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High-frequency ferromagnetic resonance on ultrafine cobalt particles

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We report on high-frequency (300–700 GHz) ferromagnetic resonance (HF-FMR) measurements on cobalt superparamagnetic particles with strong uniaxial effective anisotropy. We derive the dynamical susceptibility of the system on the basis of an independent-grain model by using a rectangular approach. Numerical simulations give typical line shapes depending on the anisotropy, the gyromagnetic ratio, and the damping constant. HF-FMR experiments have been performed on two systems of ultrafine cobalt particles of different sizes with a mean number of atoms per particles of 150 ± 20 and 310 ± 20. In both systems, the magnetic anisotropy is found to be enhanced compared to the bulk value, and increases as the particle size decreases, in accordance with previous determinations from magnetization measurements. Although no size effect has been observed on the gyromagnetic ratio, the transverse relaxation time is two orders of magnitude smaller than the bulk value indicating strong damping effects, possibly originating from surface spin disorders. [S0163-1829(99)50706-6]

I. INTRODUCTION

Magnetic nanoparticles are a subject of intensive research due to their unique magnetic properties which make them of great interest both from theoretical and technological points of view.[1] These nanometer scale species are at the border of the molecular and the solid state physics. The size reduction, i.e., the reduced coordination number, leads to an increased magnetic moment per atom[2,3] and to an enhanced effective anisotropy (K_{eff}).[4,5] At this small size the particles are single domain and present a superparamagnetic (SP) behavior.

Recently, the progress in chemical synthesis has allowed the production of systems of cobalt freelike particles stabilized in a polymer. The particle sizes are controlled during the elaboration process and their final distributions are very narrow. In addition, each particle is well isolated from all the others, i.e., without strong chemical and/or physical interactions with its environment. Their major characteristic is the enhancement of the magnetic moment for the smallest particles as in the case of free clusters.[4] This manipulable system is ideal to study other features, such as structural properties, magnetization, and ferromagnetic resonance, or thermal relaxation and quantum tunneling of the magnetization.[6]

The magnetic properties of supported nanoparticles are currently investigated using magnetization, ac-susceptibility, Mossbäuer, and magnetotransport measurements.[1] These experiments allow one to deduce the different parameters such as the magnetic moment per atom, K_{eff}, or the relaxation time associated with superparamagnetism.[7] If the latter parameter is always relatively consistent with the theoretical predictions,[8,9] to our knowledge no exact demonstration of the theoretical expressions have been done, since the microscopic parameters of the Landau-Lifshitz equation of the magnetic-moment motion [gyromagnetic ratio (γ or g) and damping parameter (α)] are unknown. The work reported here shows that one way to determine γ and α is the use of ferromagnetic resonance (FMR) experiments under high enough magnetic field. Up to now, the experimental FMR studies which are currently performed have not allowed this determination. Usually performed under low magnetic field, they are devoted to the study of the temperature variation of the spontaneous magnetization[10] (M_S) or to the evaluation of K_{eff},[11] through the temperature variation of the FMR signal or the resonance field, respectively. For diluted systems, the spectra commonly exhibit large absorption linewidths which are not well understood.[12]

Here theoretical and experimental high-frequency ferromagnetic resonance (HF-FMR) investigations on ultrafine SP particles are presented. This work leads to the determination of K_{eff}, g, and α on ultrafine cobalt particles.

II. THEORETICAL ASPECTS

In the interpretation of the FMR spectra of disordered systems, one has to take into account the angular dispersion of the crystalline axis which causes a distribution of the local direction of the anisotropy fields $\mathbf{B}_a$.[13] Thus, the apparent resonant field (B_r) and the linewidth (ΔB) of the spectra will depend on this distribution. In the case of randomly oriented particles, the natural way to calculate the FMR signal is to evaluate the dynamic susceptibility χ_p of a *single* isolated particle for a fixed direction of $\mathbf{B}_a$, and to calculate the average value of χ_p over the distribution of $\mathbf{B}_a$ to get the observable quantity $\chi = \langle \chi_p \rangle$.[14]

In the case of ultrafine SP cobalt particles, one has to take into account the strong anisotropy and the effect of the thermofluctuations of the magnetic-moment (μ) direction due to their SP properties. Indeed, because of the enhanced anisotropy, B_a could be more than 1 T. For a particle in the blocked state, with its easy magnetization axis along the applied static field **B**, the resonant pulsation given by $\omega_r = \gamma(B + B_a)$, imposes a pulsation of measurement ω above $\omega = \gamma B_a \geqslant 30$ GHz.

