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2000 J. Phys.: Condens. Matter 12 7111

(http://iopscience.iop.org/0953-8984/12/31/312)

J. Phys.: Condens. Matter **12** (2000) 7111–7115. Printed in the UK PII: S0953-8984(00)09952-5

Dipolar ferromagnetism in ensembles of ellipsoidal nanoparticles

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Received 29 November 1999, in final form 3 April 2000

Abstract. The phase diagram and mean local field theory for ensembles of dipolar interacting ellipsoidal nanoparticles randomly distributed over the sites of a tetragonal lattice are constructed. Dipolar ferromagnetism in the ensembles arises from a competition between the ferro- and antiferromagnetic interactions of the nanoparticle magnetic moments. A critical temperature is defined for these systems with magnitude depending on the shape of the nanoparticles.

1. Introduction

Recently there has been experimental evidence [1, 2] that in ensembles of magnetic nanoparticles, randomly distributed in a nonmagnetic matrix, ferromagnetic ordering can exist. There are numerical [3] and analytical [4, 5] results which show that such ordering can be attributed to the dipolar interaction between the nanoparticles. Enhanced values of the remanence and the coercivity of a random assembly of dipolar nanoparticles on a simple cubic lattice with packing density close to percolation can be also attributed to the ferromagnetic ordering of their magnetic moments [6]. For the interpretation of those experimental and numerical data a theory of dipolar ferromagnetism is necessary. It must take into account the finite size of the nanoparticles, the asphericity of their shape and the anisotropy of their spatial distribution. But at present such a theory is absent. The goal of this paper is the construction of that theory in the mean local field approximation. In the considered case dipolar interaction of any nanoparticle pair has either ferromagnetic or antiferromagnetic character. Therefore, existence or absence of dipolar ferromagnetism is determined by a competition of ferromagnetic and antiferromagnetic interactions, which, in their turn, depend on the spatial distribution of nanoparticles and their shape. Besides, similar to dipolar liquids [7], the result of that competence can depend on the shape of the sample. But here in order to avoid the demagnetizing fields, we consider the sample which is infinite in all directions.

2. Phase diagram

We consider an ensemble of uniaxial ferromagnetic nanoparticles the centres of which are randomly distributed over the sites of a tetragonal lattice. It is supposed that (1) the lattice constants in the xy-plane and along the tetragonal axis (the z-axis) are equal to d_1 and d_2,

0953-8984/00/317111+05$30.00

respectively; (2) each lattice site is occupied by a nanoparticle with a probability p; (3) the nanoparticles have the shape of ellipsoids of revolution with semiaxes R (in the plane xy) and $R + \delta$ (along the z-axis); (4) the axes of easy magnetization of the nanoparticles are parallel to the z-axis, and the anisotropy field H_a essentially exceeds the mean local field acting on each particle. In this case the mean local field has only a z-component. Placing the origin of coordinates into the centre of any nanoparticle we can represent that component in the form

$$H = \left\langle \sum_i \frac{m_{iz}}{V^2} \int_V \int \frac{3(r_{iz} + \rho_z - \rho'_z)^2 - |\boldsymbol{r}_i + \boldsymbol{\rho} - \boldsymbol{\rho}'|^2}{|\boldsymbol{r}_i + \boldsymbol{\rho} - \boldsymbol{\rho}'|^5} \, \mathrm{d}\boldsymbol{\rho} \, \mathrm{d}\boldsymbol{\rho}' \right\rangle. \tag{1}$$

Here $V = 4\pi R^3(1 + \varepsilon)/3$ is the nanoparticle volume, $\varepsilon = \delta/R$, m_{iz} is the z-component of the ith magnetic moment $\boldsymbol{m}_i$, $\boldsymbol{r}_i (\neq 0)$ is the radius vector of the ith nanoparticle centre, the integration is carried out on the nanoparticle volume and the overbar and angular brackets denote thermodynamic averaging and the average over distributions of the nanoparticles on the sites of the lattice, respectively. Notice that the double integral represents the total interaction energy of two nanoparticles of finite size.

