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Interaction and size effects in magnetic nanoparticles

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Abstract

Magnetic nanoparticles dispersed as a ferrofluid with volumetric concentrations in the range 0.4 to 10% and sizes ranging from 59–77 Å have been studied via magnetic measurements at room and low temperatures. Remanence measurements have been used to determine switching and coupling effects. Particle size and concentration effects have been investigated and we find that the samples with higher concentrations have larger coercivities than expected due to coupling effects. Interactions have been found to be demagnetising overall as expected for dipolar interacting systems. Surface effects become evident below 10 K when thermal effects are weak.

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1. Introduction

The study of fine magnetic particles continues to be of importance not only for recording technologies but also for other areas such as biological applications [1,2]. Also the study of the transition from atomic to bulk behaviour is of fundamental importance in solid state physics.

The magnetic properties of nanosize fine particles are dominated by the effects of the particle size distribution and the behaviour of the magnetic anisotropy. The particle size distribution in certain types of systems, and particularly those which we have examined in this work, is relatively simple to determine using standard transmission electron microscopy (TEM) techniques. However the behaviour of the anisotropy, which is also distributed, is somewhat more complex due to the fact that there are a number of origins of anisotropy which contribute to the total. For most ferro and ferri magnetic materials there is a contribution to the total anisotropy from standard magneto-crystalline

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effects. However for most particulate materials of practical use it is generally the case that shape anisotropy is dominant for any elongation greater than about 10%. In particles having nanometric dimensions (<10 nm) such elongations are almost invariably present. A further complexity in the behaviour derives from the fact that the surface area to volume ratio in nanoparticles is extremely large. For a typical particle of diameter 10 nm approximately one third of the atoms lie within two atomic layers of the surface. This leads to non-ideal chemical and crystallographic structures in a significant proportion of the material and hence to strong surface anisotropy effects. Surface anisotropy becomes an increasingly dominant factor as the particle sizes reduced below 10 nm. Hence the interpretation of experimental measurements involves a deconvolution of these complex contributions to the anisotropy.

The systems examined in this work were magnetite (Fe_3O_4) particles in the form of a ferrofluid with three different magnetic particle sizes of 59, 66 and 77 Å. The advantage of the ferrofluid system is that it is possible to change the concentration of the samples without changing the particle size distribution. This facilitates the study of interactions. Furthermore, the control of the particle size in ferrofluids and its determination is relatively simple via TEM or magnetic measurements as has been extensively documented [3,4]. It is also relatively easy to synthesise particles with very small particle sizes (<10 nm) and narrow distributions [5].

Magnetisation reversal in a ferrofluid proceeds via one of two mechanisms. For particles of high anisotropy where the moment is fixed in the easy direction, the moment can align with the field by physical rotation with a relaxation time of [6]

$$\tau = 6\,V\eta/kT, \tag{1}$$

where η is the fluid viscosity, V particle volume, T absolute temperature and k Boltzman's constant. When the anisotropy is low, as for the Fe_3O_4 particles studied here, alignment occurs via the usual Stoner–Wolfarth process subject to thermal activation where the relaxation time τ is given by the Néel–Arrhenius law,

$$\tau^{-1} = f_0 \exp(-\Delta E/kT), \tag{2}$$

where f_0 is the attempt frequency and ΔE the energy barrier given by

$$\Delta E = KV(1 - H/H_K)^2, \tag{3}$$

K is the particle anisotropy and H_K the anisotropy field, which for a particle system with uniaxial anisotropy and a random distribution of easy axis is, $H_K = 0.96\,\mathrm{K}/M_{\mathrm{sB}}$, where M_{sB} is the saturation magnetisation of the bulk material.

The magnetisation then proceeds by whichever process has the shorter relaxation time which, for a viscosity of 1 cpoise has been calculated by Schliomis [6] to give a critical particle diameter (D_s) above which physical rotation occurs,

$$D_s = \left[\frac{24\,kT}{\pi K}\right]^{1/3}. \tag{4}$$

Room temperature magnetisation curves for the three ferrofluids studied in this work are shown in Fig. 1.

In the case of particles in a solid matrix i.e., a frozen ferrofluid, only Néel rotation is possible. For particles of the size studied here the critical diameter for superparamagnetic behaviour for a typical relaxation time of 100 s [7] is 170 Å at room temperature falling to 40 Å at 4 K. These values assume an anisotropy constant of 5×10^5 erg/cc which is typical in such systems [8].

The particles in the fluids studied here have sizes that lie in this range and hence it is possible to

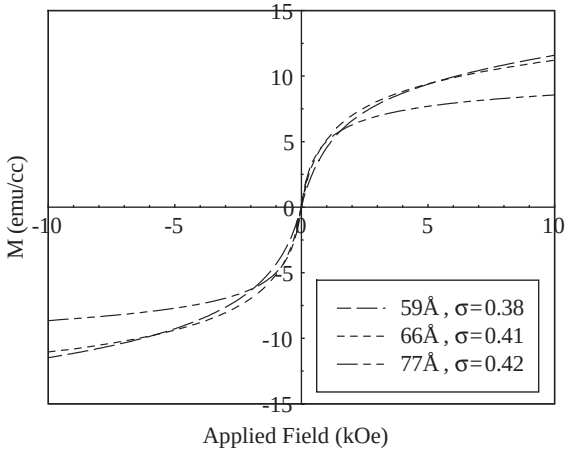

Fig. 1. Influence of the particle size on the magnetisation curves at room temperature.