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Dynamic response of magnetic nanoparticles arranged in a tubular shape

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Abstract

We have developed a model that describes the ferromagnetic resonance spectra recently observed in nanotubes formed by assembled $La_{0.67}Sr_{0.33}MnO_3$ manganite nanoparticles. The resonance line shape in these tubes resembles that of a system of randomly oriented flat particles instead of what is usually seen in elongated samples. In order to explain the experimental data we have assumed that each individual grain (or small group of grains) has an easy plane effective anisotropy which could be partially aligned in a cylindrical symmetry. The magnetization of each grain is also distributed around a mean value, and hence the magnitude of the anisotropy varies from grain to grain. Within this framework we have been able to fit reasonably well the resonance field and the overall line shape of nanotubes that were deposited on a glass substrate and were aligned in a magnetic field. From the simulations we have deduced an average effective magnetization $M = 180\,\mathrm{emu/cm^3}$ with a distribution width of $140\,\mathrm{emu/cm^3}$. This value of magnetization is smaller than that of bulk LaSr manganites at room temperature, probably due to the granular nature of the tubes.

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1. Introduction

The technique of ferromagnetic resonance (FMR) is commonly used to analyze the characteristics of magnetically ordered materials. Small particles, thin films, nanowires, and other systems with one or more reduced dimensions can be readily studied with this experimental technique due to the high signal to noise ratio that can be achieved with a very small amount of sample. The first approach in the modeling of the resonance spectra is the determination of the resonance fields. However, this analysis gives a valuable description only when the parameters that determine the magnetic behavior (e.g. magnetization, anisotropy, anisotropy direction, etc.) have a very narrow distribution. In many cases FMR spectra can be wrongly interpreted if it is considered that variables have no fluctuations. So when there are fluctuations in these variables it is necessary to analyze the complete line shape in order to account for their influence in the absorption spectrum. A few years ago it was discovered that manganite nanoparticles could be assembled in the form of nanotubes [1]. These tubes have an elongated shape with small interparticle interactions of dipolar origin [2]. The resonance line shape in these tubes resembles that of a system of randomly oriented flat particles instead of what is usually seen in elongated samples. It is then of interest to study the FMR spectra in this kind of tubes in order to find an explanation of this uncommon behavior.

2. Sample preparation and experimental setup

The preparation and structural characterization of the nanotubes have been already described in Ref. [2]. As already mentioned, the tubes are hollow structures formed by the assembly of small particles. For this study we have

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used $La_{0.67}Sr_{0.33}MnO_3$ nanotubes which have the following structural characteristics: tube length ~7 μm, tube diameter ~700 nm, wall thickness ~45 nm, particle diameter ~24 nm [2]. From the magnetic point of view the tubes are ferromagnetic at room temperature (T_C~340 K) and they have a saturation magnetization which can be less than one half of the bulk value of 580 emu/cm^3. This reduced M_S has been attributed to the presence of a paramagnetic dead layer located at the surface of the particles. This layer hinders the direct exchange interaction among particles and hence the magnetic coupling is dominated by dipolar effects.

Room temperature FMR experiments were performed at 9.5 GHz (X-band) in a Bruker ESP 300 spectrometer with a rectangular TE 102 cavity. Samples for FMR experiments were prepared by diluting the nanotubes in ethylene alcohol, placing a small drop of the solution on a glass substrate and allowing the alcohol to dry while applying a magnetic field of 1.5 kOe. In this way the tubes are partially aligned in the direction of the field which should allow to distinguish the contribution of the particle's own shape from that of the tube.

3. Model and experiment

In order to explain the resonance spectra of the nanotubes we will follow the model developed in Ref. [3]. The situation is somewhat different now because in that case the particles were forming a plane and in this case they are arranged in the form of a tube. A schematic picture of the system under study is shown in Fig. 1. We will assume that all particles have a planar shape favoring an easy plane anisotropy and are distributed in such a way that they form a tube which tends to be aligned with the x-axis. This can be done by allowing θ_p to take random values and setting $\varphi_p = \pi/2$. Explicit terms considering interparticle interactions are neglected. We will also neglect the magnetocrystalline anisotropy which is much lower [4] than terms arising from the shape anisotropy.

