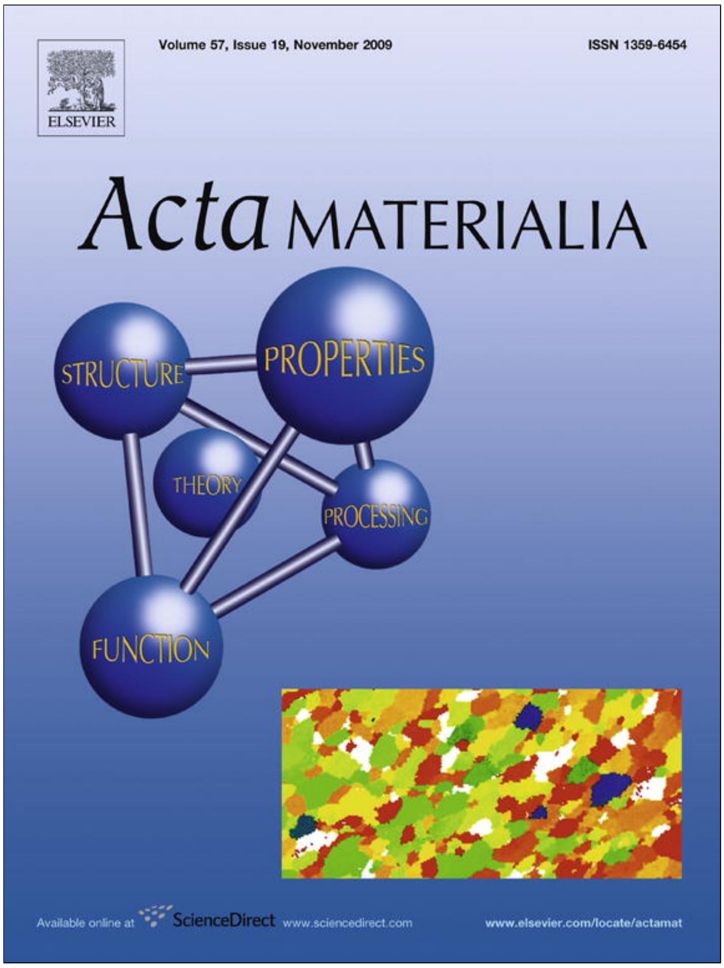
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Influence of nanopowder particle size on competition and growth of different crystallographic phases during temperature cycling

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Abstract

A model of nucleation of a new phase nucleus in an isolated nanoparticle is presented for the case of a polymorphic transition. It is shown that due to the limitation in the size of the system, a phase transition which could occur in a macroscopic sample is inhibited and situations may be realized where a metastable phase may be formed in preference to the most stable phase. We present a numerical analysis for the description of the evolution of a polymorphically transforming Fe nanoparticle ensemble subjected to temperature cycling. The time dependence of the volume fraction of the new phase is determined and the existence of a size-induced hysteresis, which is dependent on particle size, is demonstrated. The obtained results may be employed in the development of alternative methods of information processing in current and future information technologies.

Keywords: Gibbs free energy; Nanoparticle; Nucleation; Temperature cycling; Polymorphic transition

1. Introduction

Nanostructure design is a key aspect of nanotechnology. Nanotechnology is directed to achieving the ability to build materials and products at an atomic level of precision and has been one of the most active areas of scientific research in the last decade. Metal nanoparticles and nanopowders have a specific significance among nanostructured materials due to their wide range of practical applications, including catalysis, design of composite materials with specific properties such as higher tensile strength and fatigue strength, transportation, aerospace, sports products, chemical and food processing.

In order to develop nanomaterials with desired structure and properties, knowledge of the basic principles and specific features of self-organization processes at the atomic and/or molecular level is of basic importance. However, despite the widely acknowledged importance of nanomaterials, our understanding of the specific features of the evolution of first-order phase transitions in such systems is far from complete. In the present paper, we analyze first-order phase transitions in ensembles of nanoparticles both from a thermodynamic point of view and with respect to the specific features of the kinetics of such processes, specifically targeting polymorphic transitions in metallic nanoalloys undergoing temperature cycling.

Phase transformations of materials in confined volumes can deviate considerably from those observed in the bulk [1–3]. Compared with bulk materials, nanosized systems are characterized by a high ratio of the number of surface to volume atoms [4]. This peculiarity leads to the possibility of the stable existence of metastable phases, a property that can be employed in nanotechnology as a means to improve the physical properties of materials.

One of the well-known physical properties of nanomaterials is the variation of the melting temperature with the size of the samples, as theoretically predicted by Pawlow as early as 1909 [5–8]. For example, the melting temperature T_m of an isolated nanoparticle decreases when the size R of the nanoparticle reduces according to the relation:

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$$T_m \approx T_{m,\infty}[1 - C_1/R]. \tag{1}$$

Here $T_{m,\infty}$ is the bulk melting temperature, C_1 is a constant for a given material and depends on the surface tension, σ. The decrease of T_m is noticeable when R has values in the nanometer range. This kind of behaviour has been known for a long time and has been verified by recently carried out experimental, theoretical and computer investigations on melting and freezing of low-dimensional materials [9].

Experiments have demonstrated the possibility of supercooling and superheating of nanoparticles. For example, a 150 nm Bi film melts at 273 °C but solidifies at 165 °C, i.e. 107 °C below the melting temperature. In this example, the cooling rate at solidification was 600 K s^{-1} [10]. The superheating of small particles and materials is not easily observed in metallic systems and has been little reported [11]. Applying a very high heating rate, large transient superheating might be obtained by suppression of the melting kinetics. Melting generally proceeds from a free surface or interface and there should be no large nucleation barrier to the formation of a liquid, since the solid–vapour interface has generally higher energy than the sum of the liquid–vapour and solid–liquid interface energies. The result, when the liquid coats the solid part, coincides with the well-known wetting effect related to the small value of the surface tension of a liquid with respect to that for a solid [12]. The generally used critical undercooling (or critical supercooling temperature) needed for the formation of the low-temperature phase depends on the cooling (heating) rate. This implies that these quantities are determined not only by thermodynamic factors but by kinetic ones as well. In the present paper we shall distinguish the thermodynamically determined critical undercooling and superheating as functions of the size of the nanoparticles from the kinetically defined critical undercooling and superheating as functions of cooling and heating rates and nanoparticle size.

Another example in which size-induced effects and, in particular, size-induced hysteresis phenomena occur is capillary condensation (phase transitions in pores or capillaries – for some recent work in this direction, see e.g. [13,14]). Capillary condensation is important for the understanding of the properties of porous materials and represents the surface-driven phase change accompanied by shifts in the phase coexistence curves. By plotting the pressure (or temperature) vs. the total number of moles adsorbed in such materials it is possible to construct a size-dependent phase diagram similar to bulk equilibrium coexistence curves. In this respect, three aspects are important: (i) one can see different shapes of hysteresis loops in the adsorption isotherms; (ii) hysteresis effects vanish above some hysteresis critical temperature which is lower than the bulk critical temperature of the corresponding transition; (iii) there is some shift in the hysteresis critical temperatures, and these increase with decreasing pore width. Recently, one of the present authors analyzed the phase separation of a binary alloy taking into account the concentration redistribution, and demonstrated the existence of size-induced hysteresis effects [15].