For SP particles the thermofluctuations of the direction of μ reduces B_a, which then depends on the magnetic field, on the temperature, and on the volume of the particle.[15,16] Raikher and Stepanov have developed a model which takes into account these effects, but in the limiting case of $B \gg B_a$. To our knowledge, no experimental study has validated their theoretical predictions.[16] In order to reduce the number of parameters, a solution is given by performing the measurements under a magnetic field strong enough to saturate the magnetization ($B > 5$ T), with a high-frequency excitation field ($\mathbf{b}_{\rm hf}$), typically in the far infrared range (100–1000 GHz). In such a configuration the thermofluctuation effects on the value of B_a become negligible.

In these experimental conditions one can develop an independent-grain model. The motion of the magnetic moment μ of a single domain particle uniformly magnetized follows the Landau-Lifshitz equation,

$$\frac{d\mu}{dt} = -\gamma\mu\wedge\mathbf{B}_{\rm eff} - \alpha\frac{\gamma}{\mu}(\mu\wedge\mu\wedge\mathbf{B}_{\rm eff}), \quad \text{with} \;\; \mathbf{B}_{\rm eff} = -\frac{\partial F}{\partial\mu}. \tag{1}$$

Here $\mathbf{B}_{\rm eff}$ is the effective field, and F is the free energy density of the particle. For an uniaxial anisotropic ferromagnetic crystal, F is given by $F = -\mu[B(\mathbf{e}\cdot\mathbf{b}) + 0.5B_a(\mathbf{e}\cdot\mathbf{n})^2]$, where $\mathbf{e} = \mu/\mu$, $\mathbf{b} = \mathbf{B}/B$, $\mathbf{n} = \mathbf{B}_a/B_a$, and $B_a = 2K_{\rm eff}/M_S$. In general, Eq. (1) is solved using the Smit-Beljers method, leading to χ_p as an analytical function of the derivatives of F with respect to the rotational angles.[14(b),17] In this method the singular direction $\theta = 0$ has to be excluded. To overcome this disadvantage, Suran, and more recently Baselgia *et al.* have proposed an alternate method using rectangular coordinates.[18] In their model they used the rectangular coordinate system (1,2,3), 3 being set along the equilibrium direction of μ, and solved Eq. (1) in the absence of damping.

In order to derive χ_p, we start from Eq. (1) which integrates the damping effects, and solve it in the (1,2,3) system, using the Baselgia *et al.* procedure.[18(b)] We thus obtain a general set of analytical expressions for the resonant frequency ω_r, the linewidth $\Delta\omega$, and the scalar susceptibility χ_p as a function of the rectangular derivatives of F and the direction coefficients of $\mathbf{b}_{\rm hf}$ and **B**. It is then easy to calculate the derivatives of F and the directions coefficients of $\mathbf{b}_{\rm hf}$ and **B** in the (1,2,3) system using the orthogonal transformation between the (1,2,3) and the laboratory systems (x,y,z). Finally, the FMR spectra is then given by Abs$= -\chi_p''$, where χ_p'' is the imaginary part of χ_p. More details of the calculations and the analytical expressions of χ_p will be published elsewhere.[19] The major interest of this method of calculation is to suppress the $\theta = 0$ singularity in the general expressions derived by using the Smit and Beljers method. This method gives general analytical expressions which can be used in any experimental configurations encountered.

