structure having nanometric dimensions of the ferrite samples. Due to very low values of dielectric loss at high frequency, these nanoferrites are found to be useful in making microwave devices and high frequency applications. The samples are found to be having good catalytic properties showing 77%, 89% and 99% removal of methylene blue dye in one hour for Co-Zn, Ni-Co-Zn and Mg-Co-Zn ferrites respectively, this process is ecofriendly due to release of eco-friendly products in the reactions.

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Statistical-variational calculation of structural and thermodynamic characteristics of system «crystalline nanoparticle – homogeneous gaseous enviponment»

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Abstract

In this study we used the procedure developed before for system of statistical equations solution, and formula, determining structural and thermodynamic characteristics of inhomogeneous molecular systems. These equations were derived within two-level statistical approach, based on Bogolubov – Born – Green – Kirkwood – Ivon correlation function method (BBGKI), Rott condition correlative function method and thermodynamic density functionals method.

The article implements a method for the variational calculation of the density profile in the vicinity of a spherical crystalline nanoparticle in equilibrium with a gaseous medium at a temperature below the triple point, and also establishes a correlation between the structure and thermodynamic characteristics of crystalline nanoparticles, taking into account the spatial relaxation of the lattice at their boundary with the surrounding gas environment.

Keywords: heterogeneous system, nanoparticle, density field.

Introduction

Earlier, in [1–4], a technique was described for the numerical solution of the complete system of integral and algebraic equations for a heterogeneous system containing a crystalline nanoparticle inside a fluid medium (gas or liquid). This technique was developed within the framework of a two-level statistical method [5, 6]. It is based on Bogolubov – Born – Green – Kirkwood – Ivon correlation function method (BBGKI), Rott condition correlative function method [7] and

thermodynamic density functionals method. In case of inhomogeneous systems, these potentials are functionals of the density field of the medium, which is specified by the discrete field of numbers of filling with molecules of the cells of the Rott conditional distribution method. The two-level statistical method makes possible taking into account the inhomogeneous distribution of the average occupation numbers n_i of cells in the entire volume V of the system. The shape and size of the cells change significantly near the boundaries of crystalline nanoparticles. For this, the F_{11}-approximation is used, which takes into account the set of the most probable states of a condensed system of N molecules in volume V. The number of microcells M in this approximation exceeds the number N of molecules in the nanoparticle and its surrounding fluid medium. Therefore, some cells with a certain probability may be vacant. As a result, the occupation number n_i of the cells is less than 1, and the field of their distribution over the volume reflects the inhomogeneity of the density field in the nanoparticle volume and in the environment.

In the two-level statistical method the average forces potentials φ_{ij} are used [6, 7], which for inhomogeneous system are functionals of the sought field of ocupation numbers n_p of cells. The centers of the cells belong to the coordination spheres with numbers p (p = 1, 2, ..., P) relative to the center of the spherical nanoparticle.

The average forces potentials φ_{ij} are numerically determined by solving a complex system of statistical integral and algebraic equations. In a modified numerical method for solving this system, the Lennard-Jones potential and other functions are averaged over the regions of localization of distribution functions in the form of spheres with radii b_p. Unary functions $\bar{F}_{11}^{*}$ within these spheres are considered constant. The radii b_p are associated with the root-mean-square deviations of the molecules from the centers of the cells, i.e. from the nodes of the fcc lattice. As a result, the micro- and macrostructure of a spherical nanoparticle with an inhomogeneous radial density profile is described by discrete sets of occupation numbers n_p and radii b_p of spheres.

Experimental

The modified integral equation solved in this study for the average forces potentials of an inhomogeneous one-component system with vacancies has the form [1]:

$$f_{ij}(\rho_i, b_j) = n_j g_{ij}(b_i, \rho_{ij}, b_j) f_{ij}^{(a)}(\rho_i, b_j) + (1 - n_j g_{ij}(b_i, \rho_{ij}, b_j)) f_{ij}^{(a)}(b_i, \rho_{ij}, b_j). \quad (1)$$

Here $f_{ij}(\rho_i, b_j) = e^{-\beta\varphi_{ij}(\rho_i, b_j)}$ ($\beta = 1/\theta$ – return temperature, $\theta = kT$); $\varphi_{ij}(\rho_i, b_j)$ is an average force potential acting on a molecule inside a sphere of radius b_i from the side of a molecule uniformly distributed inside a sphere of radius b_j; ρ_i is the distance from a molecule in a volume $\upsilon_i = (4/3)\pi b_i^3$ to the center of a volume $\upsilon_j = (4/3)\pi b_j^3$; ρ_{ij} is the distance between the centers of the volumes υ_i and υ_j; g_{ij} is an analogue of the radial function for the heterogeneous system under study, which is anisotropic due to the inhomogeneity of the system with a radial density profile [4].

