ANISOTROPY AND SIZE DISTRIBUTION EFFECTS ON THE MAGNETIC PROPERTIES OF A SYSTEM OF FERROMAGNETIC NANOPARTICLES

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Effects of the random orientation of easy magnetization axes and the particle size polydispersity on the thermodynamic properties of a system of noninteracting magnetic nanoparticles have been studied in a three-dimensional model. The results are compared with those obtained in the framework of the classical Stoner–Wohlfarth model. The peak that is observed in the temperature dependence of the system magnetization has been shown to smear, if the orientation randomness and/or the dispersion of the particle size distribution increase.

1. Introduction

In the last two decades, a large attention in the domain of studying the magnetic materials has been paid to nano-sized systems. This interest is related, first of all, to the opportunity for a wide technological application of those objects to various branches of human life, and magnetic nanoparticles have a lot to do with it [1]. One of the promising technologies is an increasing of the magnetic recording density of information. It suggests a transition from the magnetic recording technique used nowadays, which allows one to create carriers with a record density of 100–200 Gb/sq. in., to a technology of "discrete bits", which can increase the record density by an order of magnitude [2]. An interest of modern medicine to magnetic nanoparticles should also be noted, in particular, as the components of contrast substances for magnetic resonance tomography [3] or as drug carriers toward affected sites of the body [4]. Such substances are also required from the viewpoint of their applications to chemical and other industrial branches.

Theoretical researches in this domain were started in the middle of the last century by such scientists as Néel, Bean, Stoner, Wohlfarth, and others [5–7]. Among the first papers, where the possibility for a single-domain state in nanoparticles to exist was substantiated, there was Frenkel and Dorfman's work [8], where the critical dimensions of ferromagnetic specimens, below which no ferromagnetic state can be formed in the specimen, were estimated to be of the order of tens of nanometers. For example, it is experimentally confirmed that spherical particles of nickel remain single-domain up to a diameter of 80 nm [9]. If particles in the specimen are larger, a multidomain structure can be formed.

The mechanism of magnetic reversal of single-domain particles by means of the coherent rotation of magnetic atoms was suggested by Stoner and Wohlfarth in 1949 [7]. In this case, a totality of atomic magnetic moments in a nanoparticle can be replaced by a single supermoment.

The subject of our inquiry is a system of magnetic nanoparticles embedded into a solid-state non-magnetic matrix. Note that, since particles cannot move free – in contrast to ferrofluids, i.e. ferroparticles in a liquid medium – the magnetic anisotropy of a particle in the matrix plays an important role. We considered the simplest case of uniaxial anisotropy, when a certain direction characterized by the minimal energy of anisotropy for every particle exists. This direction is referred to as the easy magnetization axis or the anisotropy axis.

This work aimed at the transition from a simple model of the Stoner–Wohlfarth type to the description of more complicated systems which takes into account the effects of various distributions of anisotropy axis

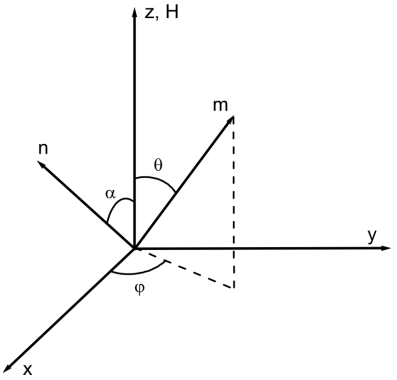

Fig. 1. A coordinate system for the description of a system of magnetic particles with the magnetic moment **m** and the anisotropy axis that is given by a unit vector **n**

orientations and the difference in the nanoparticle dimensions. We studied the influence of anisotropy in comparison with the effects of polydispersity on the magnetic properties of system in various temperature intervals. At this stage, we did no take into account internal thermal effects which are caused by the influence of the temperature on the dimension, anisotropy constant, and magnetic properties of a particle. The effects of particle-to-particle interaction, which can provoke a ferromagnet-paramagnet phase transition in the system of ferromagnetic particles, were also left beyond the scope of consideration.

2. Description of the Model

The model system Hamiltonian can be written down in the form

$$\mathcal{H} = -K\sum_i V_i \left(\frac{\mathbf{n}_i \cdot \mathbf{m}_i(T)}{m_i(T)}\right)^2 - \mu_0 \mathbf{H}\sum_i \mathbf{m}_i(T), \qquad (1)$$

where K is the anisotropy constant; V_i, $\mathbf{m}_i$, and $\mathbf{n}_i$ are the volume of the i-th particle, its magnetic moment, and a unit vector that determines the orientation of its anisotropy axis, respectively; **H** is the external magnetic field, and μ_0 is the magnetic constant. The first term describes the energy of magnetic anisotropy, while the second the energy of interaction between the magnetic moments of particles and the external magnetic field.

