Direct Measurement of Superparamagnetic Fluctuations in Monodomain Fe Particles via Neutron Spin-Echo Spectroscopy

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Using the technique of neutron spin-echo spectroscopy, we have conducted a direct measurement of the superparamagnetic relaxation of nanoscale, magnetic monodomain iron particles in the time range between 0.01 and 160 nsec and for momentum transfers q between 0.035 and 0.15 Å^{-1}. Using a phenomenological model which includes the effect of a particle size distribution, we are able to determine the temperature T and q dependence of the longitudinal superspin relaxation time spanning 4 orders of magnitude. We find that for $T \lesssim 40$ K, interparticle correlations affect the longitudinal superspin fluctuations. [S0031-9007(98)08356-2]

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The first attempt to describe the relaxation of isolated magnetic particles was made by Néel to provide a theoretical foundation for the study of paleomagnetism and the dating of ancient pottery [1]. The theory of superparamagnetic relaxation was later refined by Brown [2]. The small magnetic clusters which lie at the origin of superparamagnetism are found in many diverse systems in biology, geology, materials, and environmental science [3,4]. For a ferromagnetic system, reducing the size below that of a typical magnetic domain will drastically modify its magnetic behavior due to the lack of domain walls and lead to the existence of a superspin associated with the particle as a whole. This can be seen as a size renormalization of the paramagnetic constituents in a solid.

The relatively new nanoparticle fabrication technology makes it now possible to construct model systems for the controlled study of the parameters which influence the magnetic properties, such as size distribution and interparticle correlation effects. Of particular interest, from both a theoretical and a practical point of view, are the magnetic fluctuations associated with the whole-particle magnetization. The dynamics of these systems has been studied essentially through experimental techniques which are based on detecting the temperature at which the fluctuation rate of the system becomes slower than the excitation frequency of the probe: this point is defined as the blocking temperature T_B. Mössbauer spectroscopy can also probe the particle dynamics via a detailed analysis of the spectra observed below T_B under certain conditions [5]. Combining local probes such as Mössbauer spectroscopy with ac and dc susceptibility, one can determine the blocking temperature over a very wide frequency range (roughly 10^{-2}–10^{8} Hz) [6,7]. Qualitatively, these data are consistent with the picture of essentially isolated particles where the magnetic anisotropy creates an energy barrier against fluctuations between the equivalent easy magnetization directions. This picture is probably oversimplified [3,7] due to interparticle correlations which can appear at low temperature, and one needs to revert to more direct probes, such as inelastic neutron scattering (INS), if one is to refine this model.

A good model system for neutron scattering studies is monodomain iron clusters embedded in an insulating matrix of Al_2O_3. A substantial amount of experimental work has been performed to investigate the magnetic properties of a sample with an average Fe particle diameter of 20 Å [8]. Transmission electron microscopy (TEM) determined a body-centered cubic structure and a 4 Å standard deviation for the particle diameter. Inelastic neutron scattering showed the existence of two distinct magnetic fluctuation components both associated with the whole spin of the particle (superparamagnetic fluctuations) [9]. The faster relaxing component could be resolved using triple-axis and time-of-flight INS spectrometers and was attributed to transverse fluctuations [9]. The other component could not be resolved and appeared to be frozen due to slow fluctuations beyond the instrumental resolution.

This slow component is identified with the longitudinal superspin fluctuations, which to date have never been *directly* measured for separated monodomain ferromagnetic particles. Although the measurements of the blocking temperature are primarily governed by these slowest fluctuations, such experiments can only qualitatively infer their behavior. Neutron spin-echo (NSE) spectroscopy directly measures the dynamic structure factor $S(q,t)$ as a function of momentum transfer q and Fourier time t. $S(q,t)$ is the spatial Fourier transform of the pair correlation function $C(r,t)$, which is in principle a complete

description of the space-time behavior of a system. Furthermore, the paramagnetic NSE technique [10] is sensitive to the magnetic fluctuations only and has the advantage to be essentially a *zero-field* measurement. Modern NSE spectrometers can access a wide range of Fourier times typically between 10^{-11} and 10^{-7} sec and also provide spatial information through studies of the q dependence. NSE is therefore an ideal probe to investigate the longitudinal fluctuations in superparamagnetic systems.

The superspin fluctuations were measured on the same sample used in previous experiments [8,9]. This sample was prepared by cosputtering of iron and Al_2O_3 on an aluminum foil substrate. The volume fraction of iron is 20% and the Al_2O_3 matrix is amorphous. The mean diameter of the essentially spherical Fe particles is about 20 Å as deduced from both magnetization measurements and x-ray small angle scattering [8]. Assuming the bulk density of iron [8], this diameter corresponds to over 300 Fe atoms per particle. SQUID measurements show a well defined blocking temperature of 15 K for a characteristic measurement time of about 100 sec [11]. The total sample volume was about 150 mm^3.