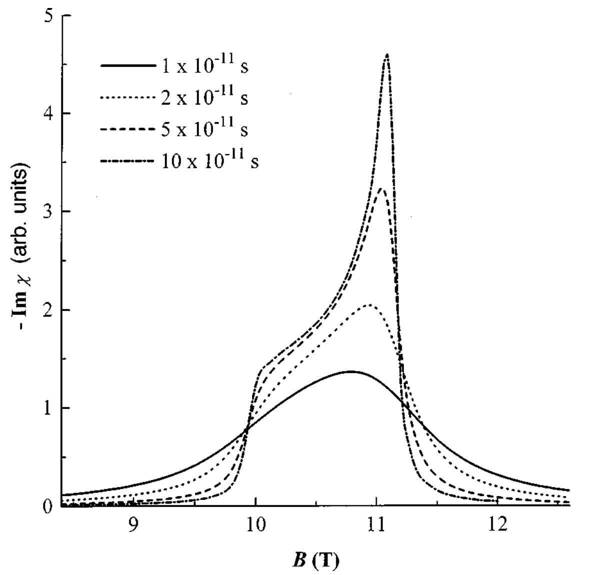

FIG. 1. Calculated high-frequency FMR spectra for three different $\tau_\perp$ values with $g = 2$, $B_a = 1$ T, $\omega = 2\pi\, 3\times10^{11}$ rad/s, and $B_0 = \omega/\gamma = 10.71$ T.

If we consider an uniaxially anisotropic ferromagnetic particle in a static field **B** along the z axis, the general expression of the resonant frequency ω_r is given by $\omega_r^2 = (1+\alpha^2)\gamma^2\{[B\cos\theta + B_a\cos^2(\theta_k - \theta)][B\cos\theta + B_a\cos 2(\theta_k - \theta)]\}$ where θ_k is the direction of the anisotropy with respect to the z axis. As ω_r, $\Delta\omega$ depends on θ_k while χ_p depends on both θ_k and on the $\mathbf{b}_{\rm hf}$ direction. For a system of particles with randomly oriented $\mathbf{B}_a$, the FMR spectra is the average of Abs over the angle distributions.

From these expressions we can derive various limits corresponding to familiar results. For $K_{\rm eff} \rightarrow 0$, we immediately obtain the classical result of an isotropic ferromagnet derived by Landau and Lifschitz. In the limit of particles made of a material with a long transverse relaxation time $\tau_\perp$ or a vanishing intrinsic FMR linewidth ($\alpha \rightarrow 0$), the inhomogeneous width of the resonance spectra is determined by the angular distribution of $\mathbf{B}_a$. If we consider an isotropic distribution of $\mathbf{B}_a$, the particles with $\mathbf{B}_a$ perpendicular to **B** have the largest resonance field $B_{\rm max}$, while the particles with $\mathbf{B}_a$ along **B** have the lowest resonance field $B_{\rm min}$. The broadening ΔB of the absorption spectra can then be well approximated by $\Delta B \approx 3B_a/2$.

Figure 1 presents the numerical simulations for an assembly of randomly oriented particles with a constant value of $B_a = 1$ T and different $\tau_\perp$ values. The other parameters have been fixed to $g = 2$ and $\omega = 2\pi 3\times10^{11}$ rad/s. It shows the sensitivity of the shape of the spectra to the damping effects, transforming the inhomogeneous broadened spectra to an asymmetric Lorentzian one as $\tau_\perp$ decrease. Our results are in perfect agreement with previous calculations,[18] and allow us to validate our method of calculation.

III. EXPERIMENT

HF-FMR experiments have been performed on two systems of ultrafine cobalt particles of different sizes (Coll-I,