Let us choose a coordinate system (Fig. 1), in which the direction of the anisotropy axis coincides with the z axis, and the vector of external magnetic field strength is directed at an angle α with respect to Oz. Then, the angles θ and φ are the coordinates of the magnetic moment of a particle in the spherical coordinate system.

Let all particles be spherical. Consequently, we can neglect the shape anisotropy and consider only the crystallographic one. Another assumption concerns the dependence of the magnetic moment on the temperature. In the general case, $m(T) = m_s f\,(T/T_c)$, where m_s is the magnetic moment of a particle at zero temperature, T_c the Curie temperature for the particle, and f is a function that equals 0, if its argument equals 1, and 1, if its argument equals 0. At $T > T_c$, this function equals zero. Usually, the function $f(T/T_c)$ is supposed to be close to unity at temperatures up to $0.4T_c$ [10]. Therefore, the magnetic moment can be considered as temperature-independent at lower temperatures. In what follows, we assume that $f\,(T/T_c) \simeq 1$ and, correspondingly, $m = m_s$.

Before the consideration of more complicated models, let us define the simplest one, where all anisotropy axes are parallel to one another, $\mathbf{n}_i = \mathbf{n}$, and all particles are identical by dimensions. For this model, if we take into account all assumptions and definitions made above, Hamiltonian (1) can be rewritten in the form

$$\mathcal{H} = -\sum_i KV\left((\cos\theta_i\cos\alpha_i + \sin\theta_i\sin\alpha_i\cos\varphi_i)\right)^2 - \\ -\sum_i \mu_0 mH\cos\theta_i, \qquad (2)$$

where $\alpha_i = \alpha$. Model (2) will be used as a reference one to compare the results obtained for more complicated systems.

Let us introduce the following notations for the temperature, magnetic field strength, and volume of particles. The relative volume of particles will be designated as

$$v = \frac{V}{V_m}, \qquad (3)$$

where V_m is the average volume of particles. In the case where the particles are distributed uniformly by their sizes, we have $V = V_m$ and, accordingly, $v = 1$.

The dimensionless temperature can be normalized by the anisotropy energy, so that

$$t = \frac{k_{\mathrm{B}}T}{KV_m}, \qquad (4)$$

where k_{B} is the Boltzmann constant.

The magnetic moment of the particle will be considered as independent of the temperature; however, in the general case, it also depends on the particle's volume. Let this dependence be linear, i.e.

$$m_s = I_s^{\mathrm{par}} V, \qquad (5)$$

where $I_s^{\rm par}$ is the magnetization of saturation for a unit volume of the substance, which ferromagnetic particles are made up of.

We can also introduce the relative strength of the magnetic field

$$h = \frac{I_s^{\rm par}\mu_0 H}{K}. \tag{6}$$

Now, the magnetization in model (2) can be written down in the form

$$I(t,h) = I_s \frac{\int\limits_0^\pi \cos\theta A(\theta,t,h)d\theta}{\int\limits_0^\pi A(\theta,t,h)d\theta}, \tag{7}$$

where I_s is the magnetization of saturation for the system of magnetic nanoparticles, and

$$A(\theta,t,h) = \sin\theta \exp\left(v\frac{h}{t}\cos\theta\right) \times$$

$$\times \int\limits_0^{2\pi} \exp\left(\frac{v}{t}\left(\cos\theta\cos\alpha + \sin\theta\sin\alpha\cos\varphi\right)^2\right) d\varphi. \tag{8}$$

For the magnetic susceptibility, we find

$$\chi(t,h) = \frac{\chi_0}{t}\Bigg[\frac{\int\limits_0^\pi \cos^2\theta A(\theta,t,h)d\theta}{\int\limits_0^\pi A(\theta,t,h)d\theta} -$$

$$- \left(\frac{\int\limits_0^\pi \cos\theta A(\theta,t,h)d\theta}{\int\limits_0^\pi A(\theta,t,h)d\theta}\right)^2\Bigg], \tag{9}$$

where $\chi_0 = v\mu_0 I_s I_s^{\rm par}/K$.

