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The influence of magnetic anisotropy on the magnetization of small ferromagnetic particles

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Abstract. We calculated the magnetization of small ferromagnetic particles with uniaxial anisotropy. The numerical data were compared with experimental results for a magnetic liquid consisting of small amorphous $Fe_{0.75}C_{0.25}$ particles in decalin. From the comparison an anisotropy constant $K \simeq 3 \times 10^5$ J m^{-3} was estimated.

1. Introduction

As a first approximation an ensemble of small magnetic particles, for instance in a magnetic liquid, can be described as a superparamagnetic gas of giant moments. The magnetization of the particles in thermal equilibrium in a static, homogeneous field may be described by a Langevin function and the initial susceptibility, χ_i, depends on temperature according to the Curie law. Any deviation from the Langevin behaviour then reveals the differences between the ideal and real physical systems. The observed deviations from an ideal superparamagnetic behaviour have, in many cases, been explained by the fact that in reality the magnetic particles are not monodisperse: there is a distribution of sizes. By taking the size distribution into account and calculating the total magnetization as a superposition of Langevin contributions from each particle size fraction, a better agreement between calculated and experimental data may be obtained (see, for instance, the work of Kaiser and Miskolczy [1] and Chantrell *et al* [2]). However, on a closer examination of the data it becomes evident that there still remain some discrepancies in the intermediate field region.

We measured the static magnetization, in fields up to 12 T, of magnetic particles in frozen magnetic liquids and found that the data cannot be fully described by Langevin behaviour, even if the size distribution is taken into account. Thus we were motivated to investigate whether some of these deviations may be explained by the influence of magnetic anisotropy. The magnetic anisotropy has been included in calculations of the magnetic hyperfine splitting in Mössbauer spectra of superparamagnetic particles by Mørup *et al* [3] and in a theory for spin relaxation in small magnetic clusters by Jensen *et al* [4]. We calculated the expectation value of the z component of the particle moment in an external field from a Hamiltonian which includes the dipole energy in the external field, as well as the second- and fourth-order anisotropy terms. The model is the same as in the superparamagnetic case of Jensen *et al* [4]. However, in order to account for the experiments on magnetic liquids our numerical calculations cover

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a wider range of magnetic moments and fields. We found that when the magnetic anisotropy is included, we can obtain a better agreement between the experimental and theoretical field dependence of the magnetization. In the following we describe how the anisotropy energy modifies the field dependence of the magnetization of an ensemble of non-interacting magnetic particles.

2. The magnetization of particles with magnetic anisotropy

2.1. The model

The total energy, E, of a magnetic particle in an external magnetic field is given by the sum of the exchange energy, E_{ex}, the dipolar energy, E_B, and the anisotropy energy, E_{an}. In the following we consider only the completely ordered magnetic state, that is at temperatures far below the Curie temperature, with parallel or antiparallel alignment of all the spins in the particle. In this case the magnetization of the particle acts as a giant magnetic moment whose magnitude is independent of temperature and field. The microscopic magnetocrystalline anisotropy is caused by the spin–orbit coupling, which has the symmetry of the actual crystal lattice. For small particles, however, the contributions to the anisotropy from shape, surface or stress, are in general much larger than the magnetocrystalline ones. In particles that are not perfectly spherical certain easy directions are favoured, and as a first approximation we consider only one easy axis. Then we calculate the expectation value of the z component of the magnetization including the terms E_B and E_{an} in the Hamiltonian.

Let $\boldsymbol{e}$ and $\boldsymbol{u}$ be unit vectors along the directions of the easy axis and the magnetization respectively and β the angle between them, cf figure 1. With the magnetic field, $\boldsymbol{B}$, applied in a direction which makes angles λ with $\boldsymbol{e}$ and α with $\boldsymbol{u}$, the external magnetic field energy becomes

$$E_B = -\boldsymbol{m} \cdot \boldsymbol{B} = -I_s V B \cos\alpha \tag{1}$$

where $\boldsymbol{m}$ is the magnetic moment of a particle with saturation magnetization I_s and volume V.