For $|\varepsilon| \ll 1$ in equation (1) the double integral (divided by V^2) to first order in ε equals

$$\frac{3r_{iz}^2 - |\boldsymbol{r}_i|^2}{|\boldsymbol{r}_i|^5} \left[1 + \varepsilon \frac{24R^2}{5|\boldsymbol{r}_i|^2} \right] \tag{2}$$

therefore in this case the mean local field is reduced to

$$H = nm_z \xi S(\gamma, \xi) \tag{3}$$

where $n = p/d_1^2 d_2$ is the packing density of nanoparticles, $m_z = \langle \overline{m_{iz}} \rangle$, $\xi = d_2/d_1$ is the parameter characterizing the deviation from a cubic lattice (the case $\xi = 1$ corresponds to a cubic lattice), $\gamma = 24\varepsilon R^2/5d_1^2$,

$$\begin{aligned} S(\gamma, \xi) &= S_{5/2}(\xi) + \gamma S_{7/2}(\xi) \\ S_r(\xi) &= \sum_{n_1, n_2, n_3} \frac{2\xi^2 n_3^2 - n_1^2 - n_2^2}{(n_1^2 + n_2^2 + \xi^2 n_3^2)^r} \end{aligned} \tag{4}$$

and n_1, n_2, n_2 are integers that are not equal to zero simultaneously. Graphs of the functions, $S_{5/2}(\xi)$, $S_{7/2}(\xi)$ and $f(\xi) = -S_{5/2}(\xi)/S_{7/2}(\xi)$ are shown in figure 1. Notice that the numerical series $S_{5/2}(\xi)$ does not converge absolutely; that is why its sum can depend on the method of summation. Consequently, the thermodynamic properties of nanoparticle ensembles can depend on their external shape [7–9]. Our calculations apply to the case when the infinite sample arises from a cubical sample, the size of which tends to infinity.

According to equation (3) ferromagnetic ordering in an ensemble of magnetic moments of ellipsoidal nanoparticles can occur if $S(\gamma, \xi) > 0$, that is $\gamma > f(\xi)$ for $0 < \xi < 1$ and $\gamma < f(\xi)$ for $\xi > 1$. The parameters γ and ξ are not fully independent since the conditions $d_1 \geqslant 2R$ and $d_2 \geqslant 2R(1+\varepsilon)$, providing the disjointness of nanoparticles, should be held. This means that at fixed values of ε and ξ the parameter γ can be changed in the interval $(0, \varphi(\varepsilon, \xi))$ for $\varepsilon > 0$, and in the interval $(\varphi(\varepsilon, \xi), 0)$ for $\varepsilon < 0$, where

$$\varphi(\varepsilon, \xi) = \begin{cases} \dfrac{6}{5} \dfrac{\varepsilon}{(1+\varepsilon)^2} \xi^2 & (0 < \xi < 1 + \varepsilon) \\ 6\varepsilon/5 & (\xi \geqslant 1 + \varepsilon). \end{cases} \tag{5}$$

Taking into account the condition $S(\gamma, \xi) > 0$, it follows that in ensembles of prolate ($\varepsilon > 0$) nanoparticles ferromagnetic ordering exists if the parameters γ and ξ belong to the region defined by the conditions $0 < \gamma \leqslant \varphi(\varepsilon, \xi)$ and $0 < \xi < 1$ (in figure 2 such a region for $\varepsilon = 0.2$ is denoted by I). That region decreases with decreasing ε (in figure 2 for

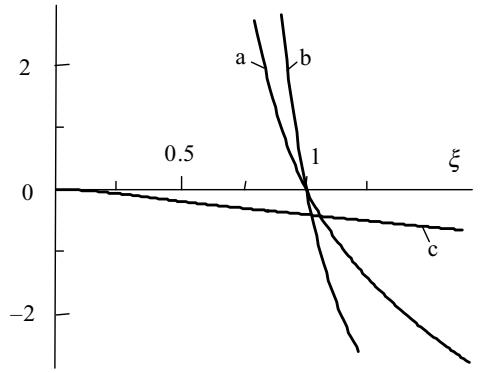

Figure 1. Dependence of the functions $S_{5/2}(\xi)$ (curve a), $S_{7/2}(\xi)$ (curve b) and $f(\xi) = -S_{5/2}(\xi)/S_{7/2}(\xi)$ (curve c), defined by equation (4), on the parameter ξ.