3. Results and Their Discussion

Before we consider the effects of anisotropy axis direction spread and polydispersity, let us analyze the properties of a simpler model, when all particles are identical and oriented in the same direction. In Fig. 2,*a*, the temperature behavior of the system magnetization in a finite magnetic field ($h = 0.01$) is shown for various values of the angle α (see Fig. 1) between the magnetic field and the anisotropy axes. One can see that all curves

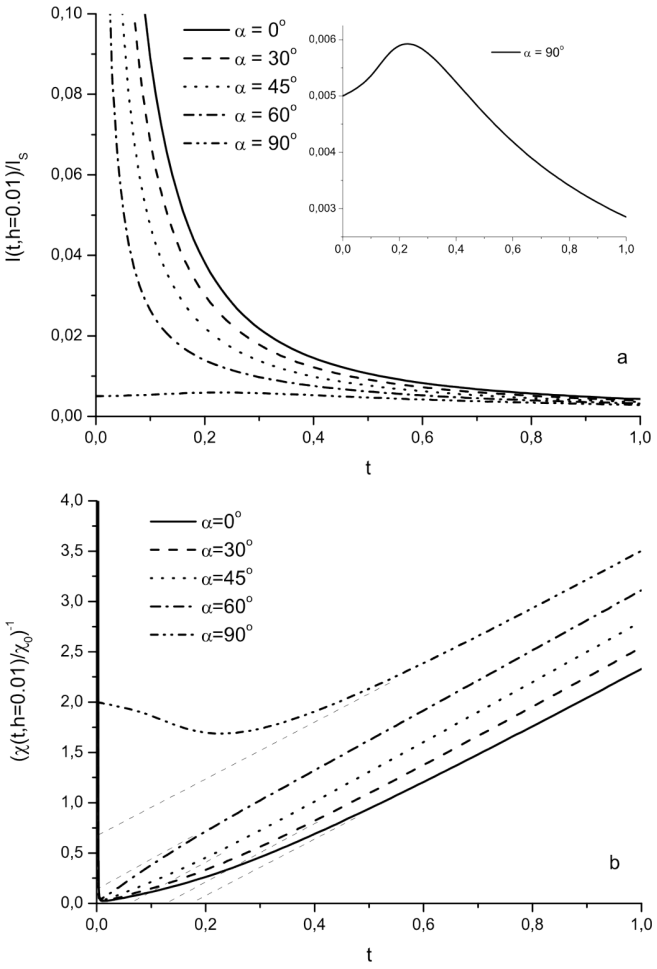

Fig. 2. Magnetization (a) and the inverse susceptibility (b) of the system of magnetic particles with parallel orientation of anisotropy axes for various angles between the anisotropy and the external field $h = 0.01$

fall down, as a rule, if the temperature grows. In the cases where the anisotropy axes are oriented almost normally to the external field, a more complicated nonmonotonic dependence can be observed (see in the scaled-up inset).

In Fig. 2,*b*, the temperature dependences of the inverse magnetic susceptibility are depicted for various α and a small field $h = 0.01$. The high-temperature linear asymptotes of those dependences intersect the temperature axis at different points, so that a deviation from the known Curie law for isotropic paramagnets is evident. Hence, from the viewpoint of the general behavior of magnetic susceptibility, two characteristic sections can be distinguished. The first section – with the linear temperature dependence $\chi^{-1}(t,h)$ – is observed

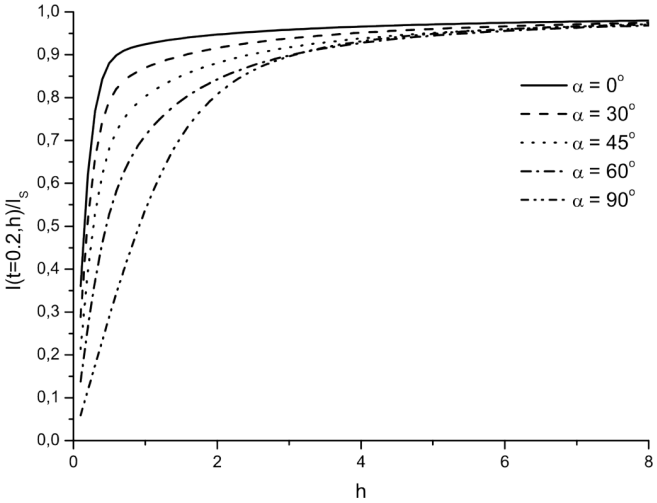

Fig. 3. Field dependences of the magnetization of the system of magnetic particles with parallel orientation of anisotropy axes for various angles α at the temperature $t = 0.2$

at temperatures that are high enough, but lower than the Curie temperature for the nanoparticle. The second section is a low-temperature one, where the dependence is nonlinear.