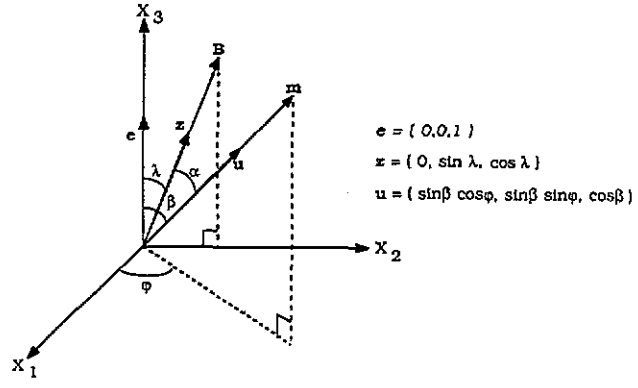

Figure 1. The Cartesian coordinate system, x_1, x_2, x_3, showing the unit vectors $\boldsymbol{e}$, $\boldsymbol{u}$ and $\boldsymbol{z}$ in the directions of the easy axis, of the magnetic moment of the particle, $\boldsymbol{m}$, and of the magnetic field, $\boldsymbol{B}$, respectively.

In uniaxial particles the anisotropy energy depends only on the angle β between the magnetization and the direction of easy magnetization in the particle. With terms up to fourth order and anisotropy constants K_0, K_2 and K_4, this gives

$$E_{an} = (K_0 - K_2 \cos^2\beta - K_4 \cos^4\beta)V. \tag{2}$$

In thermal equilibrium and for a fixed orientation of the easy axis the probability of finding the magnetization in the direction of u is proportional to the Boltzmann factor

$$f(u) = \exp(-E/kT) = \exp(-(E_B + E_{an})/kT). \tag{3}$$

The expectation value of the z component of the magnetic moment is given by

$$\langle m_z(e)\rangle = I_s V \langle \cos\alpha\rangle = I_s V \int_{\text{unit sphere}} \cos\alpha f(u)\,\mathrm{d}u \Big/ \int_{\text{unit sphere}} f(u)\,\mathrm{d}u. \tag{4}$$

Using the notations in figure 1, the following expression is obtained for the expectation value of the z component of the magnetic moment:

$$\langle m_z(e)\rangle = I_s V \int_0^{2\pi}\int_0^{\pi} \cos\alpha \exp(A\cos\alpha + B_1\cos^2\beta + B_2\cos^4\beta)\sin\beta\,\mathrm{d}\beta\,\mathrm{d}\varphi \times \left(\int_0^{2\pi}\int_0^{\pi} \exp(A\cos\alpha + B_1\cos^2\beta + B_2\cos^4\beta)\sin\beta\,\mathrm{d}\beta\,\mathrm{d}\varphi\right)^{-1} \tag{5}$$

where $A = I_s V B/kT$, $B_1 = VK_2/kT$ and $B_2 = VK_4/kT$. The factor $\cos\alpha$ can be written $\cos\alpha = z \cdot u = \sin\lambda\sin\beta\sin\varphi + \cos\lambda\cos\beta$.

Let

$$\bar{I}_0(x) = \exp(-|x|)I_0(x) \qquad \bar{I}_1(x) = \exp(-|x|)I_1(x) \tag{6}$$

where I_0 and I_1 are the modified Bessel functions of order 0 and 1. Integration over φ in the numerator and denominator of (5) then results in

$$m_z(\lambda) = T(\lambda)/N(\lambda) \tag{7}$$

where

$$T(\lambda) = \int_0^{\pi} [\cos\lambda\cos\beta\bar{I}_0(A\sin\lambda) + \sin\lambda\sin\beta\bar{I}_1(A\sin\lambda)] \times \exp(A\cos(\lambda-\beta) + B_1\cos^2\beta + B_2\cos^4\beta)\mathrm{d}\beta \tag{8}$$

and

$$N(\lambda) = \int_0^{\pi} \bar{I}_0(A\sin\lambda)\exp(A\cos(\lambda-\beta) + B_1\cos^2\beta + B_2\cos^4\beta)\,\mathrm{d}\beta. \tag{9}$$

The numerical integration over β was carried out with NAG routine D01AJF [5].