$$g_{ij} = \frac{n_{ij}}{n_i n_j}, \qquad n_{ij} = n_i - n_{ij}^{av}, \quad (2)$$

$$n_{ij}^{av} = 0{,}5B_{ij} + 0{,}5\sqrt{B_{ij}^2 + 4n_i(1 - n_j)A_{ij}^{-1}}, \quad (3)$$

$$A_{ij} = f_{ij}^{(a)}(b_i, \rho_{ij}, b_j) - 1, \qquad B_{ij} = (n_i - n_j) - \frac{1}{A_{ij}}. \quad (4)$$

Functionals $f_{ij}^{(a)}(\rho_i, b_j)$ and $f_{ij}^{(a)}(b_i, \rho_{ij}, b_j)$ are defined by the following expressions:

$$f_{ij}^{(a)}(\rho_i, b_j) = \frac{1}{\upsilon_j}\int_{\upsilon_j} e^{-\beta\Phi(r)} d\upsilon_j, \quad (5)$$

$$f_{ij}^{(a)}(b_i, \rho_{ij}, b_j) = \frac{1}{\upsilon_i}\int_{\upsilon_i} f_{ij}^{(a)}(\rho_i, b_j) d\upsilon_i, \quad (6)$$

where r is the distance between two molecules in volumes υ_i and υ_j.

The functionals of entropy S, internal energy U, and free energy F of a spherical nanoparticle and its surrounding fluid are calculated using the following formulas:

$$S\{n_p\} = -\sum_{p=1}^{P} Z_p(n_p ln\, n_p + (1-n_p) ln(1-n_p)) + \sum_{\substack{j=1 \\ j\neq p}}^{J} n_p n_j\, g_{pj} ln g_{pj}, \qquad (7)$$

$$U\{n_p\} = \sum_{p=1}^{P} Z_p \sum_{\substack{j=1 \\ j\neq p}}^{J} (n_p n_j\, g_{pj} \psi(b_p, \rho_{pj}, b_j)), \qquad F\{n_p\} = U\{n_p\} - \theta S\{n_p\}, \qquad (8)$$

$$\psi(b_p, \rho_{pj}, b_j) = \frac{\int_{v_p} \varphi_{pj}^{(a)}(\rho_p, b_j) \int_{v_j} e^{-\beta\Phi(r)} dv_j dv_p}{\int_{v_p} \int_{v_j} e^{-\beta\Phi(r)} dv_j dv_p}, \qquad (9)$$

$$\varphi_{pj}^{(a)}(\rho_p, b_j) = \frac{\int_{v_j} \Phi(\rho) e^{-\beta\Phi(r)} dv_j}{\int_{v_j} e^{-\beta\Phi(r)} dv_j}. \qquad (10)$$

Here Z_p is the number of nodes belonging to the coordination sphere with number p; $J = 42$ – the number of nodes belonging to three coordination spheres with centers coinciding with the center of the sphere v_p.

In numerical calculations, all formulas and equations are written in dimensionless form. The geometric dimensions are determined in units of the linear parameter σ of the Lennard-Jones potential, and all quantities with the dimension of energy are determined in units of the energy parameter ε of the same potential.

For a spherical nanoparticle, the density field of a heterogeneous system depends only on the distance r_p from the center of the nanoparticle. Therefore, the desired radial profile of occupation numbers $n(r_p)$ is approximated by a three-parameter function containing a hyperbolic tangent and two variational parameters a and κ, i. e.

$$n(r_p) = a - (a - n_\infty)\text{th}(\kappa \Delta x_p), \qquad \Delta x_p = r_p - r_{nano}, \qquad (11)$$

where n_∞ is the value of the occupation numbers in a volumetric homogeneous environment, r_{nano} is radius of a spherical nanoparticle.

For spherical surface, the values of the variational parameters a and k are found by solving the variational problem of finding the minimum of the functional of the large thermodynamic potential $\Omega\{n(r_p)\} = F\{n(r_p)\} - \mu \sum Z_p\ n(r_p)$ of the nanoparticle and its environment.

Results and discussion

The complete closed system of integral and algebraic equations (1)–(6) was solved numerically by the iteration method. The parameters a and κ were varied using system (7)–(11).

The functional $\Omega\{n(r_p)\}$ was varied numerically for different parameter values a и κ. Figure 1 shows the dependences of the large thermodynamic potential Ω on the variational parameter a for given different values of the parameter κ and the temperature $\theta = 0{,}6$ that corresponds to the crystal-gas phase transition ($n_\infty = 2 \cdot 10^{-5}$) [6].

The figure 1 shows that the absolute minimum of the functional $\Omega\{n(r_p)\}$ is realized at values of the parameter κ in the range from 4 to 5 and, accordingly, with values of the parameter a in the range from 0,07 to 0,08.