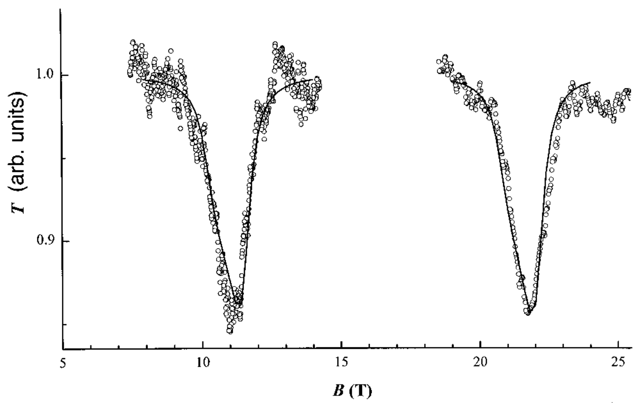

FIG. 2. Experimental high-frequency FMR spectra (symbols) of a Coll-II sample measured at 4.2 K, for two different frequencies 344 and 647 GHz corresponding, respectively, to B_0 around 11 T, and 22 T. The solid lines are the theoretical calculations.

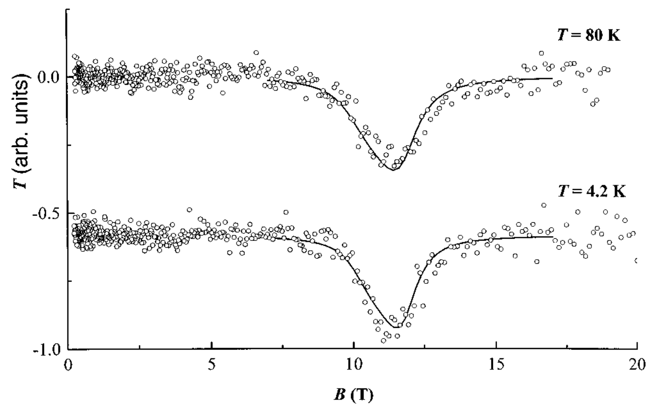

FIG. 3. Experimental high-frequency FMR spectra (symbols) of a Coll-I sample measured at different temperatures, for a frequency of 344 GHz corresponding to B_0 around 11 T. The solid lines are the theoretical calculations.

Coll-II).[4,6] These particles, prepared by a chemical method, are well dispersed in a polymer and have a very narrow size distribution. The analysis of magnetization curves evidences the presence of freelike, isolated particles with a mean number of atoms per particle of 150±20 and 310±20 for Coll-I and Coll-II, respectively.

HF-FMR measurements have been performed in the Faraday configuration using a pulsed magnetic field reaching 35 T, with a cryogenic setup where the temperature can be varied from 2 to 300 K. The high-frequency excitation field was produced by a far-infrared Fabry-Pérot cavity optically pumped by a CO_2 laser. Each of the HF-FMR spectra corresponds to the sample transmission variation vs applied magnetic field.[20]

IV. RESULTS AND DISCUSSION

In Fig. 2 are reported the typical experimental spectra collected at 4.2 K on Coll-II for two different frequencies $\omega/2\pi = 344$ and 647 GHz. Figure 3 presents the temperature dependence of the experimental spectra for Coll-I measured at the same frequency $\omega/2\pi = 344\,\mathrm{GHz}$. All these spectra show a rather large linewidth and are relatively homogeneously broadened, indicating strong damping effects.

These spectra have been analyzed using the above described model. Using the sensitivity of the model to the three parameters, and by fitting all the absorption curves, we can determine accurately K_{eff}, g, and $\tau_\perp$ (see Table I). For Coll-II, both spectra have been fitted using a single set of parameters allowing us to determine accurately B_a, γ, and $\tau_\perp = 1/(\omega\alpha)$. For Coll-I, the temperature dependence of the spectra and its narrowing with increasing temperature illustrate the temperature variation of B_a, and $\tau_\perp$.

In these systems the size-induced B_a distributions must be taken into account. For the two particle systems, we have computed the B_a distributions starting from the size distribution obtained by high-resolution transmission electronic microscopy and magnetization measurements,[4] and using the phenomenological law giving the diameter (ϕ) dependence of K_{eff} in ultrafine particles, i.e., $K_{\mathrm{eff}} = K_V + 6K_S/\phi$.[4,21] K_V and K_S are the volume and the surface contribution of the anisotropy, respectively, estimated with our experiments. Finally, it turns out that the distribution of B_a does not change significantly the fitting parameters, since they are very narrow. The K_{eff} values are found to be enhanced compared to bulk value and decrease as the particle size increases. The g factors are closed to bulk value and seem to be insensitive to the particle sizes.[22] On the other hand, the $\tau_\perp$ values are considerably lowered (two orders of magnitude) compared to bulk value.[23] They are decreasing with decreasing particle size.

