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Phase transitions in an ordered 2D array of cubic nanoparticles

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The study of phase transitions in an ordered cubic nanoparticles 2D array was carried out by computer modeling. The study was performed for the Ising model. The Wolf cluster algorithm is used to simulate the phase transition in the system. The interaction between the nanoparticles is exchange. The interaction between spins for different particles is less in one particle. Cases of different energy values for the interaction between particles are considered. The particles are single-domain. The ferromagnetic phase transition is investigated. The total magnetization in the system is used as an order parameter. The phase transition temperature is calculated based on finite dimensional scaling theory using Binder cummulants. A computer experiment was performed. The phase transition temperature dependence on energy of interaction between particles is obtained. The temperature changes according to the logarithmic law. The parameters for the Curie temperature change law from the interaction energy of nanoparticles are calculated. Critical exponents of the system were calculated. The critical exponents are independent from the interaction energy between the particles. The critical exponent for magnetic susceptibility is equal $\gamma = 2.21 \pm 0.09$. This value is different from the critical exponents for a solid film.

Keywords: nanoparticles array, computer simulation, phase transition, Ising model, critical phenomena.

1. Introduction

Modern nanotechnologies can create metamaterials with new properties that are absent from conventional materials. Recently, metamaterials consisting of ferromagnetic nanoparticles collected in an ordered 2D structure on the substrate surface have been actively investigated. Ordered 2D arrays of nanoparticles can be obtained in various ways. The first method consists in deposition of nanoparticles from a liquid medium onto a structured substrate [1, 2, 3, 4]. In this case, the structure of the system is determined by the substrate symmetry. The second method consists in lithographic division of thin ferromagnetic film into rectangular areas with equal size [5, 6, 7, 8].

An ordered array of ferromagnetic nanoparticles has magnetic properties similar to conventional magnetic materials [9].

Nanoparticles are small in size. Small particles are single-domain. Therefore, the particles can be considered as one macrospin at a temperature below the blocking temperature. If all particles have the same size, then all macrospins have the same magnetic moment. An ordered nanoparticles' array can be considered as a 2D system consisting of macrospins located in the square lattice nodes. Three phases are possible in this system. The first phase is present when all particles are in the paramagnetic state. With a decrease in temperature, spins in each particle transition to an ordered state. Particles become macrospins. These macrospins are randomly oriented. The total magnetization in the system is zero. The system is in a superparamagnetic state. With a further decrease in temperature, macrospins are ordered. The magnetization in the system becomes greater than zero. The system goes into a superferromagnetic state. The interaction between the nanoparticles is exchange. The surface spins in the nanoparticle interact. The purpose of this article is to study the transition from a paramagnetic state to a superferromagnetic state.

The magnetic properties of the nanoparticles array have been experimentally investigated in several papers. Article [10] examines heterostructures Co/CaF_2/Si (001) with corrugated surface (110) of buffer layer CaF_2. The system is an ensemble of superparamagnetic weakly interacting nanoparticles for a cobalt film thickness below some critical value at $T = 294$ K. The authors demonstrate that when the temperature decreases, the system goes into a superferromagnetic state. Phase transitions in $GeSb_2Te_4$ arrays were studied by irradiation of samples with electron beam using high-resolution transmission electron microscopy [11]. Article [12] investigated magnetic response and anisotropy of epitaxial nanoparticles Co/Cu (110) arrays. Phase transition from paramagnetic to ferromagnetic was detected. Uniaxial anisotropy induced by nano-sized Co particles was observed. Magnetometric characteristics of self-organizing magnetic iron oxide nanoparticles arrays are investigated in the paper [13]. Magnetic phase transitions have been investigated in this system.

Quasi-2D periodic arrays of Co-nanocrystals with a diameter 12 nm self-organize on carbon substrates [14]. Dipole bonding between particles results in collective magnetic behavior at temperatures below 300 K. The residual magnetization and uniaxial anisotropy indicate the isinglike nature of this magnetic material. Micromagnetic modeling for iron nanocubes showed that the macrospin model is applicable at sizes less than 20 nm [15]. With nanoparticles

of more than 40 nm, surface phenomena must be considered. The magnetic behavior of nanoparticles Fe/Fe_3O_4 on the ultra-thin film CoFeB surface was visualized by comparing images of atomic force and magnetic force microscopes [16]. Ferromagnetic resonance spectra showed the effects of particle and film interaction on the magnetic behavior in the system. Studies of ferromagnetic nanoparticles of ZnO arrays doped with various transition metals demonstrate magnetic phase transition at room temperatures [17–24]. Computer simulation of hysteresis in magnetic nanoparticles assembly [25] showed dependence of hysteresis loop shape and dimensions on temperature and interparticle interaction intensity. Rectangular magnetite nanoparticles assemblies on lithographic substrates demonstrate collective magnetic behavior [26]. Micromagnetic modeling for these systems shows the possibility of different behavior for the system in the magnetic field. The properties of the nanoparticle array depend on the interparticle interaction.

