Determination of magnetic characteristics of nanoparticles by low-temperature calorimetry methods

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ABSTRACT

At low temperatures, the heat capacity of a superparamagnetic "ideal gas" determined by magnetic degrees of freedom can greatly exceed the lattice heat capacity. It is shown that in the presence of an external magnetic field, the temperature dependence of the magnetic part of the heat capacity has two maxima. The relations between the temperature at which these maxima are achieved, the magnetic moment of the nanoparticles and the magnetic anisotropy constant have been obtained. Measuring the heat capacity maxima temperatures by low-temperature calorimetry methods and using the obtained relations, we can obtain the numerical values both of the magnetic moment of nanoparticles and the magnetic anisotropy constants.

1. Introduction

Over the past decades, the field of research and development of physical characteristics of magnetic nanomaterials has undergone dramatic changes. This is due to the development of efficient methods for preparation and stabilization of nanometer sized magnetic particles (nanoparticles), and to the development of physical methods for their investigation [1–3]. When reducing the particle to a single domain size, the impact of thermal fluctuations on the rotational dynamics of the magnetic moment **m** of nanoparticles begins to grow. This type of the random motion of the magnetic moment is called superparamagnetism, and the system consisting of macroscopic amounts of this type of nanoparticles − a superparamagnetic.

One of the distinguishing features of superparamagnetics from conventional paramagnetic materials is that not individual atoms (or molecules) are carriers of the magnetic properties of elementary particles contained therein but magnetic nanoparticles containing a large number of atoms in the magnetically ordered state. The magnetic moments of nanoparticles are much larger than the magnetic moments of single particles of a conventional paramagnetic of the order of only a few Bohr magnetons. Another distinguishing feature of superparamagnetics is related to the presence of the magnetic anisotropy energy of their particles.

The magnetic characteristics of bulk samples – the anisotropy ratio A and the magnetic moment m – depend on the volume [4]. However, in the nanostructured magnetic particles A and m, the characteristics, besides the volume, also depend on the surface area of the nanoparticle

[5]. The surface contribution complicates significantly the development of theoretical methods for calculating these characteristics. The known numerical values of the magnetic characteristics were obtained by measuring the blocking temperature [6], or are known from the experiments with cluster beams [7] and the total magnetization relaxation studies [8].

In recent years, to determine the macroscopic characteristics of materials (including superparamagnetics), the adiabatic calorimetry allowing precise determination of the temperature dependence of the heat capacity has been successfully used [9–18]. In [19], the idea of determining the magnetic anisotropy constant by high-precision low-temperature calorimetry methods has been suggested. In this paper, methods for determining the magnetic characteristics (coefficient of anisotropy and magnetic moment) of nanoparticles by means of low-temperature heat capacity measurements are developed.

2. Magnetic energy of a nanoparticle and equations of rotation

If nanoparticles in a superparamagnetic are obtained by nanostructuring easy-axis ferromagnetics, they will also possess a magnetization easy axis (anisotropy axis). The particle energy with uniaxial magnetic anisotropy can be represented as [1–4]:

$$H_A(\theta) = A\sin^2\theta, \tag{1}$$

where θ is the angle between the vector direction of the magnetic moment **m** of the nanoparticle and the anisotropy axis **n** (Fig. 1).
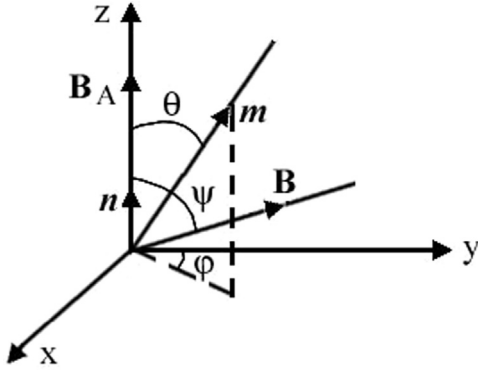
Fig. 1. Orientation of the vectors of the magnetic moment **m** and magnetic induction **B** with respect to the easy-axis magnetization, B_A is the magnetic induction of the anisotropy field, ψ is the angle between the easy-axis **n** and the magnetic induction vector **B**, θ and φ are the polar and azimuthal angles of the vector **m**, respectively. At $\varphi \neq 0$ the angles θ and ψ lie in different planes.

Usually, the anisotropy factor and the magnitude of the magnetic moment of the nanoparticle are represented as [1–4] $A = K_V V_m$ and $m = |\mathbf{m}| = M_S V_m$, where K_V and M_S are the densities of the corresponding quantities. The nanoparticle is supposed to be of spherical shape, consists of a central magnetic sphere of diameter d_m (magnetic diameter of the nanoparticle) and a nonmagnetic shell. $V_m = \frac{\pi}{6} d_m^3$ is the central magnetic sphere volume.

The anisotropy energy of one form or another is common to all magnetization nanoparticles. Its highest value ($K_V = 4.5 \cdot 10^5$ J/m^3) is observed in hexagonal-structure cobalt [20], whereas in nanoparticles of magnetite [21] (Fe$_3$O$_4$) it is smaller by an order of magnitude ($K_V = 4.8 \cdot 10^4$ J/m^3).