The melting behaviour of nanoparticles of Pb–Bi alloys, observed by hot stage transmission electron microscopy, shows a similar size-induced hysteresis loop [16]. At the same time the theoretical consideration of structural phase transitions in nanomaterials undergoing temperature changes still remains an open question [17,18]. Bearing in mind Eq. (1), such hysteresis cannot be explained by thermodynamics alone but has to involve a description of the kinetics of melting and crystallization as well. In order to develop a theoretical description of the above-mentioned hysteresis effects in cyclic melting and crystallization, in the present paper we perform a thermodynamic analysis of the formation of a nucleus in a nanoparticle and apply the thermodynamic approach to the study of the kinetic "decoding" the transition back and forth during the temperature cycling of a nanopowders. Herein, our particles are assumed to be relatively large, and the number of atoms, N_0, in each particle is of the order 10^3–10^7, so that (i) thermodynamic arguments remain valid; and (ii) each surface may be characterized by a single value of the specific surface energy (taken as independent of size). These conditions are met for metallic particles when their radius is equal to or larger than about 2 nm.

The paper is arranged in the following way. First we develop a model of phase transition in an isolated nanoparticle and derive general thermodynamic results (Section 2). We then introduce the kinetic model (Section 3) and demonstrate by numerical analysis the existence of a size-induced hysteresis. We show the dependence of this hysteresis on the rate of temperature change and properties of the nanopowders, and how it results in a polymorphic transformation of an ensemble of Fe nanoparticles subjected to a temperature cycling (Section 4). Section 5 completes the paper with the summary and conclusions.

2. Thermodynamic model and results of the thermodynamic analysis

2.1. The model

Our analysis is based on two ideas, which seem to be very simple, but have so far not been taken into account generally in the analysis of the kinetics of phase transitions of nanoparticles (cf. also Ref. [19]). First, it is clear that an "anomalous" appearance of metastable phases in small systems is related to the change in the conditions of phase equilibrium. In bulk materials, the stable phase (say, phase 1) is the one which has the lowest bulk Gibbs free energy (per volume of the system), g: $g_1 < g_2$. The subscripts 1 and 2 refer here to phases 1 and 2, respectively. In the description of nanoparticles one has also to take into account, in addition to bulk contributions, the surface (and/or interfacial) free energies, σ_1 and σ_2. Then the Gibbs free energy G of the transforming system has the form: $G_1 = 4\pi R^3 g_1/3 + 4\pi\sigma_1 R^2$ for phase 1 and

$G_2 = 4\pi R^3 g_2/3 + 4\pi\sigma_2 R^2$ for phase 2. Here the particles are assumed to be of spherical shape with radius R (Fig. 1). Due to the different surface energy contributions of the phases, the equilibrium conditions may be changed so that the metastable (from the usual, "bulk" point of view) phase 2 becomes the stable one: $G_1 > G_2, g_1 + 3\sigma_1/R > g_2 + 3\sigma_2 R$. For nanosystem sizes of $R < R^* = 3(\sigma_1 - \sigma_2)/(g_2 - g_1)$ the metastable phase 2 will be the thermodynamically more advantageous. Here R^* is the system's transition size, i.e. the size of the whole system transforming from phase 1 to phase 2 and vice versa. Based on such considerations it becomes clear that the decrease in the system's size R may lead to a situation in which the phase with smaller surface tension becomes more probable and stable. Thus, size constraints may be the main reason for the formation of a metastable instead of a stable (from the macroscopic point of view) phase.

The second argument, which is equally important for nanosystems but usually disregarded, is related to nucleation, i.e. the formation of a new phase inside the initially supersaturated ambient phase. Nucleation implies the reconstruction of the structure of the system and yields the appearance of a new interface (with corresponding values of σ_{12}). Owing to the competition between bulk driving force and surface terms, the Gibbs free energy required to form a nucleus of a new phase goes through a maximum G_c (the so-called nucleation barrier). Here, the size of the nucleus – corresponding to the maximum (maximum points in Figs. 3 and 4) or more generally to the saddle-point of the thermodynamic potential – is called the critical size of the new phase nucleus and does not coincide with the transition size R^* of the whole system as defined above. If the value G_c is very high compared with the energy of thermal motion $k_B T$ (where k_B is the Boltzmann constant and T is the temperature of the system), then a phase transition via homogeneous nucleation is impossible. Since the above-mentioned (interface and external) surfaces exist at the transition, they will affect the value of G_c, and it is thus to be expected that as the surface energies contribute to the size-dependent transition temperature, they will play an important role in the transition of nanoparticles.

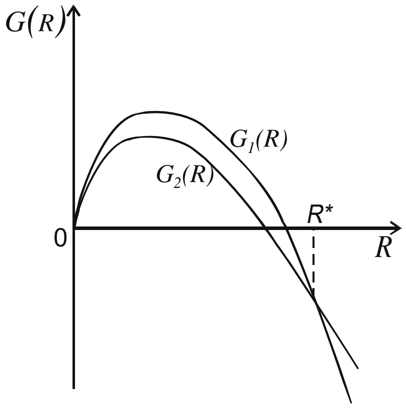

Fig. 1. Qualitative representation of the size effect on the change of phase equilibrium conditions. R^* is a system's transition size at which metastable phase 2 becomes stable.

Let us assume that a small, isolated, initially supersaturated particle of a given alloy exists as α-phase and then is quenched into the two-phase region (say, α-phase is stable at low temperatures, whereas the β-phase exists at higher ones). Then a phase transition may take place from the single α-phase state: (i) to the β-phase state, say at temperature T_1; and (ii) to a two-phase $\alpha + \beta$ state, say at temperature T_2. A single nucleus of a new phase can form inside the particle as shown on Fig. 2.

It is now possible to evaluate the Gibbs free energy of the corresponding transition. The reasoning is based on the calculation of the temperature variation of the Gibbs free energy for the involved phases, $G(T)$, performed under isobaric conditions. Let N_0 be the number of atoms in the particle. At fixed temperature T, the total energy, $G\alpha$ of the initial α-phase nanoparticle is given by:

$$G_\alpha = N_0 g_{\infty\alpha} + f_\alpha N_0^{2/3}\sigma_\alpha \tag{2}$$

In this equation, $g_{\infty\alpha}$ is the bulk Gibbs free energy density of the α-phase, σ_α is the surface tension (related to one surface atom), $f_\alpha N_0^{2/3}$ is the number of surface atoms, and f_α is the shape factor. In a similar way one can write the Gibbs free energy of the transformed (into β-phase) nanoparticle:

$$G_\beta = N_0 g_{\infty\beta} + f_\beta N_0^{2/3}\sigma_\beta \tag{3}$$

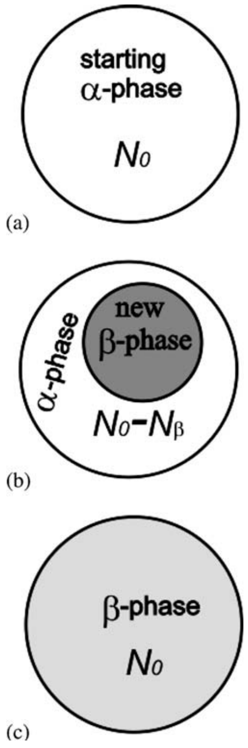

Fig. 2. Transition modes: (a) initial nanoparticle with α-phase inside; (b) the same particle after the nucleation of the β-phase; (c) the same particle after the polymorphic α–β transition. N_0 is the number of atoms in a given particle.

where the symbol β refers to the β-phase.