Computer simulation of critical behavior for a two-dimensional system with a one spin thickness, divided into square areas, is performed in the article [27]. It is shown that the critical behavior of such system is different from the 2D Ising model. The phase transition temperature depends nonlinear on the energy of the interaction between the nanoparticles. Theoretical-field description of critical behavior for 3D nanoparticles array is performed in article [28]. Calculations in a two-loop approximation showed that such systems have a new class of universality for critical behavior. Analytical calculations for two-dimensional systems are impossible, since a renormalization group approach does not apply to them.

In this article, the study of magnetic phase transitions in the cubic ferromagnetic nanoparticles array by computer modeling is carried out. Dependence of phase transition temperature and critical exponents on intensity of interaction between particles is investigated.

2. Model

The system under investigation is a square matrix of nanoparticles. Nanoparticles are placed in units of square lattice. The geometry for the system under study is shown in Fig. 1.

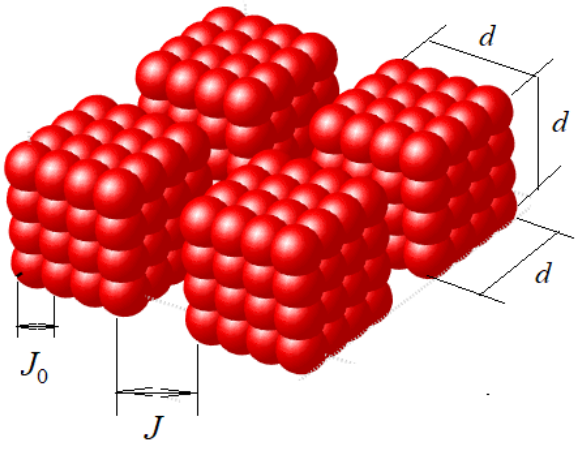

Fig. 1. (Color online) Geometry of the system.

The Ising model is used. Each atom has a spin S_i, which can take one of two values (1/2 or −1/2). The interaction between the spins is exchange. The exchange integral of the interaction between spins in one particle is J_0. The exchange integral is J for adjacent spins from different particles. The exchange integral decreases with increasing distance. Inequality is $J \le J_0$ performed for exchange integrals. The rate of decrease for the exchange integral as the distance increases may be subject to different laws. The exchange integral changes according to the exponential law in the most common case. Long-range effects are present in a large number of substances. In this case, the exchange integral depends on the distance according to the power law. In this article, the law of dependence for exchange forces on distance is not specified. The ratio of exchange integrals $R = J/J_0$ is used as a model parameter. Changes in the physical properties of the system are considered depending on the parameter R. This system models an ordered ferromagnetic nanoparticles array.

The Hamiltonian of the Ising model with a changing exchange integral is used.

$$H = \sum J_{ij} S_i S_j. \tag{1}$$

$$J_{ij} = \begin{cases} J, & S_i \in D_k, S_j \in D_k. \\ J_0, & \text{overwise.} \end{cases} \tag{2}$$

D_k is a nanoparticle with the number k. Particles have the size $d \times d \times d$. Systems with $L \times L$ size are studied in a computer experiment. The system must contain an integer number of nanoparticles, so L is proportional to d. The exchange interaction is short-acting, so we consider the interaction only of the nearest neighbors.

The magnetic phase transition is described based on the order parameter. Magnetization is a parameter in this system. Magnetization m is calculated as the average spin value per atom in computer simulation.

$$m = \sum S_i / N. \tag{3}$$

N is the total number of atoms.

The Wolf cluster algorithm to study the magnetic properties of a system at different temperatures is used [29]. Second-order phase transitions occur only in infinite systems. The finite-dimensional scaling theory is used to obtain the magnetic characteristics for finite systems in a computer experiment [30]. The finite-dimensional scaling theory considers systems of various sizes. The properties of infinite systems are approximated based on the sequence of properties for finite systems with increasing size. One of the parameters for the system is the fourth order Binder cummulant [31].

$$U_4 = 1 - \frac{\langle m^4 \rangle}{3 \langle m^2 \rangle^2} \tag{4}$$

The values in the angle brackets indicate their average thermodynamic values. The value of the Binder cummulant does not depend on the size for the system at the phase transition point. This property is used to determine the phase transition temperature. Several systems with different size L are modeled. Plots for Binder cummulants' dependence on

temperature will intersect at one point. This point determines the phase transition temperature T_C.

Magnetic susceptibility is calculated from the fluctuation ratio.

$$\chi = NK\left(\left\langle m^2\right\rangle - \left\langle m\right\rangle^2\right), \quad (5)$$

$K = |J_0|/(k_B T)$, k_B is Boltzmann's constant.