The measurements of $S(q,t)$ were performed on two NSE spectrometers IN11 and IN15 at the Institut Laue-Langevin in the time range of $t = 0.01-160$ nsec in an applied field of about 5 G. Three different incident neutron wavelengths, 6.26 Å (IN11), 8.5 Å, and 14.88 Å (IN15) were used to take advantage of the cubic dependence of t with wavelength ($t \sim \lambda^3$) [10] and thus providing the measurement range which extends over 4 orders of magnitude in t. The data were mainly collected at $q = 0.07$ $Å^{-1}$but also at $q = 0.035$ and 0.15 $Å^{-1}$, for various temperatures between 2 and 300 K. Polarization analysis was performed at each T and q in order to normalize the echo amplitude (see Fig. 1). The data were corrected for instrumental spin-echo resolution by normalizing each scan to the reference scan at 2 K where the system is frozen on the time scales of interest here.

The choice to measure at these three q values is motivated by the work presented in Ref. [8], where the magnetic small angle scattering was separated into three components: at $q = 0.035$ $Å^{-1}$ one is sensitive to the signal arising from ferromagnetic interparticle (short range) correlations, whereas $q = 0.15$ $Å^{-1}$ probes essentially only the dynamics arising from the single particle (see Fig. 5 in Ref. [8]).

Figure 2 shows the normalized spin-echo amplitude at $q = 0.07$ $Å^{-1}$ as a function of t for various temperatures. For 300 and 200 K, $S(q,t)$ is well described by a simple exponential decay $\exp(-t/\tau)$ [12]. The relaxation time τ is in agreement with the quasielastic linewidth Γ previously measured by time-of-flight (TOF) INS ($\Gamma = \hbar/\tau$) [9] (at 200 K, $\tau = 0.062 \pm 0.003$ nsec). For $T \lesssim 100$ K the dynamics changes drastically with decreasing temperature and $S(q,t)$ can no longer be described by a simple exponential decay. This coincides with the appearance of the resolution-limited slow component seen in the TOF experiment. However, it is also not possible to fit the $T \lesssim 100$ K data to a sum of two exponentials; the apparent stretched-exponential-like decay is reminiscent of a system with a distribution of relaxation times. In order to illustrate the origin of the stretched relaxation and to extract a characteristic relaxation time from these curves, we present a simplified model based on an idealized description of

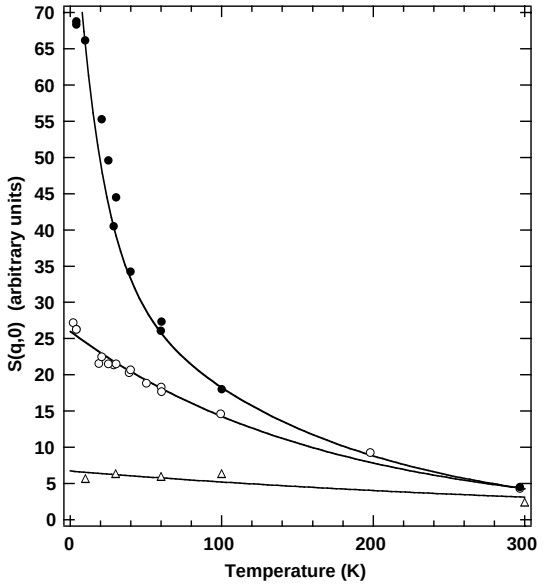

FIG. 1. $S(q,0)$ as deduced from the polarization analysis vs temperature for the three different q values: 0.035 $Å^{-1}$ (●), 0.07 $Å^{-1}$ (○), and 0.15 $Å^{-1}$ (△). Lines are a guide for the eye.

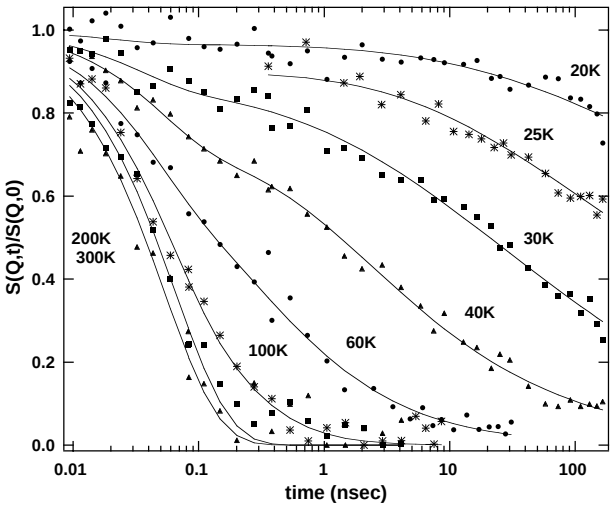

FIG. 2. Normalized $S(q,t)$ for $q = 0.07$ $Å^{-1}$ as a function of time for various temperatures. The lines represent the fit to the model described in the text, except at $T = 200$ and 300 K where a single exponential law is used.