On the other hand, if such first-order phase transition (from α-phase to β-phase) takes place it should proceed via nucleation. This means that when the new phase crystal nucleates, the Gibbs free energy dependence has to be written for the $\alpha + \beta$ configuration shown on Fig. 2b. We get:

$$G_{\alpha\beta} = N_\alpha g_{\infty\alpha} + N_\beta g_{\infty\beta} + f_\alpha N_\alpha^{2/3}\sigma_\alpha + f_\beta N_\beta^{2/3}\sigma_{\alpha\beta}, \tag{4}$$

where N_α and N_β are the number of atoms in the α- and β-phases, respectively; $g_{\infty\beta}$ is the bulk energy density of the β-phase; and $\sigma_{\alpha\beta}$ is the interfacial tension at the boundary of the α-phase and β-phase. In addition, one has to take into account the conservation of matter in the considered finite system, i.e.

$$N_\alpha + N_\beta = N_0 \tag{5}$$

The change in the Gibbs free energy ΔG of the nanoparticle related to the formation of a new nucleus is then:

$$\Delta G = G_{\alpha\beta} - G_\alpha = N_\beta(g_{\infty\beta} - g_{\infty\alpha}) + f_\beta N_\beta^{2/3}\sigma_{\alpha\beta} \tag{6}$$

The condition that the Gibbs free energy of the whole system is equal to the free energy of the initial single-phase state can be taken as the $\alpha \to \beta$-phase transition criterion (which gives the system's transition size R^* if nucleation is omitted from the account).

For the following thermodynamic discussion, we need to specify the specific interfacial energy $\sigma_{\alpha\beta}$ between the two phases. In experiments, $\sigma_{\alpha\beta}$ is a poorly determined quantity. For qualitative estimations, the absolute value of this quantity is not necessary, and we can write in our case of the α–β interface the relation:

$$\sigma_{\alpha\beta} \approx |\sigma_\beta - \sigma_\alpha| \tag{7}$$

The qualitative estimation Eq. (7) is related to the coherence between α-phase and the β-phase, yielding a small interface energy $\sigma_{\alpha\beta}$, and it also corresponds to the Fe system, which we want to use in the third part of the work for the kinetic analysis [20–24]. We assume in agreement with experimental data that $\sigma_{\alpha\beta}$ is only slightly dependent on temperature and we neglect such dependence. In contrast, we use a nonlinear temperature dependence of bulk driving force for the phase transition. The bulk driving force obeys a quadratic law as:

$$(g_{\infty\beta} - g_{\infty\alpha}) = AT^2 + BT + C \tag{8}$$

where the parameters A, B and C are fitting constants which can be determined from experimental data. This relation is a direct consequence of a Taylor expansion with respect to temperature including second-order terms and can be employed, in particular, for the description of a polymorphic transforming Fe system discussed as an example in the further analysis (see Refs. [20–24] and references therein). The relation (8) includes the effect of stress energy as well. It is also important for the understanding of first-order phase transitions at low temperatures [25].

2.2. Results

2.2.1. Polymorphic phase transition temperature in a bulk system

Having outlined the basic features of the thermodynamic model, we can now perform a theoretical evaluation of the size-dependent temperatures of the structural phase transitions of nanoparticles.

At the structural transition for bulk system, $G_\beta = G_\alpha$, $N_0 \gg N_0^{2/3}$ and $g_{\infty\beta} - g_{\infty\alpha} = 0$ holds. This relation represents the conditions for phase equilibrium. It turns out that the bulk transition temperature for a macrosystem, T_∞, should then satisfy:

$$T_\infty^2 + \chi T_\infty + \eta = 0 \tag{9}$$

Here $\chi = B/A$ and $\eta = C/A$ and the solution of the quadratic equation Eq. (9) for T_∞ gives the interrelations between T_∞ and the parameters A, B, and C as:

$$\begin{aligned} T_\infty &= -\chi/2 \pm 0.5(\chi^2 - 4\eta)^{1/2} \\ &= -0.5B/A \pm 0.5(B^2 - 4AC)^{1/2}/A \end{aligned} \tag{10}$$

From these two values one must choose the one which corresponds to the experimental value T_∞ in a given temperature interval and represents the physically reasonable solution.

2.2.2. Polymorphic phase transition temperature in a nanosystem

The value of T_∞ determines the polymorphic phase transition temperature for a macroscopic system. Let us now analyze how this temperature changes in samples of finite size.

The system is considered to be an isolated metal sphere at uniform temperature, in a state of mechanical equilibrium. Gravitational effects are neglected. At the $\alpha \to \beta$ structural transition point for a nanosystem totally transformed from α-phase to β-phase, $G_\beta - G_\alpha = 0$ [8,26] holds. Due to this transition criterion one can find the transition size R^* for transforming particles, which determines the limiting transition temperature T_1. The case when the α-phase has the same free energy as the β-phase gives the condition that the difference between the Gibbs free energy of the initial, entirely α-phase, and final, entirely β-phase, vanishes. This leads to:

$$N_0(g_{\infty\beta} - g_{\infty\alpha}) + N_0^{2/3}(f_\beta\sigma_\beta - f_\alpha\sigma_\alpha) = 0 \tag{11}$$

It turns out that the transition temperature T_1 for a given nanosystem is found from the equations:

$$T_1^2 + \delta_1 T_1 + \mu_1 = 0 \tag{12}$$

$$\delta_1 = \chi = B/A, \quad \mu_1 = C/A + N_0^{-1/3}(f_\beta\sigma_\beta - f_\alpha\sigma_\alpha)/A$$

resulting in:

$$T_1(N_0) = (\delta_1/2 \pm 0.5(\delta_1^2 - 4\mu_1)^{1/2} \tag{13}$$

It is easy to show that this formula can be represented to depend on the size of the sample. The respective equation is:

$$T_1(N_0) = -0.5B/A \pm 0.5\left\{[B/A]^2 - 4\left[C/A + N_0^{-1/3}(f_\beta\sigma_\beta - f_\alpha\sigma_\alpha)/A\right]\right\}^{1/2} \quad (13a)$$

This relation is similar to the Thomson equation for melting with contribution from the surface energies of both phases [4,6,9,27]. It leads in the limit of large sample sizes to the macroscopic result, Eq. (10); i.e.

$$T_1(N_0 \to \infty) \cong -0.5B/A \pm 0.5\{[B/A]^2 - 4[C/A]\}^{1/2} = T_\infty \quad (14)$$

The quantity $T_1(N_0)$ is important for the understanding of the behaviour of a transforming nanosystem and usually has the form given by Eq. (1) for melting of nanoparticles.