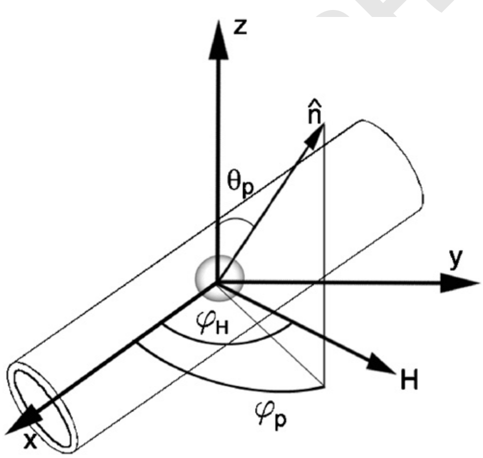

Fig. 1. Schematic drawing of the system under study. The particles lay on a cylinder which has its larger axis parallel to x. Each individual particle is assumed to have an easy plane anisotropy determined by the angles θ_p and φ_p. It also has a magnetization vector M with spherical angles θ and φ (not shown). The magnetic field H is rotated within the xy plane and forms an angle φ_H with the x-axis.

The magnetic free energy density per particle can then be written as

$$F = -\mathbf{M}\cdot\mathbf{H} + \frac{1}{2}\mathbf{M}\cdot\mathbf{N}\cdot\mathbf{M}. \quad (1)$$

In this expression $\mathbf{M}$ is the magnetization vector and $\mathbf{H}$ is the external magnetic field. In the particle reference frame the components of the demagnetizing tensor $\mathbf{N}$ are $N_{ij} = 4\pi$ if $i = j \| \hat{n}$, $N_{ij} = 0$ otherwise. If $\mathbf{N}$ is written in the xyz fixed reference frame the free energy can be written as a function of the angular variables,

$$F = -MH\sin\theta\cos(\varphi - \varphi_H) + 2\pi M^2(\sin\theta\sin\theta_p\cos(\varphi - \varphi_p) + \cos\theta\cos\theta_p)^2, \quad (2)$$

where θ and φ are the polar and azimuthal angles of the particle magnetization vector, and φ_H is the angle between the field $\mathbf{H}$ and the x-axis. For simplicity $\mathbf{H}$ is rotated in the xy plane (see Fig. 1).

The dispersion relation is obtained by applying the Smit and Beljers formula [5] to the above expression of the free energy resulting in [3]

$$\left(\frac{\omega}{\gamma}\right)^2 = \frac{1+\alpha^2}{M^2\sin^2\theta}\left(\frac{\partial^2 F}{\partial\theta^2}\frac{\partial^2 F}{\partial\varphi^2} - \frac{\partial^2 F}{\partial\theta\partial\varphi}\right), \quad (3)$$

$$\frac{\Delta\omega}{\gamma} = \frac{\alpha}{M}\left(\frac{\partial^2 F}{\partial\theta^2} + \frac{1}{\sin^2\theta}\frac{\partial^2 F}{\partial\varphi^2}\right). \quad (4)$$

α is a phenomenological factor introduced in the equation of motion to account for damping effects and $\gamma = g\mu_\beta/\hbar$.

In an experiment of magnetic resonance the absorbed power is proportional to the imaginary part of the scalar magnetic susceptibility [3]

$$\chi''(\omega) = \frac{\omega_0}{\gamma}\frac{\left(\frac{\Omega}{\gamma}\right)^2\alpha M\sin^2\theta - (1+\alpha^2)\frac{\Delta\omega}{\gamma}\frac{\partial^2 F}{\partial\varphi^2}}{\left(\frac{\Omega}{\gamma}\right)^4 + \left(\frac{\omega_0}{\gamma}\frac{\Delta\omega}{\gamma}\right)^2}, \quad (5)$$

with ω_0 the excitation microwave frequency and $(\Omega/\gamma)^2 = (\omega/\gamma)^2 - (\omega_0/\gamma)^2$. In the present case we assumed that all variables, except M, θ_p and φ_p, have a very narrow distribution. The average susceptibility is then obtained by integrating χ'' in these variables weighted by the distribution function f,

$$\langle\chi''\rangle = \frac{1}{C}\int_0^\infty\int_0^{2\pi}\int_0^\pi \chi''(M,\varphi_p,\theta_p)f(M,\varphi_p,\theta_p)\,d\theta_p\,d\varphi_p\,dM. \quad (6)$$

With the model presented above it is possible to estimate the effective anisotropy field (and the effective magnetization) from the analysis of the resonance field and the overall line shape. For this purpose we have simulated the line shape for a collection of randomly oriented planar particles in which the angle θ_p is randomly distributed and

φ_p has a gaussian distribution centered at $\varphi_p = \pi/2$ with a width σ_{φ_p}. The magnetization is also assumed to be gaussian distributed around a mean value $\bar{M}$ with a spread σ_M. Details of the computational simulation can be found in Ref. [3].