The system exhibits critical behavior near the phase transition point. Thermodynamic parameters for the system can be described by power functions depending on temperature. Finite-dimensional scaling theory allows to write power dependencies on the system size for thermodynamic functions. Magnetic susceptibility is approximated by power law.

$$\chi \sim L^{\gamma/\nu}. \quad (6)$$

Studying systems with various sizes allows to calculate the ratio of critical exponents γ/ν. The dependence of Binder cummulants on temperature is used to find the critical exponents ν.

$$\frac{dU_4}{dT} \sim L^{-1/\nu}. \quad (7)$$

3. Results and Discussion

Systems with nanoparticles $d = 4$ are investigated in a computer experiment. The particles are not single-domain when $d \geq 8$ in a computer experiment. Size $d = 6$ is borderline. Particles with $d = 4$ are selected for single domain. The linear dimensions of the system varied from $L = 24$ to $L = 56$ in increments of $\Delta L = 8$. The ratio of exchange integrals varied from $R = 0.1$ to $R = 0.9$ with step $\Delta R = 0.1$.

A plot of the phase transition temperature T_C versus the ratio of exchange integrals R is shown in Fig. 2. The phase transition temperature increases with the increase in the ratio of exchange interaction between nanoparticles. Nanoparticles are small in size, so they are single-domain. The exchange integral J can be considered as the amount of interaction between whole particles. The stronger the interaction between the particles, the higher the temperature is necessary for disordering the spins. The R value in real systems is determined by the distance between the particles and the descending law of the exchange integral with the distance.

The dependence of the Curie temperature on the ratio of exchange integrals with high accuracy is approximated by the logarithmic function. The plot of phase transition temperature T_C versus $\ln R$ is shown in Fig. 3. The system is an array of single-domain non-interacting nanoparticles at $R = 0$. Phase transition in such a system does not occur.

This dependency is written as a formula.

$$T_C = 3.516 + 0.611 \cdot \ln(R). \quad (8)$$

This dependence can be written as a function of the distance between nanoparticles if the law of the dependence for R on distance is known. The interaction between the particles may be different. The exchange integral decreases by exponential law with increasing distance r in exchange interaction.

$$J = J_0 \exp(-(r-a)/r_0). \quad (9)$$

r_0 is a constant, a is the lattice constant, $J_0 = J(a)$.

Substituting this expression into the formula for Curie temperature results in a linear law.

$$T_C = 3.516 - 0.611 \cdot (r-a)/r_0. \quad (10)$$

If long-range forces are present in the system, then exchange interaction decreases according to power law.

$$J = J_0 r^{-\sigma}. \quad (11)$$

The law for decreasing the phase transition temperature from distance is logarithmic.

$$T_C = 3.516 - 0.611\sigma \cdot \ln(r). \quad (12)$$

These results are consistent with experimental data. Most studies demonstrate the qualitative dependence of Curie temperature on the distance between particles [32, 33]. Curie temperature decreases with distance. This result is easily explained. The Curie temperature is directly proportional to the spin interaction energy. The interaction energy of particles is determined by the interaction of their spins. This energy decreases as the distance between particles increases. The phase transition temperature also decreases. Some studies contain information about the Curie temperature at several values of the distance between nanoparticles. For Co

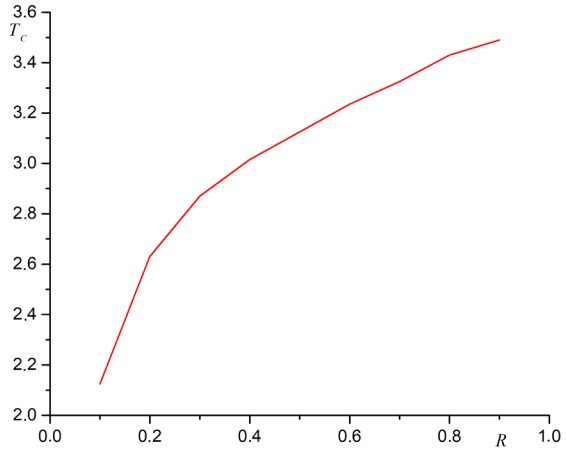

Fig. 2. Dependence of phase transition temperature T_C on ratio of exchange integrals $R = J/J_0$.