One can introduce the notion of size-induced "critical supercooling" (size-induced "critical superheating") as the difference between the temperatures defined via the transition criterion in a nanomaterial and in bulk: $\Delta T^* = T_1 - T_\infty$. We see from Eq. (13) that size-induced "critical supercooling" is a thermodynamic characteristic which depends on system parameters and the size of the system. The notion of critical supercooling implies that a phase transition is possible only (at some fixed size) if the supercooling $\Delta T = T - T_\infty$ is larger than ΔT^*. If the supercooling is less than this critical value $\Delta T < \Delta T^*$, then a transition is prohibited. In other words, a phase transition may occur in a given nanosystem only beyond a certain "critical supercooling" larger than the macroscopic one. A similar notion of size-induced "critical supersaturation" was introduced by the authors in the thermodynamic analysis of the problem of phase separation in solutions of nanosizes taking into account redistributions of the atoms [1,28]. A similar situation exists for the nucleation in pores [1,14,29].

2.2.3. Two-phase states in a nanosystem

We now investigate the possibility of a two-phase state appearance in a nanosystem. Such a situation may occur when the inequality $\Delta G = G_{\alpha\beta} - G_\alpha \leqslant 0$ holds. It corresponds to the case of equal free energies of the initial α-phase state and the two-phase $\alpha + \beta$ state. It is worth noting that it does not mean that the $\alpha + \beta$-phase state is the thermodynamically stable one (the situation is similar to that shown in Fig. 1 at the system's transition size R^*; see below) because the equality of Gibbs free energies does not signify coexistence. The temperature T_2 is the temperature at which the necessary condition for the possibility of development of a $\alpha + \beta$ two-phase state becomes fulfilled. It leads to:

$$N_\beta(g_{\infty\beta} - g_{\infty\alpha}) + f_\beta N_\beta^{2/3}\sigma_{\alpha\beta} = 0 \quad (15)$$

It turns out that the temperature T_2 for a nanosystem can be found from:

$$T_2^2 + \delta_2 T_2 + \mu_2 = 0 \quad (16)$$

$$\delta_2 = B/A, \quad \mu_2 = C/A + N_\beta^{-1/3}(f_\beta\sigma_{\alpha\beta})/A$$

A detailed analysis shows that the temperature T_2 depends on T_∞ and varies with N_β in the following way:

$$T_2 = -0.5B/A \pm 0.5\{[B/A]^2 - 4[C/A + N_\beta^{-1/3}(f_\beta\sigma_{\alpha\beta})/A]\}^{1/2} \quad (17)$$

Again, in the limit, when $N_\beta \to \infty$, we obtain $T_2 = T_1 = T_\infty$. Hence, in accordance with the law of conservation of matter, Eq. (5), $N_\beta \leq N_0$ in the above-mentioned case, and the condition $N_0 \to \infty$ is fulfilled as well. This means that in the bulk system the condition for the appearance of a two-phase state coincides with the phase transition condition.

2.2.4. Work of cluster formation for nucleation in macroscopic and nanosized samples

In accordance with the classical theory of nucleation, the free energy change ΔG_{cl} related to the $\alpha \to \beta + \alpha \to \beta$-phase transition in bulk material, at T_∞, may be estimated by the relation:

$$\Delta G_{c1} = N_\beta(g_{\infty\beta} - g_{\infty\alpha}) + f_\beta N_\beta^{2/3}\sigma_{\alpha\beta} \quad (18)$$

The Gibbs free energy change related to the formation of a critical nucleus of a new phase ΔG_c (nucleation barrier) is calculated from the condition $(\partial\Delta G_{cl}/\partial N_\beta) = 0$:

$$\Delta G_c = (4/3)\{f_\beta\sigma_{\alpha\beta}\}^3/\{g_{\infty\alpha} - g_{\infty\beta}\}^2 \quad (19)$$

This maximum is reached at a critical nucleus size. The critical size of the nucleus is determined as:

$$N_{\beta c} = \{(2/3)f_\beta\sigma_{\alpha\beta}/g_{\infty\alpha} - g_{\infty\beta}\}^3 \quad (20)$$

In the case of nucleation in a nanosystem, the change in the Gibbs free energy ΔG, related to the $\alpha \to \beta$-phase transition, must be estimated by Eq. (6). From this, one can find the free energy barrier from the condition $\partial\Delta G/\partial N_\beta = 0$, $\partial^2\Delta G/\partial N_\beta^2 < 0$. Here, N_β has values in the interval from 0 up to N_0. The nucleation barrier, as well as the number of atoms in the critical nucleus, have the same form as expressed by Eqs. (19) and (20), respectively. The difference between nucleation in nanosystems compared to bulk samples is caused by the fact that nucleation and phase transition become impossible for particles consisting of fewer particles than the number of atoms in the critical nucleus of the new phase, i.e. $N_{\beta c}$ atoms (when $N_0 < N_{\beta c}$).

2.2.5. The influence of varying T and N_0 on ΔG

Let us now consider Eq. (6) in more detail and plot the dependence of ΔG on N_β at different fixed values of T and N_0. The results of the computations are shown in Figs. 3 and 4. They represent general thermodynamic qualitative

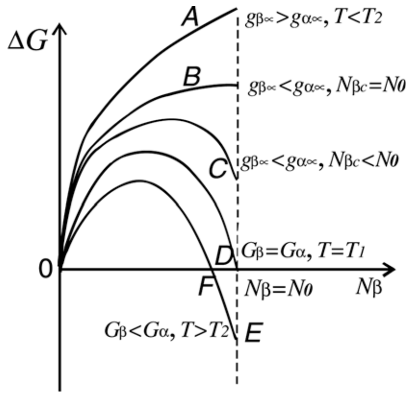

Fig. 3. Qualitative dependences of energy change for polymorphic transition in a nanoparticle. Zero point denotes the initial α-phase; points *A*, *B*, *C*, *D*, and *E* correspond to the β-phase (for the details, see the main text).

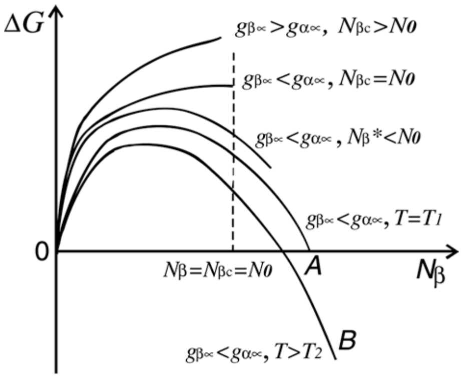

Fig. 4. Qualitative dependences of energy change for a polymorphic transition in the nanoparticle. Zero point denotes the initial α-phase; points *A* and *B* correspond to the β-phase state (for the details, see the main text).

results that should occur independently of the particular properties of any real material.

Let us look in detail first at the effects of variation of the temperature of the nanoparticles on the driving force $g_{\infty\alpha} - g_{\infty\beta}$ and ΔG by investigating the dependence of Eq. (6), taking into account the nucleation conservation of matter (Eq. (5)). Typical ΔG vs. N_β curves corresponding to the same fixed number of atoms N_0 and other parameters except T are shown in Fig. 3. The different curves are drawn at the following conditions: 0*A*, phase transition is impossible when $g_{\infty\alpha} - g_{\infty\beta} < 0$; 0*B*, phase transition is impossible, the critical nucleus size $N_{\beta c}$ coincides with the total number of atoms N_0 in the nanoparticle; 0*C*, an α–β-phase transition into the metastable β-phase state occurs at point C; 0D, an α→β-phase transition takes place at $T = T_1$ at point D when $N_{\beta c} < N_0$ and $G_\beta = G_\alpha$; 0*FE*, a phase transition occurs at a high temperature $T > T_2$ into the stable β-phase. Note that the point F corresponds to the transition criterion at $T = T_2$ for appearance of a two-phase state in a nanosystem, when $\Delta G = G_{\alpha\beta} - G_\alpha = 0$. At the same time the α + β-phase state at point F is an unstable state; the only stable state is the β-phase at point E. Note also that Fig. 3 may be considered for different interfacial energies $\sigma_{\alpha\beta}$ as well as the ΔG curves with other parameters being fixed and $g_{\infty\alpha} - g_{\infty\beta} < 0$.