For a random distribution of easy-axis directions the z component of m is finally obtained from the statistical average

$$m_z = \frac{1}{4\pi}\int_{\text{unit sphere}} m_z(e)\,\mathrm{d}e = \frac{1}{2}\int_0^{\pi} m_z(\lambda)\sin\lambda\,\mathrm{d}\lambda. \tag{10}$$

The integration of (10) was carried out with NAG routine D01ARF [5].

Should there be a preferential orientation of the directions of the easy axes of the magnetic particles, this may be taken into account by modifying the spatial distribution of the angle λ in (10).

2.2. *Numerical results*

Let $M_z = M_z(I_s, V, K_2, K_4, T, B)$ be the expectation value of the magnetization of an ensemble of particles with saturation magnetization I_s, volume V, and anisotropy constants K_2 and K_4 at temperature T in field B. We carried out numerical calculations of M_z from the integrals (5) and (10) for different sets of particles, for instance with the values

$$V_1 = 1.9 \times 10^{-25}\ \mathrm{m}^3 \qquad I_{s1} = 3.4 \times 10^5\ \mathrm{A\ m^{-1}}$$

and

$$V_2 = 1.8 \times 10^{-26}\ \mathrm{m}^3 \qquad I_{s2} = 1.4 \times 10^6\ \mathrm{A\ m^{-1}}.$$

These values are characteristic of iron oxide particles [6] and amorphous iron–carbon particles [7] in magnetic liquids, respectively. The anisotropy constants K_2 and K_4 were varied in magnitude and sign in the range 10–10^6 J m^{-3}. The results were compared with the corresponding values of the Langevin function, $L = L(I_s, V, T, B)$. Let the relative difference between the values in a given field be $\Delta(B) = (L - M_z)/L$. The numerical calculations showed the following:

(i) The magnetization decreases for all fields when the anisotropy is turned on, with the same amount for negative and positive values of K_2. This is an effect of the averaging over a random distribution of the angle λ.

(ii) In the limits of high and low fields M_z approaches the Langevin value. The largest influence of the anisotropy is observed in the intermediate field region. For small values of the anisotropy the maximum of $\Delta(B)$ occurs in a field where the ratio $mB/kT \simeq 3$. The position of the maximum remains mainly independent of the anisotropy until $\Delta(B)$ approaches values of the order of 10%. Then the maximum is shifted towards significantly higher fields.

(iii) For a given set of particles $\Delta(B)$ increases roughly quadratically with K_2 when $K_4 = 0$. This quadratic dependence on K is also found when we calculate m_z from a series expansion of (5) for low fields and small K_2 with $K_4 = 0$.

(iv) The influence of the fourth-order anisotropy term was studied for the particles with $V_2 = 1.8 \times 10^{-26}$ m^3 and $I_{s2} = 1.4 \times 10^6$ A m^{-1} for K_2 in the range 2×10^5–3×10^5 J m^{-3}. Almost the same effect on the magnetization may be obtained by increasing or decreasing the value of K_2 as by increasing or decreasing that of K_4. The main effect of K_4 was to slightly modify the shape of the magnetization curve. (We did not include this term in the comparison with the experimental data.)

Figure 2 illustrates how the anisotropy modifies the magnetization of the particles. The calculated field dependence of the magnetization at 100 K is plotted for a set of different values of K_2 and with $K_4 = 0$ for magnetic particles with $V_2 = 1.8 \times 10^{-26}$ m^3 and $I_{s2} = 1.4 \times 10^6$ A m^{-1}. $K_2 = K_4 = 0$ yields the Langevin function. As can be seen in the figure, the deviation from Langevin behaviour is largest in the intermediate field region, around 0.2 T. This is the region where we also observe the largest differences between the experimental data and the corresponding Langevin function.