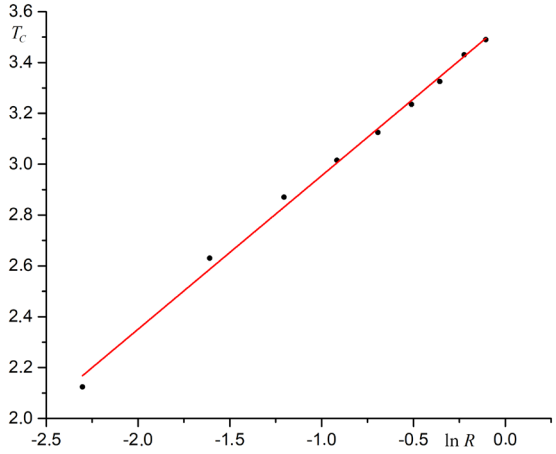

Fig. 3. Plot of phase transition temperature T_C versus $\ln R$.

nanoparticles, this relationship obeys a linear law with good accuracy [34]. This means a short-range interaction between nanoparticles.

Fig. 4 shows the value of the critical exponent's ratio γ/ν at different values R.

Fig. 4 shows that the critical exponents ratio is independent on the parameter R. The ratio of the critical susceptibility exponent to the critical correlation radius exponent is $\gamma/\nu = 2.10 \pm 0.02$. Fig. 5 shows the value of the critical exponent ν at different values R.

The critical correlation radius index is independent of R and equal to $\nu = 1.05 \pm 0.06$. The susceptibility critical exponent is $\gamma = 2.21 \pm 0.09$. The approximation of the results demonstrates that the critical exponents for the ordered nanoparticles array should match the critical exponents for continuous films. This conclusion is supported by experimental data. The magnetic susceptibility critical exponent is $\gamma = 2.39 \pm 0.08$ for the ordered array of Co nanoparticles [11]. This value is consistent with the simulation result. Critical exponents of thin films have similar values (Co/Cu, $\gamma = 2.40 \pm 0.07$ [35], Co/Cu $\gamma = 2.39 \pm 0.08$ [36, 37], Fe/InAs $\gamma = 2.21 \pm 0.25$ [38]). The critical exponent for magnetization is $\beta = 0.13 \pm 0.02$.

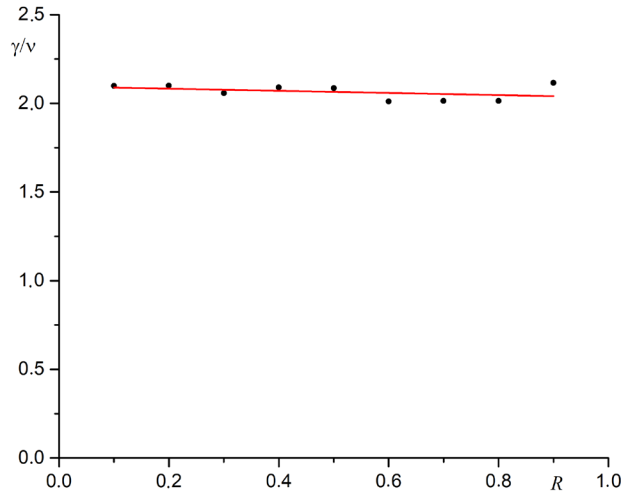

Fig. 4. The ratio of critical exponents γ/ν at different values R.

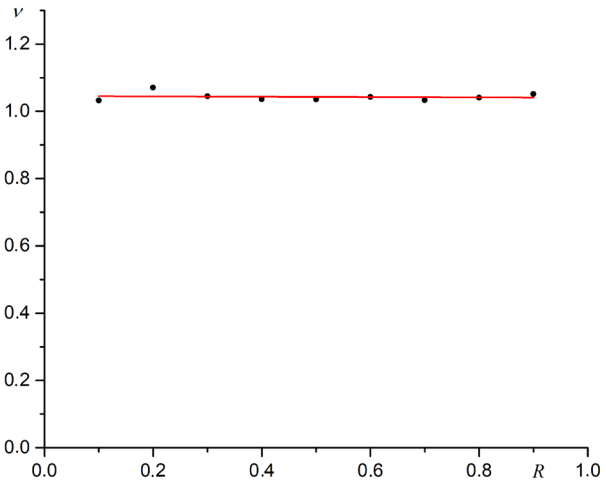

Fig. 5. The value of the critical exponent ν at different values R.

4. Conclusion

Computer simulations showed that collective magnetic phenomena are observed in the cubic ferromagnetic nanoparticles array. These phenomena lead to a ferromagnetic phase transition of the second kind. The phase transition temperature depends on the interparticle interaction energy according to the logarithmic law. Phase transition does not occur in the array of non-interacting particles. This is due to the fact that the nanoparticles are single-domain. The Curie temperature increases as the energy of the interaction between the particles increases. The dependence of the phase transition temperature on the distance between particles is determined by the law of decreasing the interaction energy. The Curie temperature tends to the value of the phase transition temperature in thin films with an increase in interparticle interaction energy. The change in Curie temperature with increasing particle spacing is consistent with experimental data.

Critical exponents of the nanoparticles array near the phase transition point do not depend on the interaction energy between particles. This pattern is observed only in systems of interacting particles. Critical exponents match the values for thin films.

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