The values of K_{eff} are consistent with those deduced from magnetization using the approach to saturation law, or from the fitting of the thermal dependence of the susceptibilities.[4] It allows us to discard definitively the method based on the estimation of K_{eff} from the blocking temperature without taking into account the size distribution which leads in a general manner to overestimated values.[4]

The most surprising result concerns the strong damping phenomena. We suppose that the very short $\tau_\perp$ originates from canted surface spin which can induce inhomogeneous precessions. Indeed, high-field magnetization measurements

TABLE I. Adjustment parameters obtained from the HF-FMR spectra for the two samples Coll-II and Coll-I.

Sample:	Coll-II		Coll-I	
$\langle n \rangle$ (atoms)	310		150	
T (K)	4.2	4.2	80	250
g	2.22±0.02	2.20±0.02	2.20±0.02	2.20±0.02
K_{eff} (10^6 erg/cm^3)	7.5±0.5	9.0±0.5	9.0±0.5	8.5±0.5
$\tau_\perp$ (10^{-12} s)	15±2	7±1	8.5±1	10±1

up to 35 T do not evidence magnetization saturation.[4] The differential high-field susceptibility which increases as particle size decreases can be explained in the light of recent micromagnetic calculations which predict in zero magnetic field the presence of canted surface spins, with a hedgehog-like spins structure, reflecting the competition between the exchange phenomena and the strong perpendicular surface uniaxial anisotropy in zero magnetic field.[24] Very high fields are necessary to reach a collinear spin structure.[24] This phenomenon which is more important as the particles are smaller can induce inhomogeneous precessions and increasing damping effects with decreasing particle size.

α can be now estimated using the relation $\alpha=1/(\tau_\perp \omega_0)$, where $\omega_0 \approx \gamma B_a$. With the parameters determined above, α is in the range of 0.3 and 0.55 (± 0.05) for Coll-II and Coll-I, respectively. These experimental estimations will be of great interest to test the analytical expressions predicting the relaxation time of the magnetization due to superparamagnetism. They confirm that the convenient value of $\alpha=1$ which was already adopted in the theoretical works on the relaxation phenomena of SP nanoparticles is a rather good approximation.[8,9] Since now all the parameters (microscopic and macroscopic parameters) are known, measurements of the experimental relaxation time τ associated with the SP phenomena should be done in order to test the validity of the theoretical models predicting τ.

V. CONCLUSION

In randomly oriented dispersed ferromagnetic particles, FMR measurements are a powerful method to determine the magnetic anisotropy and the microscopic parameters, as shown both theoretically and experimentally. We have developed a method of calculation based on independent-grain contributions averaged over angle distributions by generalizing the Baselgia *et al.* rectangular method. This original approach, which can be used for other systems and suppress the problem of the singular direction $\theta=0$, was applied to the case of highly anisotropic ferromagnetic SP particles. Our theoretical investigations showed that the ideal configuration is the use of a high-frequency excitation (>100 GHz) in high magnetic fields (>5 T), the latter being strong enough to saturate the magnetization. The numerical simulations evidence the strong sensitivity of the FMR spectra to both anisotropy and damping effects.

Experimentally, HF-FMR spectra have been obtained on ultrafine cobalt particles. Applying our model to the experimental results, we deduced K_{eff} of the particles in agreement with previous data from magnetization measurements. In addition, this procedure allows us to determine g and $\tau_\perp$. We show that g is insensitive to particle size and is of the same order as for bulk samples, while $\tau_\perp$ is two orders of magnitude below the bulk value and decreases with decreasing size. We suppose that these weak values could be due to inhomogeneous precession phenomena. Further studies on cobalt particles of different size are necessary in order to understand this unexpected result.

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