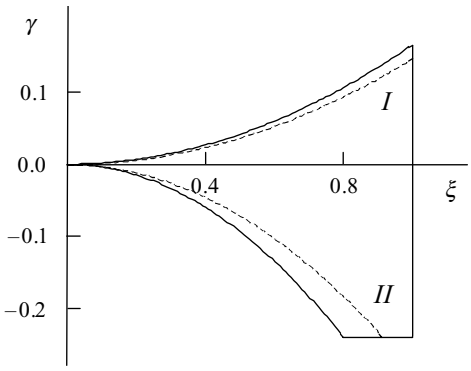

Figure 2. Phase diagrams for ensembles of prolate ($\varepsilon = 0.2$) and oblate ($\varepsilon = -0.2$) nanoparticles. In the case of prolate nanoparticles dipolar ferromagnetism can exist in region I, and in the case of oblate ones in region II. Dotted curves restrict region I for $\varepsilon = 1/6$ and region II for $\varepsilon = -1/6$.

$\varepsilon = 1/6$ region I is limited by the dotted curve), and in the limiting case of spherical ($\varepsilon = 0$) nanoparticles the condition of ferromagnetic ordering is $0 < \xi < 1$. Notice that the absence of ferromagnetic ordering at $\xi = 1$ is in agreement with the known result of Luttinger and Tisza [10] according to which the dipoles (magnetic or electric) on a simple cubic lattice are ordered antiferromagnetically.

In the case of oblate ($\varepsilon < 0$) nanoparticles ferromagnetic ordering can formally exist in two regions of the $\gamma\xi$-plane. The first region is defined by the conditions $\max(f(\xi), \varphi(\varepsilon, \xi)) < \gamma < 0$ and $0 < \xi < 1$, and exists for any value of ε (in figure 2 such a region for $\varepsilon = -0.2$ and $\varepsilon = -1/6$ is denoted by II). The second region is defined by the conditions $\varphi(\varepsilon, \xi) \leqslant \gamma < f(\xi)$ and $\xi > 1$, and appears only at $\varepsilon < 5f(1)/6 \approx -0.34$. Since for the derivation of equation (2) the condition $|\varepsilon| \ll 1$ was used, the question of whether dipolar ferromagnetism really exists requires special consideration.

3. Phase transition

Within the local mean field approximation the stationary distribution function $P(\theta)$ for the polar angle θ of a nanoparticle magnetic moment has the same form as for a separated particle in an external magnetic field oriented along the easy axis [11]

$$P(\theta) = \sin\theta \exp(\sigma \cos^2\theta + 2\sigma h \cos\theta)/Z(\sigma, 2\sigma h) \tag{6}$$

where $\sigma = H_a m/2kT$, $h = H/H_a$, m is the module of nanoparticle magnetic moment, k is the Boltzmann constant, T is the absolute temperature and

$$Z(\sigma, 2\sigma h) = \int_{-1}^{1} \exp(\sigma x^2 + 2\sigma h x)\,\mathrm{d}x \tag{7}$$

is the normalizing constant (partition function). Though the analytical expression for the quantity Z is known [12, 13], for numerical calculations we will use equation (7). Defining the order parameter of a nanoparticle system as $\mu = m_z/m$ and using the relation

$$\mu = \int_0^{\pi} \cos\theta P(\theta)\,\mathrm{d}T \tag{8}$$

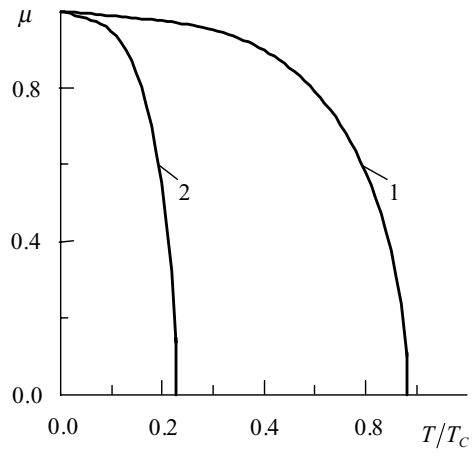

Figure 3. Temperature dependence of the order parameter μ for ensembles of prolate ($\varepsilon = 0.2$, curve 1) and oblate ($\varepsilon = -0.2$, curve 2) Co nanoparticles.