The Hamilton function of the particle with uniaxial magnetic anisotropy in the magnetic field has the form [1]

$$H(\theta, \psi, \varphi) = A\sin^2\theta - E(\cos\theta\cos\psi + \sin\theta\sin\psi\cos\varphi), \quad E = mB, \quad A > 0. \tag{2}$$

The first term in formula (2) represents the single axis magnetic anisotropy energy (1), and the second term corresponds to the interaction of the magnetic moment of the particle with the magnetic field. In superparamagnetics, the angles θ and ψ are random variables. The randomness of the variable θ is due to thermal fluctuations, and the random nature of the variable ψ is caused by the initial spread of the anisotropy axes of nanoparticles. Therefore, in equilibrium the angles θ and ψ determining the magnetic moment direction are taken from the minimum energy condition (2) with respect to the φ variable:

$$\frac{\partial H}{\partial \varphi} = E\sin\theta\sin\psi\sin\varphi = 0. \tag{3}$$

For powder nanoparticles, the anisotropy axes are oriented randomly and are not able to rotate, and the angle θ in the magnetization process varies in the range $0 < \theta \leq \pi$. Therefore, neither of these angles is identically equal to zero, and the minimum condition (3) reduces to the identity equation $\varphi \equiv 0$, which means that in equilibrium the angles θ and ψ lie in the same plane. Applying this condition to the energy (2), we get for the Hamiltonian function of the powder magnetic nanoparticle:

$$H(\theta, \psi, \varphi = 0) = A\sin^2\theta - E\cos(\theta - \psi). \tag{4}$$

As follows from the analysis [1] of the Hamiltonian function (4), the energy of the nanoparticle in the range $0 < \theta \leq \pi$ has two minima (or two potential wells) of different depth with the energy barrier between them of the order of A. For the magnetic moment to rotate (to transfer from one potential well to another), it is necessary to overcome this energy barrier. At temperatures below the blocking temperature ($T < T_B$), the magnetic moments are blocked in the potential wells

and hence do not change their orientation. At $T > T_B$, over-barrier fluctuating transitions occur, and after some time τ_N the whole ensemble of nanoparticles forms a single magnetothermodynamic system. The formula for the characteristic time of the fluctuating over-barrier transitions at $a = A/k_B T \geq 1$ was first derived by Néel [1,3]. The Néel relaxation process is related to the relaxation process inside the particle. Due to this relaxation the magnetic moment of the particle changes its direction, whereas the particle itself may remain fixed. Therefore, the Néel relaxation process is particularly important for powder magnetic nanoparticles.

For magnetic fluids, along with Néel, there is also another relaxation mechanism associated with the possibility of rotation of a particle (change in the variable ψ). This mechanism is characterized by the Brownian relaxation time (or the time of rotational diffusion)

$$\tau_B = \frac{3V\eta}{k_B T}, \tag{5}$$

η is the base fluid viscosity. Since the particle is able to rotate, the minimum energy condition (2) can be fulfilled for θ

$$\frac{\partial H}{\partial \theta} = A\sin 2\theta - E(-\sin\theta\cos\psi + \cos\theta\sin\psi\cos\varphi) = 0. \tag{6}$$

With allowance for the minimum condition (3)($\varphi = 0$), we get from (6):

$$A\sin 2\theta = E\sin(\psi - \theta). \tag{7}$$

Beside the relaxation forces proportional to the velocity $\dot{\psi}$, the nanoparticle of the magnetic fluid is also affected by the magnetic force moment

$$\frac{\partial H(\theta, \psi)}{\partial \psi} = E\sin(\psi - \theta). \tag{8}$$

As a result, the equation for the angle variable ψ with allowance for (7) for two different limiting cases can be written as

$$I\ddot{\psi} + 6V\eta\dot{\psi} + E\sin\psi = 0, \quad \theta \approx 0, \quad E \ll A, \quad I\ddot{\psi} + 6V\eta\dot{\psi} + A\sin 2\psi = 0,$$
$$\theta \approx \psi, \quad E \gg A, \tag{9}$$

where I is the moment of inertia of the nanoparticle.

3. Mechanical anisotropy state

The analysis of the rotational motion of the magnetic fluid nanoparticle under the action of the above forces made on the basis of the Eqs. (9) has shown [21] that in sufficiently strong magnetic fields the anisotropy axes can be parallel to the magnetic field induction ($\psi = 0$). The resultant state is called the state of mechanical anisotropy. The characteristic times of rotation of the particle axis, or of the establishment of the mechanical anisotropy state are given by the formulas

$$\tau_r = \frac{V}{V_m} \cdot \frac{6\eta}{M_S B_A}, \quad \text{for} \quad B \gg B_A, \tag{10}$$

$$\tau'_r = \frac{V}{V_m} \cdot \frac{6\eta}{M_S B} = \tau_r \frac{B_A}{B}, \quad \text{for} \quad B \ll B_A, \tag{11}$$

where $B_A \equiv 2K_V/M_S = 2A/m$ is the magnetic induction of the anisotropy field.

The necessary condition for the state of mechanical anisotropy to be realized is that the process of alignment of the anisotropy axes is more rapid than its destruction by rotational-diffusion processes, i.e. $\tau_r/\tau_B \ll 1$, for $B \gg B_A$, or $\tau'_r/\tau_B \ll 1$, for $B \ll B_A$. Substituting the values (10) and (11) into these equations, we get $\tau'_r/\tau_B = 1/a \ll 1$ for $B \gg B_A$ and $\tau'_r/\tau_B = (1/a)(B_A/B) \ll 1$ for $B \ll B_A$. It is obvious that the realization of the second condition is much more difficult.

Assuming that the condition of realization of the mechanical anisotropy has been fulfilled, we substitute $\psi = 0$ into the energy expression (4). Then we get for the Hamiltonian function