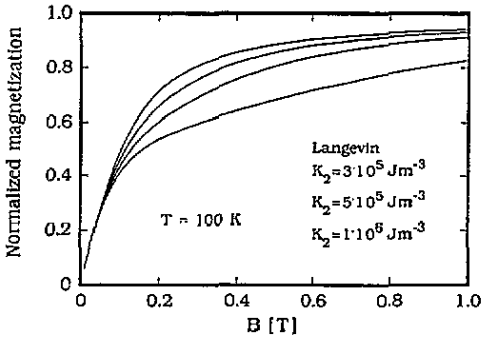

Figure 2. The influence of second-order anisotropy on the magnetization of small ferromagnetic particles. The calculations were made with equations (5) and (10) for the particle volume 1.8×10^{-26} m^3 and saturation magnetization 1.4×10^6 A m^{-1} at 100 K. The curves appear in the same order as the anisotropy constants in the figure. In all cases $K_4 = 0$.

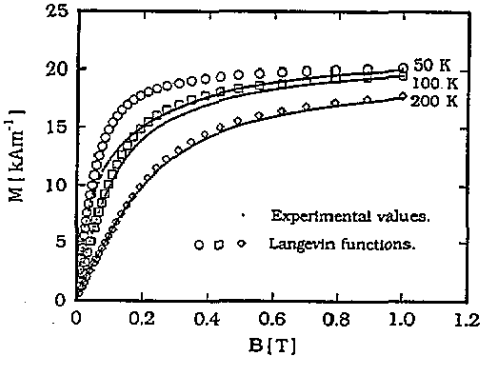

Figure 3. The magnetization of a (frozen) magnetic liquid with saturation magnetization 21 kA m^{-1} measured at 200 K, 100 K and 50 K and the corresponding Langevin functions calculated for monodisperse particles with volume 1.8×10^{-26} m^3 and saturation magnetization 1.4×10^6 A m^{-1}.

3. Comparison with experiments

The model described above may be applied to describe the properties of a magnetic liquid if the following conditions are fulfilled:

(i) The temperature must be low enough to prevent the particles from rearranging themselves spatially, that is the liquid should have a high viscosity or be frozen.

(ii) The thermal energy must be sufficient for the particles to reach thermal equilibrium within the measuring time, that is the temperature should be above the superparamagnetic blocking temperature.

(iii) The concentration of magnetic particles must be low enough to make the interactions between the particles negligible in the actual temperature range.

For a comparison between experimental and theoretical data we chose a magnetic liquid consisting of small, amorphous particles of $Fe_{1-x}C_x$ in decalin. In this liquid particle interactions are negligible for saturation magnetizations between 0.7 kA m^{-1} and 21 kA m^{-1} [7]. The magnetization of a sample cooled in zero field and measured in a constant field of 0.002 T during warming has a maximum at about 20 K, which is interpreted as due to blocking of the superparamagnetic relaxation in single particles. At temperatures above the maximum the liquid is superparamagnetic, with χ_i obeying a Curie law. Thus, for $T \geqslant 50$ K the liquid is well above the superparamagnetic blocking temperature. No particle rearrangement was observed in the liquid. The estimated diameters of the amorphous $Fe_{1-x}C_x$ particles (with $x \simeq 0.25$) are 3.2 nm with a very narrow size distribution [7]. The liquid was cooled in zero field to a crystalline state at 10 K [8]. Then the sample was successively warmed to 50 K, 100 K and 200 K. At each of these temperatures the static magnetization was measured with a vibrating sample magnetometer in magnetic fields of up to 12 T.