The figure 2 shows the results of calculations of the structural characteristics of a spherical crystalline molecular nanoparticle in equilibrium with the surrounding gas medium at a temperature $\theta = 0.6$. The obtained dependences of the radii b_p of the spheres, the root-mean-square deviations σ_p, the radial displacements Δr_p of the nodes, the quantities $q_p = \ln Q_p$ (Q_p are normalizing factors of unary functions in the cells of the coordination spheres with numbers p) and the radial profile of the occupation numbers n_p correspond to the minimum of the functional $\Omega\{n(r_p)\}$, which takes place at

the values $\kappa \approx 4,5$ and $a \approx 0,075$. It can be seen from the figure 2 that in the case of a crystalline nanoparticle with occupation numbers $n \approx 0,999$, an adsorption gaseous layer with increased density values is formed at its boundary (for example, $n_{16} = 0,095$). In this case, in the bulk of the crystalline nanoparticle, a gradual increase in the root-mean-square deviations σ from the value $\sigma_0 = 0.15$ at the center of the nanoparticle to the value $\sigma_{15} = 0,36$ at its boundary is observed. Value $p = 15$ corresponds to the boundary of a crystalline nanoparticle. Simultaneously with this, the sites of the fcc lattice shift in the radial direction, which is described by the dependence Δr_p (at $p = 15$ the value $\Delta r_{15} = 0.20$).

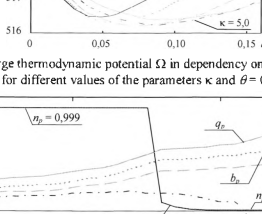

Figure 1. Plot of the large thermodynamic potential Ω in dependency on the variation parameter a for different values of the parameters κ and $\theta = 0.6$

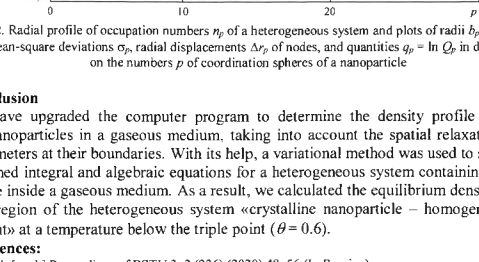

Figure 2. Radial profile of occupation numbers n_p of a heterogeneous system and plots of radii b_p of spheres, root-mean-square deviations σ_p, radial displacements Δr_p of nodes, and quantities $q_p = \ln Q_p$ in dependency on the numbers p of coordination spheres of a nanoparticle

Conclusion

We have upgraded the computer program to determine the density profile of crystalline spherical nanoparticles in a gaseous medium, taking into account the spatial relaxation of the fcc lattice parameters at their boundaries. With its help, a variational method was used to solve a system of transformed integral and algebraic equations for a heterogeneous system containing a crystalline nanoparticle inside a gaseous medium. As a result, we calculated the equilibrium density field in the interphase region of the heterogeneous system «crystalline nanoparticle – homogeneous gaseous enviponment» at a temperature below the triple point ($\theta = 0.6$).

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Features of electrochemical formation of metal and semiconductor nanowires in anodic alumina matrices with variable pores

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Abstract

Methods for the porous membranes formation from anodic alumina with periodically alternating pore diameters along the membrane depth and the electrochemical nanowires formation of complex morphology from various materials have been developed and tested. The features of the electrochemical deposition of indium and copper antimonide into pores with varying diameters under different chemical conditions and electrical modes have been investigated. The electron microscopic studies of the created nanosystems have been carried out, the elemental composition has been investigated, the current-voltage characteristics of InSb nanowires of complex morphology have been measured.

Keywords: porous anodic alumina oxide, variable pores, electrochemical deposition, semiconductors, nanowires.

Introduction

Inasmuch as quantum laws operate at the nanoscale, any change in the composition or geometry of a nanoobject can lead to a fundamental change in the physical and chemical properties of the entire structure [1]. This necessitates the creation of more complex structures (nanotubes and nanowires with different diameters at different heights, with branching, etc.). This result can be achieved by means of electrochemical template synthesis of nanostructures in porous matrices with complex nanopore geometry [2, 3]. Of particular interest are nanostructures with periodically varying pore diameters from the surface to the base.

This article presents the series of laboratory experiments in which the technology of creating anodic aluminum oxide matrices with alternating pore diameters has been worked out. Such a matrix consists of several layers of adjustable depth with specific pore diameters along the entire height of these layers and was used as template for electrochemical deposition of metal and semiconductor nanowires.

Experimental

An anodic alumina (AA) membrane with alternating pore diameters was formed by anodizing aluminum foil (99.999%) and contained four layers 10 μm thick with alternating pore diameters. The anodizing voltage determined the pore diameter, as well as other geometric parameters of the