Next we discuss the dependence of the behaviour of the system for different values of N_0 and otherwise constant values of the parameters, i.e. we analyze the size effect. In Fig. 4 we plot the qualitative dependences of energy of transition ΔG on the size of the nucleus N_β when the other parameters are fixed. Each curve is drawn for different values of N_0. As it is shown, when N_0 has values below a critical number $N_{\beta c}$, nucleation is impossible. Thus, the limited volume of the nanopowder particles constrains the fluctuations of the new phase, and allows one to keep the alloy nanosystem in a state that would have been unstable in a bulk sample. Another thermodynamic result, illustrated in Figs. 3 and 4, consists of the existence of three possibilities: (i) the prohibition of phase transition for small particles (e.g. cases *OA*, *OB* in Fig. 3); (ii) the possibility of metastable states in small volumes instead of stable ones in the same bulk system (e.g. case *OC* in Fig. 3); (iii) the possibility of phase transition into the stable phase due to nucleation (e.g. cases *OE* in Fig. 3 and *OB* in Fig. 4).

3. Polymorphic transitions at temperature cycling in an ensemble of nanoparticles: basic kinetic model

3.1. The model

The previous discussion was devoted to a thermodynamic description of polymorphic transitions in a single nanoparticle. Under experimental conditions, one generally deals with a large number of particles. In order to be able to interpret the behaviour of such ensembles, one has to study the phase transition of an ensemble of nanoparticles using statistical approaches, i.e. it is necessary to introduce size distribution functions with respect to particle sizes of the ensemble of nanoparticles and with respect to the sizes of the aggregates forming in them (cf. Fig. 5). In the present analysis, we will assume that the nanoparticles are characterized by a monodisperse size distribution.

The ensemble of nanoparticles is subjected to a cyclic change of temperature. We will study here the behaviour of the system at such temperature cycling. In the case considered, the temperature T will change in time as a linear function with constant rate $|dT/dt| = const$ for cooling and heating. First, we start from the single-phase state at high temperatures T (Figs. 2 and 5) and then decrease the temperature at a finite rate (cooling). We then stop the temperature change at some point, when the alloy is quenched into the two-phase region (curve *OFE* in Fig. 3 or curve *OB* in Fig. 4), and reverse the direction of change of temperature, i.e. increase the temperature (heating) at the same rate. One cycle refers to a complete change in temperature from some initial value back to the same point. From these considerations, we may determine $T = T(t)$ and, as a consequence, the Gibbs free energy change (Eq. (6)) may be expressed as the function of time (via the time

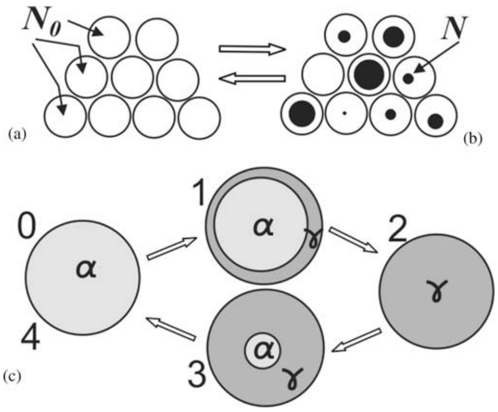

Fig. 5. Schematic representation of a polymorphic transition in a nanopowder during temperature cycling: (a) ensemble of particles of N_0 size before transformation; (b) the same particles after the new phase formation; (c) the schematic representation of one complete α-Fe → γ-Fe → α-Fe circle for one particle of the Fe nanopowder. N is the number of the atoms in the newly formed phase; it is assumed here that in each nanoparticle only one aggregate of the new phase can be formed.

dependence of temperature and, correspondingly, the bulk driving force):

$$\Delta G(N_\beta) = \Delta G(N_\beta, T) = \Delta G(N, t). \tag{21}$$

3.2. Kinetic equations

The corresponding "decoding" of "back and forth" transformation is performed here within the framework of the kinetic equation approach. For these purposes, we introduce a size distribution function $f(N,t)$ being equal to the number of new phase nuclei, consisting at time t of N atoms. The evolution of the ensemble of such clusters formed by nucleation and growth processes will be described by the standard kinetic equation of the theory of nucleation-growth processes:

$$\frac{\partial f(N,t)}{\partial t} = f(N-1,t)\cdot v_+(N-1) + f(N+1,t)\cdot v_-(N+1) - f(N,t)\cdot(v_-(N)+v_+(N)) \tag{22}$$

The frequencies of attachment $v_+(N) \equiv v_+(N, T)$ and detachment $v_-(N) \equiv v_-(N, T)$ of atoms to a cluster of size N are interrelated as:

$$v_-(N,T) = v_+(N,T)\exp\left(\frac{\Delta G(N,T) - \Delta G(N-1,T)}{k_B T}\right) \tag{23}$$

The value $\Delta G(N)$ is determined by Eq. (6).

Further, the quantity $v_+(N)$ will be assumed to be proportional to the surface of the nucleus $v_+(N) = D \cdot N^{2/3}$. Here, D is a constant of the material and depends on the shape of the nucleus and the mechanisms of nucleation.

The conservation of number of particles results in boundary conditions for the cluster size distribution function $f(N,t)$. As mentioned, we assume that in one nanoparticle only one nucleus can appear. Hence, one may write both the boundary and initial conditions as:

$$f(N_{\min},t) = Z - \sum_{N=N_{\min}+1}^{N_{\max}} f(N,t),\ \ f(N,t=0) = \begin{cases} Z, N = N_{\min} \\ 0, N \neq N_{\min} \end{cases} \tag{24}$$

where $N_{\min}$ is the minimum number of atoms in the nuclei, $N_{\max} = N_0$ is the maximum possible number of atoms in each particle, and Z is the number of particles in the nanopowder. Because of the constraint on the number of atoms in the nucleus of the new phase, the size distribution function on the right boundary $N = N_{\max}$ was calculated from Eq. (22) as:

$$\frac{\partial f(N_{\max},t)}{\partial t} = f(N_{\max}-1,t)\cdot v_+(N_{\max}-1) - f(N_{\max},t)\cdot v_-(N_{\max}) \tag{25}$$

The main task we would like to solve with this kinetic model is to describe the volume fraction ρ of the new phase during the temperature cycling of the non-interacting nanoparticle ensemble. This value is determined by the formula:

$$\rho = \frac{\sum_{N=N_{\min}}^{N_{\max}} N\cdot f(N,t)}{N_0 Z}. \tag{26}$$

In fact, we shall compute the evolution of the volume fraction ρ in the process of temperature cycling with different fixed constant cooling and heating rates $v=|dT/dt|$ assuming different sizes N_0 of the particles in the ensemble where the transition occurs.