The analytic solution for the linear section (the high-temperature limit) gives the following temperature dependence for the inverse magnetic susceptibility:

$$(\chi(t,h)/\chi_0)^{-1}\Big|_{t\to\infty} = \frac{3}{v^2}t + \frac{2}{5v}\left(1 - 3\cos^2\alpha\right). \qquad (10)$$

According to Eq. (10), if $\alpha = \arccos\sqrt{1/3} \approx 55°$, the system is similar to an isotropic paramagnet by its inverse magnetic susceptibility. Respectively, the continuation of the linear section intersects the temperature axis above zero, if $\alpha < 55°$, and in the range of negative temperatures, if $\alpha > 55°$.

In each case, the system is in the superparamagnetic state, which can be seen from the field dependence of magnetization at a constant temperature (Fig. 3). Every magnetization curve passes through zero, irrespective of the angle between the field and the anisotropy axes. Moreover, there is no hysteresis in the system. Those two phenomena are typical attributes of superparamagnetism [6, 11]. At smaller angles α, the magnetization saturates more quickly.

Hence, we have a superparamagnetic system. Some specific properties of such systems should be noted. In particular, besides the absence of hysteresis mentioned above, there is a high potential barrier at low temperatures which is caused by magnetic anisotropy and which hampers the system to transit into the equilibrium state. Therefore, nanoparticles can remain long enough in a blocked nonequilibrium state, different from the superparamagnetic one. Depending on the experimental situation, it is possible to determine the blocking temperature [6] by the formula

$$T_b = \frac{KV}{k_{\rm B}\ln\frac{\tau}{\tau_0}}, \qquad (11)$$

where τ_0 is a constant of the order of $10^{-10} - 10^{-8}$ s for a system with magnetic nanoparticles [12], and τ is the characteristic time of measurement. Expression (11) allows the temperature interval, where the system is observed in the blocked state, to be estimated. For instance, if $\tau = 100$ s, we have $T_b = KV/(25k_{\rm B})$. In the experimental temperature dependences of magnetization and magnetic susceptibility, the maxima are observed, the position of which also makes it possible to estimate the blocking temperature. Thus, if $T < T_b$, the particles are in the blocked superparamagnetic state, which originates from the domination of anisotropy effects over thermal ones at a small external field. If $T > T_b$, it is an equilibrium superparamagnetic region. In the case which is examined in this work, the observation time should be long enough for the system to transit into the equilibrium state. Consequently, it is supposed that $T_b \to 0$, so that the equilibrium nonblocked superparamagnetic state is observed in the whole temperature range.

3.1. Distribution of anisotropy axes

The systems of magnetic nanoparticles can be formed either in a natural way or artificially, making use of certain technologies. The most widespread case is a chaotic orientation of easy magnetization axes. For instance, it takes place, if a system of magnetic clusters is cooled down quickly in a liquid medium. However, with the help of the corresponding techniques applied at various cooling rates and using a controlled external magnetic field, the formation of such systems with a dominating orientation direction of magnetic anisotropy axes becomes possible. This provokes the study of the properties of ferromagnetic nanoparticle systems at various distributions that describe the orientation of anisotropy axes.

Let the distribution of easy magnetization axes be uniform within some spherical angle Ω around the selected direction (α_0, β_0)—this region is depicted in Fig. 4. Then, the magnetization in the system of

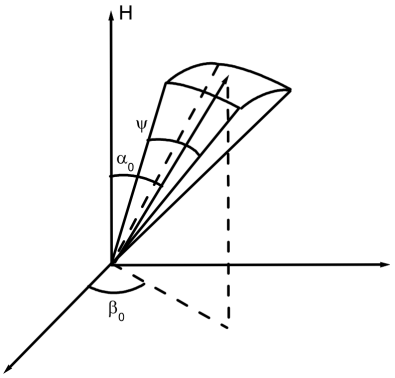

Fig. 4. The distribution region of easy magnetization axes in the spherical angle Ω

magnetic particles is determined by the expression

$$I(t,h) = \frac{\int I(\Omega,t,h)d\Omega}{\int d\Omega}$$

or, in the spherical coordinates,

$$I(t,h) = \frac{1}{2\sin(\psi/2)} \int\limits_{\alpha_0-\psi/2}^{\alpha_0+\psi/2} \cos(\alpha-\alpha_0) I(\alpha,t,h)d\alpha, \tag{12}$$

where ψ is an angle that determines the segment of random spread in the vector $\mathbf{n}$ orientation.