on the basis of equations (3), (6)–(8) we obtain the following equation for μ

$$\mu = \frac{1}{2\sigma}\left[\frac{2e^{\sigma}}{Z(\sigma, 3T_0\mu/T)}\sinh\left(\frac{3T_0}{T}\mu\right) - \frac{3T_0}{T}\mu\right] \tag{9}$$

($T_0 = nm^2\xi S(\gamma,\xi)/3k$). For $S(\gamma,\xi) > 0$ equation (9) has nonzero solution for μ (at $S(\gamma,\xi) < 0$ it has only zero solution), i.e. in a nanoparticle system a spontaneous order exists, if $T < T_{cr}$. The critical temperature $T = T_{cr}$ of the phase transition is determined as a solution of the equation

$$\frac{3T_0}{2\sigma T}\left[\frac{2e^{\sigma}}{Z(\sigma,0)} - 1\right] = 1. \tag{10}$$

Notice, since $m \neq 0$ for $T < T_C$ (T_C is the Curie temperature), the condition $T_{cr} < T_C$ must hold. If in the temperature range $(0, T_{cr})$ the dependence of m on T is weak, then equation (10) has the solution $T_{cr} = T_0$ for $a|_{T=T_0} \ll 1$ (the case of weak anisotropy), and $T_{cr} = 3T_0$ for $a|_{T=3T_0} \gg 1$ (the case of strong anisotropy).

Dependences of the order parameter μ on T/T_C for ensembles of prolate ($\varepsilon = 0.2$) and oblate ($\varepsilon = -0.2$) Co nanoparticles characterized by the parameters [14], $T_C = 1400$ K $M_s = 1400$ emu cm^{-3} (M_s is the saturation magnetization of bulk Co), $H_a = 7650$ Oe (for $\varepsilon = 0.2$), $H_a = 4790$ Oe (for $\varepsilon = -0.2$) (the values of the anisotropy field are different because the shape anisotropy of the particles is taken into consideration), $p = 1$, $\xi = 0.5$ ($S_{5/2}(0.5) \approx 23.64$, $S_{7/2}(0.5) \approx 126.28$), $d_2 = 3R$ and $R = 30$ Å are shown in figure 3. For these ensembles the spontaneous magnetization at $T = 0$ and the temperature of phase transition in the ferromagnetic state equal 65 emu cm^{-3} and 952 K in the case of prolate nanoparticles, and 43 emu cm^{-3} and 322 K in the case of oblate ones. The dependence of the transition temperature T_{cr} on a nanoparticle shape is conditioned both by a shape anisotropy and dipolar interaction. According to equations (4) and (10) dipolar interaction leads to increase of T_{cr} for ensembles of prolate nanoparticles and to decrease of T_{cr} for ensembles of oblate ones. Specifically, for the considered ensembles of Co nanoparticles the increase of T_{cr} is equal to 98 K, and the decrease 42 K; the increase of dipolar field for prolate nanoparticles and its decrease for oblate ones is approximately the same and is equal to 220 Oe.

4. Conclusion

Magnetic properties of an ensemble of uniaxial ellipsoidal nanoparticles randomly distributed on the sites of a tetragonal lattice are considered. The mean local field acting on a nanoparticle from the other nanoparticles is found, the phase diagram for such ensembles is constructed and the regions where the ferromagnetic ordering exists are defined. The equation for the dipolar order parameter is derived and the temperature of paramagnetic–ferromagnetic phase transition is calculated.

Acknowledgments

We appreciate valuable comments of anonymous referees of the paper.

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