3.3. Equilibrium statistical distribution

At equilibrium, when the temperature T is fixed, in the nanopowder some particles will be in single-phase states, and the others in two-phase states (Fig. 2a and b). The corresponding number of particles, $f_{eq}(N,T)$, may be found by the Boltzmann distribution in the statistical mechanical sense:

$$f_{eq}(N,t) = \frac{Z}{\sum_{N=N_{\min}}^{N_{\max}} \exp(-\Delta G(N,T)/k_B T)} \cdot \exp(-\Delta G(N,T)/k_B T) \tag{27}$$

In this case, the thermodynamic observables of the system become averaged over the equilibrium distribution, Eq. (27). From this, one can find the equilibrium value for the volume fraction ρ of the new phase at any fixed T as:

$$\rho_{eq} = \frac{\sum_{N=N_{\min}}^{N_{\max}} N\cdot f_{eq}(N,t)}{N_0 Z} \tag{28}$$

3.4. Specification of the parameter values

In the following, we will apply the theory and kinetic model outlined in Section 2 to the case of phase coexistence and phase transformations between the γ-Fe and α-Fe crystallographic phases. It is well known that in bulk solid state pure Fe can exist in three crystallographic modifications: α-phase (body-centred cubic (bcc)), γ-phase (face-centred cubic) and δ-phase (also called by some authors α-phase, bcc). The α-Fe phase appears within the temperature interval $T < 1183$ K. For $1183\text{ K} < T < 1665$ K, γ-Fe is more preferable, and for $T > 1665$ K up to the melting point the δ-phase appears. This means that in the bulk case the energy of α-Fe at T < 1184 K is lower than that of γ-Fe.

One can estimate the energy barrier for the nucleation of γ-Fe from α-Fe. Taking for bulk Fe material the well-known data [20,30], namely $|n\cdot(g_{\infty\alpha} - g_{\infty\gamma})| = 1.2 \times 10^8\text{ J m}^{-3}$, atomic density $n = 8.58 \times 10^{28}\text{ m}^{-3}$ and $\sigma_{\gamma\alpha} = 4 \times 10^{-2}\text{ J m}^{-2}$, one obtains the energy barrier value $\Delta G_c = 7.424 \times 10^{-20}$ J and the critical nucleus size $R_c = 6.64 \times 10^{-10}$ m. This leads to an estimate of the number of atoms $N_{\alpha c}$ in the critical nucleus of the order $N_{\alpha c} = 4/3\pi\{R_c\}^3 n \approx 103$ atoms. For a more precise quantitative analysis one has to know the temperature dependence of free energy density for this transformation. Using experimental data, we approximated the bulk driving force by a parabolic dependence as shown in Fig. 6.

Employing the above-mentioned considerations, the corresponding set of parameters of the Fe system have been obtained and then employed in the computations: $n = 8.58 \times 10^{28}\text{ m}^{-3}$, $\sigma_{\alpha\gamma} = 0.04\text{ J m}^{-2}$, $\sigma_\alpha = 2.21\text{ J m}^{-2}$, $\sigma_\gamma = 2.17\text{ J m}^{-2}$, $f = 2.486 \times 10^{-19}\text{ m}^2$, $\Delta g = g_{\infty\gamma} - g_{\infty\alpha} = k_B(-0.00365T^2 - 10.3952T + 7191.1424)$ J, $k_B = 1.38 \times 10^{-23}\text{ J K}^{-1}$ [20–24,30]. The order of rates of cycling are taken as $\upsilon_1 = 0.04\text{ K s}^{-1}$, $\upsilon_2 = 0.02\text{ K s}^{-1}$ and will be specified in each simulation; the constants for numerical simulation are: $D = 10^{11}\text{ s}^{-1}$, $N_{\min} = 1$, $Z = 10^{10}$.

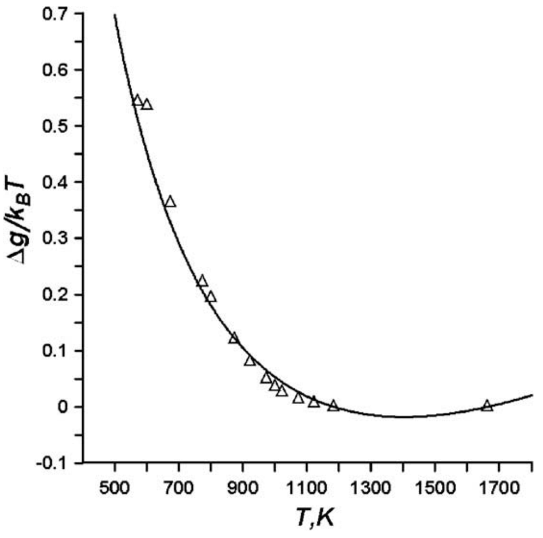

Fig. 6. Experimental points (Δ) of different authors [20–24] for the γ-Fe to α-Fe transformation and the parabolic approximation $\Delta g = g_{\infty\alpha} - g_{\infty\gamma} = A\ T^2 + B\ T + C$ for the bulk driving force of the transformation (solid curve) employed here in the calculations.

4. Competition of different Fe-phases during temperature cycling and size-induced hysteresis

4.1. Hysteresis of γ-Fe to α-Fe transformation: size effects

The change in the volume fraction of newly formed α-Fe during temperature cycling as obtained by the theoretical method (Eq. (28)) as outlined in Eq. (26) above is presented in Fig. 7. It clearly exhibits a new result: a size-induced hysteresis of the γ-Fe → α-Fe → γ-Fe transformation. Fig. 7 shows the different hysteresis loops in the volume fraction vs. temperature diagram. Our model shows that the width and shapes of hysteresis loops depend on N_0, dT/dt, σ and D. In particular, we traced the influence of the system's size N_0 on the hysteresis loop. It turned out that the greater is the size of a system, the greater is the effective width of

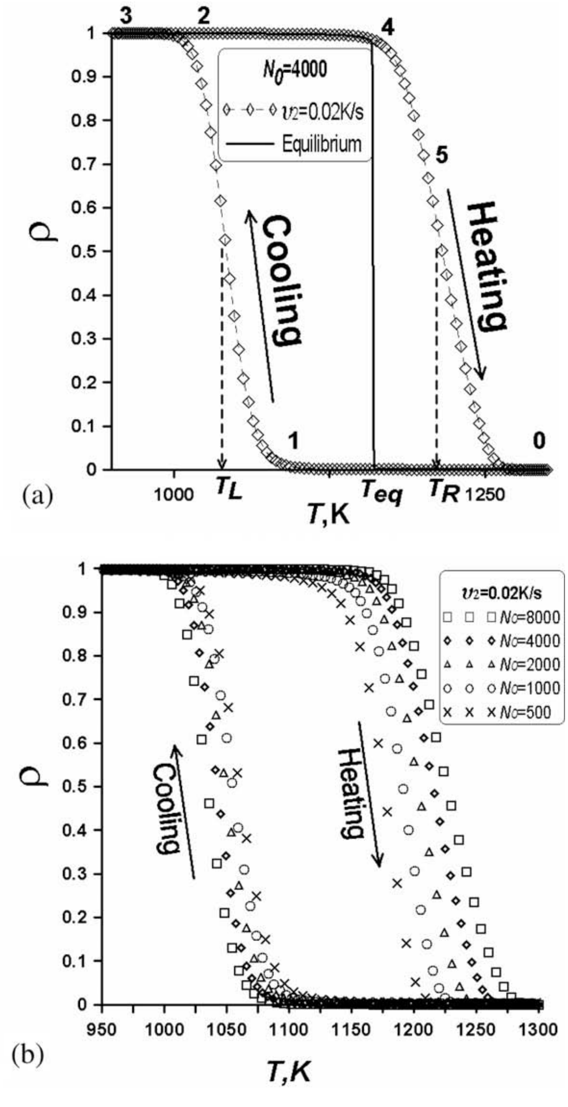

Fig. 7. Effect of size on hysteresis: loops for the fixed rate $\upsilon_2 = 0.02\text{ K s}^{-1}$ of temperature cycling of Fe nanoparticles between 1300 and 950 K and different numbers of atoms in the particles: ×, $N_0 = 500$; ○, $N_0 = 1000$; Δ, $N_0 = 2000$; ◇, $N_0 = 4000$; □, $N_0 = 8000$. The solid curve ρ represents the equilibrium values ρ_{eq} from Eq. (24) for each fixed temperature.