In Fig. 2 we show the experimental spectra of the nanotubes with the external magnetic field applied parallel and perpendicular (within the film plane) to the direction of preferential alignment, together with the fits obtained from the model. When the field is applied normal to the glass substrate the spectrum was quite similar to that obtained in the perpendicular direction, indicating that the inter-tube dipolar interaction is small. First of all it is observed that the positive part of the absorption is narrower and has a larger amplitude than the negative part. This experimental line shape is typical for flat particles that are randomly oriented in three dimensions [6]. For this reason we have assumed that the particles have a planar shape. For the simulations of Fig. 2 we have used the following parameters: $\bar{M} = 180\,\mathrm{emu/cm^3}$, $\sigma_M = 140\,\mathrm{emu/cm^3}$, θ_p random, $\varphi_p = \pi/2$, $\sigma_{\varphi_p} = \pi/3$, $\alpha = 0.035$ (which gives an intrinsic line width $\Delta H_{\mathrm{int}} \sim 300\,\mathrm{Oe}$). The angular variation of the resonance field and the fit obtained with the same set of parameters is shown in the inset of Fig. 2. Note that the spectrum asymmetry as well as the angular variation of the resonance field are well reproduced by the model. The fit is not so good in the region of fields around 3 kOe. However, it should be remembered that the particles have a paramagnetic dead layer which can contribute to the spectrum with a signal in this field range. Although the addition of a second line of paramagnetic origin will give a much better fit to the experimental data, it was not considered in the present analysis because no new information on the ferromagnetic phase will be obtained. The average value of magnetization is in agreement with the results obtained from dc magnetization measurements [2]. The experimental peak to peak line width $\Delta H \sim 1500\,\mathrm{Oe}$ is considerably larger than the intrinsic line width ΔH_{int}, indicating a large extrinsic contribution to the relaxation. We have also measuredthe line width at Q-band (34 GHz) and obtained $\Delta H \sim 2000\,\mathrm{Oe}$ consistent with the measurements at lower frequencies. The large values of ΔH are indicating that there is a large spread of resonance fields originated by the angular distribution of particles and by a magnetization that fluctuates from particle to particle. In order to reproduce the measured spectra it was necessary to use a rather large value of σ_M. This is not unexpected because the particles forming the nanotubes are not monosized and have a distribution width of approximately 50% [2]. Also the particle shape varies from grain to grain giving different values of the effective demagnetization field. Another important aspect that needs discussion is the spread in the angular variable φ_p. If perfect alignment of the tubes were assumed ($\sigma_{\varphi_p} = 0$) the difference between the parallel and perpendicular resonance would have been considerably larger. The high value of σ_{φ_p} confirms the experimental observation of a partial tube alignment during the fabrication process and also that the flat side of the particles is not necessarily parallel to the tube surface.

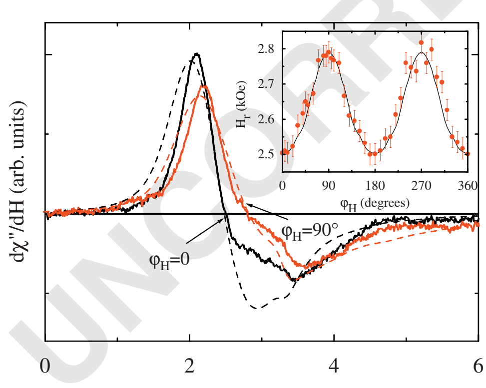

Fig. 2. (Color online) Experimental (continuous lines) and simulated (dashed lines) spectra for LaSr nanotubes and a collection of flat particles, respectively. The two cases correspond to the external field applied parallel and perpendicular to the direction of tube alignment. In the present case we have used for the simulation $\nu = 9.5\,\mathrm{GHz}$, $\bar{M} = 180\,\mathrm{emu/cm^3}$, $\sigma_M = 140\,\mathrm{emu/cm^3}$, θ_p random, $\varphi_p = \pi/2$, $\sigma_{\varphi_p} = \pi/3$, and $\alpha = 0.035$. In the inset we show with full circles the experimental angular variation of the average resonance field (defined as the zero crossing of the absorption derivative) and the corresponding fit (continuous lines).

4. Conclusions

Using FMR techniques and a model for a collection of particles arranged in a cylindrical symmetry we have been able to estimate the average magnetization of partially aligned LaSr nanotubes. The resonant spectra can be well explained if we assume that the particles have an easy plane of anisotropy and are randomly distributed in one of the angular variables while keeping the other fixed around a mean value. The value that we have obtained for the average effective magnetization is in good agreement with the results from static measurements. However, we have observed a relatively large distribution in the magnetization values which could be originated in particles with different sizes and shapes that are forming the nanotubes.

Acknowledgments

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