Let us analyze the case where $\alpha_0 = \pi/2$. Provided that all particles have the same orientation type, the temperature dependence of magnetization demonstrates a maximum. In Fig. 5,*a*, we present the curves which were obtained at different values of ψ. One can see that the gradual increase of ψ is accompanied by a smearing of the region, where the orientation of the easy magnetization axis dominates, and the magnetization maximum disappears.

The magnetic susceptibility of a system of magnetic nanoparticles, where the orientations of the easy magnetization axes were uniformly spread over a spherical angle Ω, was determined in a similar way:

$$\chi(t,h) = \frac{1}{2\sin(\psi/2)} \int\limits_{\alpha_0-\psi/2}^{\alpha_0+\psi/2} \cos(\alpha-\alpha_0) \chi(\alpha,t,h)d\alpha. \tag{13}$$

The growth of the region, in which the magnetic anisotropy axes are oriented, also gives rise to a reduction of the region of nonlinear behavior at small t

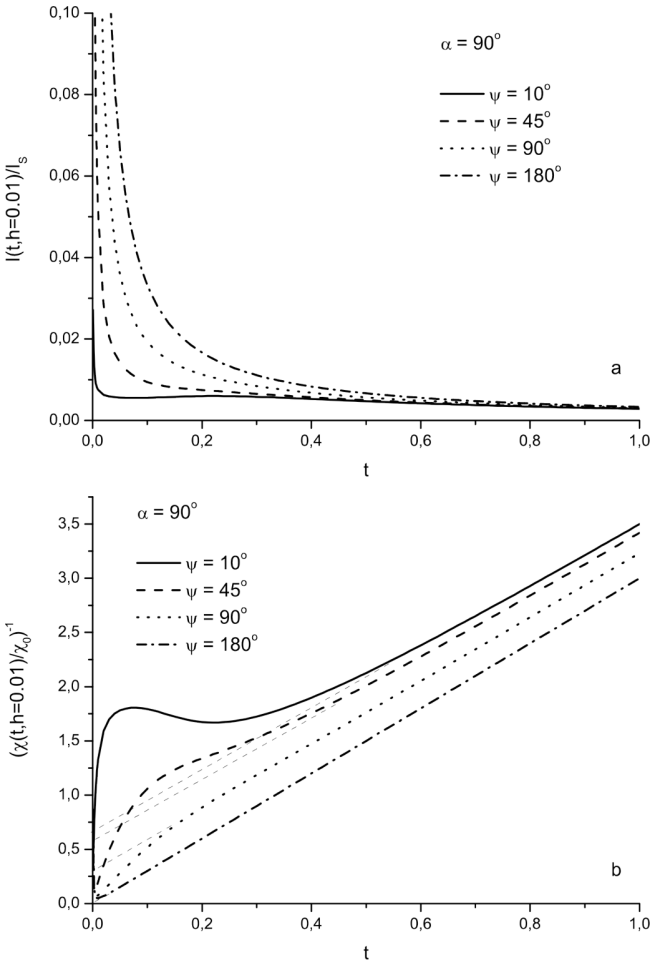

Fig. 5. Magnetization (*a*) and the inverse susceptibility (*b*) of the system of magnetic particles at various sizes of the region, where the orientations of the magnetic anisotropy axes are randomly distributed

and its gradual smearing (see Fig. 5,*b*). At the angle $\psi = \pi$, i.e. in the case of the isotropically uniform distribution of anisotropy axes, we come to the linear dependence of $\chi^{-1}(t,h)$ on the temperature.

3.2. Polydispersity

In most real cases, we deal with a nonuniform distribution of particles over their dimensions. Therefore, important is a problem to take the particle polydispersity into account and to study its influence on the magnetic properties of the system. On the basis of the results of experimental works [13–15], which were devoted to studying the properties of magnetic