the hysteresis loop at the same rate of cooling (respectively, heating), υ (Fig. 7b).

As was mentioned concerning first-order phase transitions, a minimum undercooling and superheating (dependent on the cooling rate) are needed for the formation of the new phase. The new result here is the fact that these critical undercoolings and superheatings are functions of the size of the nanoparticles as well.

In more detail, the temperature cycling of a Fe nanopowder, 1300 K → 950 K → 1300 K, leads to a loop-like $\rho(t)$ curve – the evolution path 0123450 in Fig. 7a. Here, one may distinguish the following stages: 01, supersaturated single-phase states (parent γ-Fe phase) of the nanopowder (see also Fig. 5a); 12, phase transition from the point 1 of single-phase states to a two-phase states (parent γ-Fe phase + new α-Fe phase) at point 2 (this event indicates nucleation) due to two-phase α-Fe + γ-Fe phase states; 34 and 45, cooled and/or superheated two-phase α-Fe states; 50, back-transition from α-Fe phase states at point 5 to α-Fe + γ-Fe states and then to γ-Fe phase states.

Let us introduce the phase transition criterion into the kinetics of considered process. For this we assume that a phase transition did proceed when half of the volume is transformed, i.e. when $\rho = 0.5$ is reached. This criterion determines the value of the transition temperature T_L at the left branch of the hysteresis loop, and similarly T_R at right branch. The difference T_R–T_L is the width of the hysteresis loop, which is a function of size and the rate υ (Figs. 7 and 8). For the first time, as far as we know, the tendency of a narrowing of the hysteresis loop with a decrease in the size of a system (at a given rate of change of external parameters) is observed here in the kinetics of a polymorphic transformation. The respective results are presented in Fig. 8.

If one extrapolates similar arguments concerning a phase transition criterion for the equilibrium volume fraction of the new phase, $\rho_{eq} = 0.5$, then one obtains the temperature of this transition, T_{eq}, related to the equilibrium distribution (Eqs. (27) and (28)). Generally speaking, T_{eq} is defined from the thermodynamically averaged value ρ_{eq} and due to this fact it represents the averaged transition temperature and also depends on the size of the particles in a nanopowder (cf. Fig. 8). The approximation of corresponding points in Fig. 8 (indicated by symbols ×) by one curve gives the fit function:

$$T_{eq} = 1183(1 - 0.31/N_0^{-1/3}) \quad \text{or} \quad T_{eq} = T_\infty(1 - 4.27 \times 10^{-11}/R) \tag{29}$$

Eq. (29) shows the stabilization of γ-Fe phase at small sizes. Recently the size effect on the Fe nanocrystalline phase transformation by means of dilated crystal model in thermodynamics has been described in terms of excess volumes [31]. The effect of interface energy on the stability of γ-Fe at room temperature was emphasized. Our result coincides with this finding, in which the authors showed that the γ-Fe phase can stably exist in nanocrystalline Fe at 300 K when its grain size is below about 50 nm.

Similar results have been reported for the competition and growth of different crystallographic phases during the crystallization process in limited volumes of liquid and in the case of phase equilibrium in two-phase stressed coherent solids using direct thermodynamic equilibrium conditions [32,33].

4.2. Effect of rate $dT/d\tau$ on hysteresis curve

In Fig. 9, the hysteresis curves are shown for different rates of change of temperature at otherwise identical conditions. As can be seen, the width of the hysteresis loop T_R–T_L, i.e. the effective distance between left and right branches of the curve $\rho(t)$ in intermediate temperature intervals, depends on the rate of temperature change, i.e. the greater the rate υ, the bigger is the effective width of hysteresis loops. As the value of υ decreases, the hysteresis loop narrows. The dashed lines connecting the different experimental points are the approximations derived from the corresponding formula devoted to a statistical generalization of the presented results:

$$(T_R - T_L)/T_{eq} \approx \ln(N_0)\{a + b\upsilon^{1/2} + c\upsilon^{2/5}\} + \{d\upsilon 1/2 + e\upsilon^{2/5}\} + h,$$

where the values a, b, c, d, e, h are the same constants for all realizations.

The statistical generalization of the critical superheating, defined as $\delta_R = (T_R - T_{eq})/T_{eq}$, gives the approximation: $\delta_R \approx ln(N_0/12)\{p_1 + p_2\upsilon^{1/2}\} + p_3$. Here $\mathrm{p}_1 = 2.94 \times 10^{-4}$, $\mathrm{p}_2 = 5.47 \times 10^{-2}$, $\mathrm{p}_3 = 2.2 \times 10^{-3}$.

For the critical supercooling, $\delta_L = (T_{eq} - T_L)/T_{eq}$, this study yields: $\delta_L \approx ln(N_0/2)\ \{p_4 + p_5\upsilon^{2/5}\} + p_6$ with $p_4 = 4.94 \times 10^{-3}$, $p_5 = 5.31 \times 10^{-2}$, $p_6 = -1.9 \times 10^{-2}$.

It can also be observed that the hysteresis characterizes the nonsteady behaviour of the transforming system and the ρ value is not equal to ρ_{eq}. If we stop and fix T, then

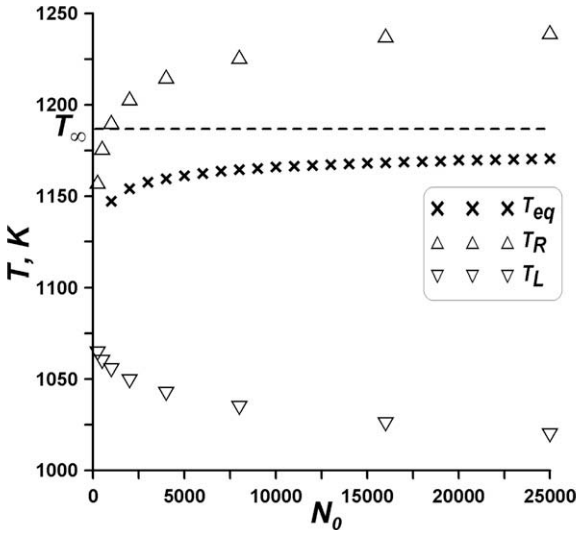

Fig. 8. Size-induced temperature dependences of the phase transition in Fe nanopowder at fixed rate $\upsilon_2 = 0.02\ \mathrm{K\ s^{-1}}$: ×, the values of T_{eq} from the number of atoms N_0 in each particle of the nanopowder; Δ, the superheating temperatures T_R; ▽, the values of T_L.