The magnetization of the liquid increases faster than does the Langevin function in high fields. It does not saturate even in fields as high as 12 T. This implies that the particles have a field dependent intrinsic magnetization. The experiments show that the magnetization increases linearly with the field above 4 T. We know that in liquids prepared with this method there are Fe^{2+} and Fe^{3+} ions present, which can account for at least part of this slope [9]. In the normalization of the calculated data we made a correction for this increase and used an extrapolated value for the spontaneous magnetization. The magnetization of polydisperse particles, calculated from a superposition of Langevin contributions, is larger than for monodisperse particles and the largest differences occur in low fields [2]. In this region the influence of the anisotropy is small. In fields of the order of 0.2 T, where $\Delta(B)$ has its maximum, and for a small variation in particle size, the increase for polydisperse particles above the monodisperse Langevin value is partly compensated by a larger value of $\Delta(B)$. We found that for our particle sizes and values of anisotropy constants the particles may be treated as monodisperse with the volume V_2 and the saturation magnetization I_{s2} given above. This corresponds to the mean values of volume and magnetic moment of the particles.

In figure 3 the experimental data for the liquid with saturation magnetization 21 kA m^{-1} are plotted together with the Langevin function. The largest values of $\Delta(B)$ are about 3%, 8% and 19% at the temperatures 200 K, 100 K and 50 K respectively. The positions of the maxima of $\Delta(B)$ are 0.1 T, 0.2 T and 0.35 T respectively. We have already shown above that for these particles the numerical calculations yield the largest values of $\Delta(B)$ in this field range. The value of K_2 was then adjusted to yield the same decrease below the Langevin function. This was obtained for $K_2 \simeq 3\times10^5$ J m^{-3}. It can be seen in figure 4 that we obtain a substantial improvement of the description of the experimental data in the intermediate field region when we include the anisotropy compared to that obtained with the simple

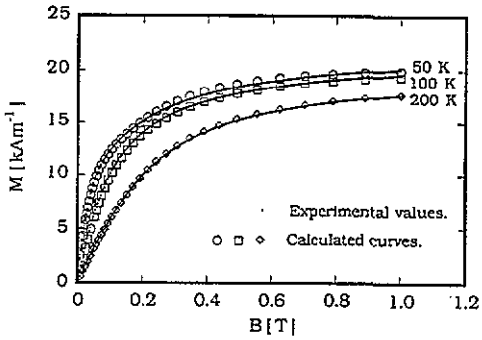

Figure 4. The magnetization of a (frozen) magnetic liquid with saturation magnetization 21 kA m^{-1} measured at 200 K, 100 K and 50 K, and the corresponding magnetizations calculated from equations (5) and (10). The calculations were made for particles with volume 1.8×10^{-26} m^3, saturation magnetization 1.4×10^6 A m^{-1} and anisotropy constants $K_2 = 3 \times 10^5$ J m^{-3} and $K_4 = 0$.

Langevin function, shown in figure 3.

An anisotropy constant $K = 2.7 \times 10^5$ J m^{-3} was obtained from a comparison between the superparamagnetic blocking temperatures observed by Mössbauer spectroscopy and magnetization measurements, with different measuring times [7]. Thus we conclude that the magnetic anisotropy of the particles can explain the deviations of their magnetization from Langevin behaviour in an intermediate field, of the order of 0.2 T.

4. Conclusions

We calculated the magnetization for small ferromagnetic particles, including the effect of magnetic anisotropy and found that this gives the same kind of deviations from Langevin behaviour as observed in experiments. The effect of anisotropy is small: less than 1% deviation at 100 K for anisotropy constants less than 10^4 J m^{-3} for particles with sizes and magnetic properties that are characteristic of magnetic liquids. In order to explain the largest experimentally observed deviations, 3–19% in the actual temperature range, the anisotropy must be of the order of 10^5 J m^{-3}. This value is high compared to bulk values for crystalline materials. It is, however, in excellent agreement with the value obtained from other experiments on the same liquid.

In the analysis of small particles magnetization curves are often used to extract particle sizes. Our results show that then one has to consider not only the particle size distribution, but also the influence of anisotropy. In particular one should ascertain that the saturation magnetization is estimated in a field that is high enough to make any deviation from Langevin behaviour negligible.

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