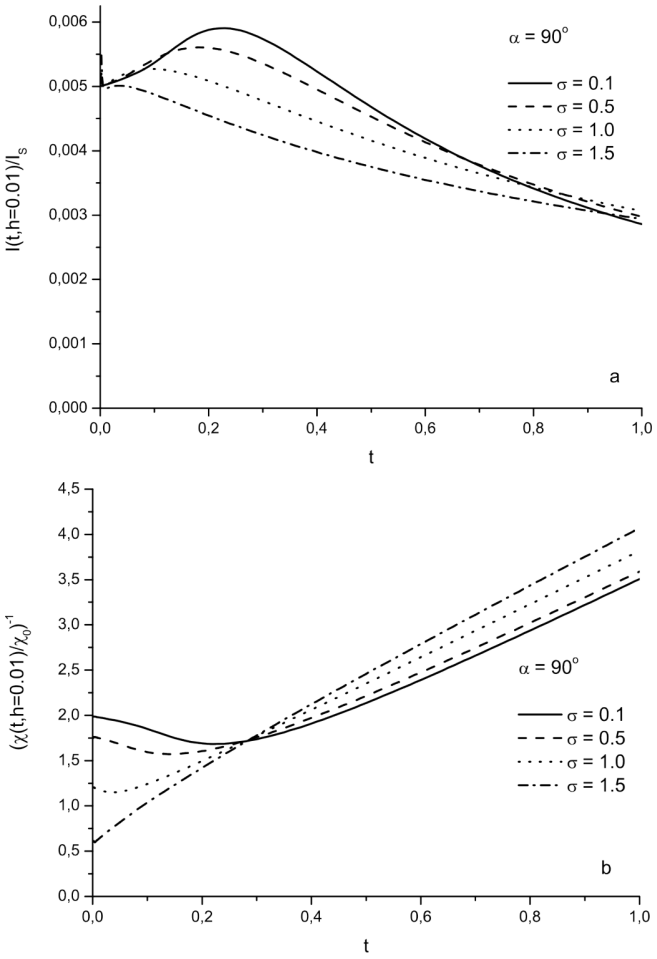

Fig. 6. Magnetization (a) and the inverse susceptibility (b) of the system of magnetic particles as the functions of the temperature for various widths of the log-normal distribution of particles over their dimensions

nanoparticles, we can choose a log-normal distribution over the size which looks like

$$f(v) = \frac{1}{\sqrt{2\pi}\sigma v} \exp\left(-\frac{\ln^2(v)}{2\sigma^2}\right), \tag{14}$$

where σ is the distribution width. Let us consider this case in more details. The magnetization of the system is equal to

$$I(t,h) = \int_0^\infty f(v) I(v,t,h) dv, \tag{15}$$

where $I(v)$ is defined by expression (7).

In Fig. 6,a, the magnetization of the system as a function of the temperature is depicted for various widths of the log-normal distribution. If the polydispersity grows, the peak becomes smeared.

For the magnetic susceptibility, we have

$$\chi(t,h) = \int_0^\infty f(v)\chi(v,t,h) dv. \tag{16}$$

The results of calculations are exhibited in Fig. 6,b. In particular, one can see that the inverse susceptibility does not change the properties of the system considerably at linear sections.

4. Conclusions

When considering the influence of the anisotropy and polydispersity effects, we have obtained the temperature dependences for the magnetization and the magnetic susceptibility of the system for various values of parameters that describe the distributions of ferromagnetic nanoparticles over the orientation of their magnetic anisotropy axes and their dimensions. By analyzing the magnetic susceptibility in the framework of the model with parallel orientation of easy magnetization axes, we have determined the parameters of linear sections in the dependence of the inverse magnetic susceptibility on the temperature. The field dependence of magnetization testifies that the system is in the superparamagnetic state, irrespective of the distribution over the anisotropy axis orientations. The smearing of the peak, which is observed in the case of identically oriented anisotropy axes, is observed when the disorientation effects and the width of the size distribution of particles increase. The results obtained can be useful for the interpretation of experimental data for systems with magnetic nanoparticles.

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ВПЛИВ АНІЗОТРОПІЇ І ПОЛІДИСПЕРСНОСТІ НА МАГНІТНІ ВЛАСТИВОСТІ СИСТЕМИ ФЕРОМАГНІТНИХ НАНОЧАСТИНОК

І.М. Мриглод, В.В. Соколов

Р е з ю м е

Для тривимірної моделі невзаємодіючих магнітних наночастинок досліджено вплив випадкової орієнтації осей найлегшого намагнічення та полідисперсності у розмірах феромагнітних наночастинок на термодинамічні властивості системи. Проведено порівняння з результатами класичної моделі Стонера–Вольфарта. Показано, що максимум, який спостерігається на залежності намагніченості системи від температури, розмивається при збільшенні області, у якій орієнтовані осі найлегшого намагнічення та ширини розподілу частинок за розмірами.