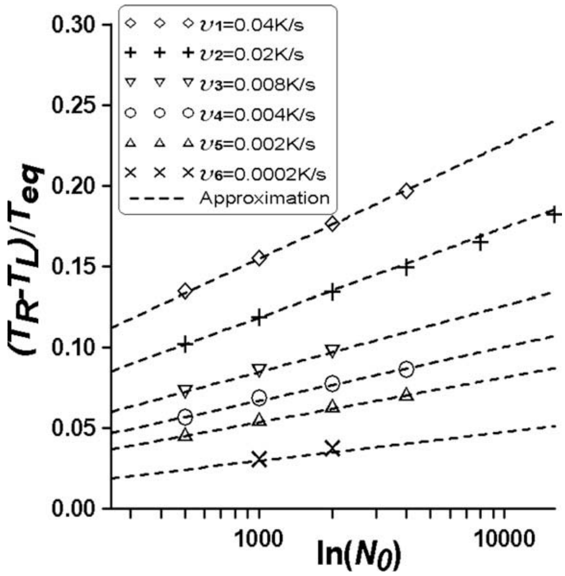

Fig. 9. Representation of the hysteresis effect in powder of nanosized Fe particles related to the finite size and temperature cycling between 950 and 1300 K: the specific width of thermal hysteresis for different fixed rates of temperature circling. The dashed lines connecting the different numerical simulation points are approximations derived from the common formula: $(T_R - T_L)/T_{eq} \approx ln(N_0)\{a + b\upsilon^{1/2} + c\upsilon^{2/5}\} + \{d\upsilon^{1/2} + e\upsilon^{2/5}\} + h$, where the values a, b, c, d, e, and h are the same constants for all realizations.

the solution of Eq. (22) begins to coincide with the equilibrium distribution function $f_{eq}(N,T)$ (Eq. (27)) and the value of ρ tends to the corresponding value ρ_{eq} given by Eq. (28).

5. Discussion and concluding remarks

In this paper, first, we presented a general thermodynamic analysis for nucleation of one nucleus in a nanoparticle. It is shown that three possibilities exist: occurrence of a polymorphic $\alpha\rightarrow\beta$-phase transition, prohibition of transformation and formation of metastable states. This model describes a size-induced change in the critical temperatures of phase transitions in small, isolated nanoparticles and is then applied to the γ-Fe to α-Fe polymorphic phase transformations.

Secondly, a kinetic model of polymorphic phase transformations in a nanopowder under temperature cycling is presented. For finite rates of temperature changes one observes hysteresis loops. Such hysteresis is demonstrated in the framework of a kinetic equation approach (recently one of the authors obtained similar results for the description of phase separation kinetics in a binary alloy by taking into account the concentration redistribution [15]). The computations show that the width of the hysteresis loop depends on the number of atoms in the particles of the powder, interfacial tension and the rate of temperature change. In particular, the greater the size of the Fe system and/or the rate of temperature changes, the greater is the width of the hysteresis loop and vice versa. As these values decrease, the hysteresis loop narrows.

It is worth noting that for the Fe system qualitative estimations from different experimental data give the relations for specific surface energies [20–24,30]. Such specification leads to the consideration of nucleation of the new phase occurring only inside the existing nanoparticle for the γ-Fe → α-Fe transformation and at the external boundaries of the particle for the α-Fe → γ-Fe transition. One can expect interesting possibilities if the nanoparticles transform due to different modes. For example, there are many other cases where the growth of the new phase occurs at the surface of the nanoparticle, so additional terms would appear in the thermodynamic expressions, including a three-phase contact line. In these cases the free energy curves could potentially cross more than once depending the values of the various surface tensions and line tension. The analysis of this problem in a general form is in progress and will be discussed elsewhere [34].

In contrast to these findings, in the experimental analyses performed by Alivisatos et al. the hysteresis width for polymorphic transition in the CdSe nanostructured system turns out to be almost independent of nanocrystal size, whereas our kinetic model and simulations predict a considerable increase in the width of the hysteresis loop with increasing particle size [17,18]. Why? This is the question we want to answer in future analysis. First, there is a difference between these problems. We treat the size-induced temperature hysteresis, whereas Alivisatos et al.'s group performed size-induced pressure hysteresis experiments. Secondly, we think that in the case of semiconductor CdSe nanocrystals, which Alivisatos et al. considered, the equilibrium conditions may be weakly dependent on the size. Also, in our opinion, the pressure change leads to the redistribution of grain sizes and the boundaries between grains.

Recent work indicates that for nanocrystals, the grain size variation of the transition temperature may exhibit two characteristic regions. This feature has been demonstrated for the case of nanocrystalline Ag [35]. In particular, as soon as the mean grain size is above about 4 nm, the melting temperature decreases with decreasing grain size and as the mean grain size becomes smaller than about 4 nm, the melting temperatures become almost keep constant. The corresponding explanation is based on the assumptions that: (i) a nanocrystal can be viewed as a composite of a grain boundary phase and an embedded grain phase; (ii) with mean grain size decreasing to a certain degree, the grain boundary phase becomes dominant in melting. A similar situation may be the reason for the peculiarities of the CdSe nanosystem.

Pure Fe exhibits a magnetic transformation at the Curie point $T_C = 1043$ K. This point is located inside the interval of cycling of 950–1300 K considered here. Therefore, it would be interesting to trace the cross-coupling of magnetic transformation and size-induced temperature hysteresis. This work is not included here and will be examined in due course. Nevertheless, some prior discussion may be done. It is known that the decrease in the size of the samples to the nanoscale can lead to an increase in the pressure inside the particle, a change in density and deformation. All these factors may become crucial for the shift of T_C. From this point of view, one may expect a para → ferro → para magnetic transformation due to simultaneous influence of the Laplace pressure and Curie point. Another interesting related phenomenon is the influence of the size-induced shift of the temperature of the fcc–bcc phase transition (T_L in Fig. 7). This may be the reason for the existence of low-temperature para- and ferromagnetic fcc γ-Fe.

On the other hand, co-operative orientation of spins in a material can result in magnetoelastic effects, e.g. in a change of the form of magnetic influence on thermal expansion (which is sensitive to the energy of atomic interaction) or on Young's modulus. In the latter case, there was even a relative decrease in the Young's modulus of about 400% for the alloy of Fe–Rh in the vicinity of the Curie point and in the temperature interval of the polymorphic transformation (cubic lattice → rhombic lattice) [36]. Hence one may expect that the magnetic transformation can change the shape of the phase hysteresis loop in the temperature interval at which the magnetic and phase transformations coincide (left branch of the hysteresis loop in Fig. 7). Thus, in our opinion, the size-induced phase and magnetic transformations must mutually influence each other.

It is also worth noting that the hysteresis shown is very similar to magnetic (such as paramagnetic–ferromagnetic) phase transitions under an applied magnetic field. This behaviour should allow one to use the size-induced hysteresis effect in a way similar to that of magnetic materials for a variety of applications such as high tech-DVD and CD technologies, coatings, shape memory systems and many other important applications.

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