments are also related to the well-known relationships between the melting temperature and the binding energy and the energy of vacancy formation. The conclusion about an increase in the energy of vacancy formation in nanoparticles with decreasing nanoparticle size points to the presence of a critical size below which the sign in these relationships changes. Moreover, we could also mention the appearing contradiction between an increase in the energy of vacancy formation and the enhancement of diffusion processes in nanoparticle systems [7]. However, as follows from the conclusion that the energy of vacancy formation increases with decreasing nanoparticle size, diffusion processes should be retarded.

CONCLUSIONS

Our analysis demonstrates that the conclusion about a decrease in the energy of vacancy formation and, correspondingly, an increase in the vacancy concentration with decreasing nanoparticle size is most strongly grounded. This conclusion seems to be natural, since it agrees with the well-known concepts of the relation between the melting temperature, the binding energy, and the energy of vacancy formation and with the results of studying numerous relaxation processes in nanosystems. These processes are controlled by diffusion processes, which are directly dependent on the energy of vacancy formation, the vacancy concentration, the catalytic and chemical activity of nanoparticles, and so on.

ACKNOWLEDGMENTS

REFERENCES

1. Ya. I. Frenkel, *Kinetic Theory of Liquids* (Akad. Nauk SSSR, Moscow–Leningrad, 1945; Clarendon, Oxford, 1946).

2. J. Fridel, *Dislocations* (Pergamon, Oxford, 1964; Mir, Moscow, 1967).

3. P. Pawlov, Z. Phys. Chem. **65**, 1; 545 (1909); **68**, 316 (1910).

4. I. D. Morokhov, S. P. Chizhik, N. T. Gladkikh, et al., Dokl. Akad. Nauk SSSR **248**, 603 (1979) [Sov. Phys. Dokl. **24**, 674 (1979)].

5. I. D. Morokhov, S. P. Chizhik, N. T. Gladkikh, et al., Dokl. Akad. Nauk SSSR **248**, 1376 (1979) [Sov. Phys. Dokl. **24**, 769 (1979)].

6. I. D. Morokhov, S. P. Chizhik, N. T. Gladkikh, et al., Izv. Akad. Nauk SSSR, Met., No. 5, 210 (1979).

7. S. P. Chizhik, N. T. Gladkikh, et al., Izv. Akad. Nauk SSSR, Met., No. 6, 180 (1983).

8. Pj. Buffat and J. P. Borel, Phys. Rev. A **13**, 2287 (1976).

9. I. D. Morokhov, V. I. Zubov, and V. B. Fedorov, Fiz. Tverd. Tela (Leningrad) **25**, 312 (1983) [Sov. Phys. Solid State **25**, 178 (1983)].

10. I. D. Morokhov, S. P. Chizhik, N. T. Gladkikh, et al., Izv. Akad. Nauk SSSR, Met., No. 6, 159 (1979).

11. V. I. Gorchakov, E. L. Nagaev, and S. P. Chizhik, Fiz. Tverd. Tela (Leningrad) **30**, 1068 (1988) [Sov. Phys. Solid State **30**, 620 (1988)].

12. E. L. Nagaev, Phys. Status Sol. B **167** (2), 381 (1991).

13. Yu. I. Nagaev, Usp. Fiz. Nauk **162** (9), 49 (1992) [Sov. Phys. Usp. **35**, 747 (1992)].

14. Yu. I. Petrov, Zh. Fiz. Khim. **63**, 2757 (1989).

15. Yu. I. Petrov, Izv. Ross. Akad. Nauk, Ser. Fiz. **62**, 1142 (1998).

16. N. T. Gladkikh and A. P. Kryshtal, Fiz. Met. Metalloved. **85**, 1576 (1998).

17. N. T. Gladkikh and A. P. Kryshtal, Vopr. At. Nauki Tekh. **3** (4), 45 (1998).

18. N. T. Gladkikh and A. P. Kryshtal, Funct. Mater. **6**, 823 (1999).

19. N. T. Gladkikh and O. P. Kryshtal, in *Proceedings of the Topical Conference on Microstructures and Surface Morphology Evolution in Thin Films, Triest, 1999*, p. 26.

20. N. T. Gladkikh and O. P. Kryshtal, in *Proceedings of the 18th European Conference of Surface Science (ECOSS-18), Vienna, 2003*.

21. S. I. Bogatyrenko, N. T. Gladkikh, A. P. Kryshtal, and A. A. Filippov, Izv. Ross. Akad. Nauk, Ser. Fiz. **66**, 120 (2002).

22. W. H. Qi and M. P. Wang, J. Mater. Sci. **39**, 2529 (2004).

23. D. Xie, M. P. Wang, and L. F. Cao, J. Mater. Sci. **40**, 3565 (2005).

24. W. H. Qi, M. P. Wang, M. Zhou, and M. Y. Hu, J. Phys. D **38**, 1429 (2005).

25. M. Müller and K. Albe, Acta Mater. **55**, 3237 (2007).

26. F. Ruffino, V. G. Grimaldi, F. Giannazo, F. Roccaforte, and V. Raineri, Nanoscale Res. Lett. **3**, 454 (2008).

27. S. I. Bogatyrenko, N. T. Gladkikh, A. P. Kryshtal, A. L. Samsonik, and V. N. Sukhov, Fiz. Met. Metalloved. **109**, 585 (2010).

Translated by K. Shakhlevich