the magnetic particles: In an independent particle picture, the superparamagnetic relaxation time τ is generally described by [1,2]

$$\tau = \tau_0(T, V) \exp(KV/k_B T), \tag{1}$$

where $\tau_0(T, V)$ is the inverse of a microscopic attempt frequency, *a priori* temperature and volume dependent [1,2,13–15], K is the magnetic anisotropy energy per unit volume, V is the particle volume, and k_B is Boltzmann's constant. Equation (1) implies that even a small spread in particle size will generate a significant distribution of relaxation times. In the following we outline how the size distribution influences the line shape of $S(q, t)$. We assume that the intrinsic relaxation for a monodisperse system remains exponential for all T, since the magnetic correlations are short range. As a first approach one can therefore suppose that any correlations simply lead to a renormalization of τ and not of the line shape itself. The cosputtering technique gives rise to a log-normal distribution $P(V)$ of the particle volume [7,16]:

$$P(V) = \frac{1}{\sigma V \sqrt{\pi}} \exp\left\{\frac{-[\ln(V/V_m)]^2}{\sigma^2}\right\}, \tag{2}$$

where σ is a measure of the size distribution and V_m is the mean volume. As a first approach one can therefore model the stretching of the relaxation for a given q as follows:

$$\frac{S(q, t)}{S(q, 0)} = \frac{\int_0^\infty V^2 P(V) \exp[-t/\tau(V)]\, dV}{\int_0^\infty V^2 P(V)\, dV}. \tag{3}$$

Using Eq. (1) for $\tau(V)$, one can rewrite Eq. (3) as a function of only three parameters $\beta \equiv k_B T/KV_m$, $\tau_m \equiv \tau_0 \exp(1/\beta)$, and σ:

$$\frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \exp\left(-x^2 - \frac{t}{\tau_m} \times \exp\left\{\frac{1}{\beta}\left[1 - \exp(\sigma x + \sigma^2)\right]\right\}\right) dx, \tag{4}$$

where we neglect any possible volume dependence of τ_0. This is justified, since by far the main effect of the size distribution is felt in the exponential term of Eq. (1). It is important to note that Eq. (4) makes no assumptions about the q and T dependence of τ_m or β. We now have a phenomenological expression which allows one to extract the characteristic longitudinal relaxation time from a measurement of $S(q, t)$, without the artifact of the size distribution.

To take into account the presence of the fast (transverse) component, we add to Eq. (4) a (particle volume independent) term $R \exp(-t/\tau_t)$ and normalize the entire expression by $(1 + R)$. This adds two extra parameters to the fit: the transverse relaxation time τ_t and the ratio R between the two components. In any case, the weight of this term to the fit is fairly small below 60 K. The fitted values for τ_t and R are consistent with the TOF results, and the resultant fit using this model is in excellent agreement with the data as can be seen in Fig. 2. Independent of any quantitative analysis, it is clear from the data that on a time scale of the order of 0.1 μsec, a measurable relaxation exists at 20 K. This is to be contrasted with the observation by SQUID magnetometry of a 15 K blocking temperature for a 100 sec characteristic measurement time [11]. Since the magnetization is the magnetic response at $q = 0$, the most evident explanation for this discrepancy is that the relaxation is q dependent, most likely due to interparticle correlations.

As expected, the size distribution σ is T independent, which for the final fits discussed below, we have fixed to the average value found: $\sigma = 0.6 \pm 0.1$. This corresponds to a standard deviation in the diameter of about 3 Å, consistent with the particle-size spread estimated from our TEM measurements.

We know from small angle neutron scattering measurements [8] that the system is weakly interacting so that β is not in principle simply proportional to T as in the isolated particle picture. Therefore we fit each temperature separately and plot the resultant effective longitudinal relaxation time $\tau_m(T)$ in Fig. 3. From this semilog plot vs $1/T$, one can see that $\tau_m(T)$ is nearly linear at $q = 0.07$ Å^{-1} but exhibits a pronounced curvature at $q = 0.035$ Å^{-1}. The coefficient β (inset in Fig. 3) is also highly linear in temperature but has a negative

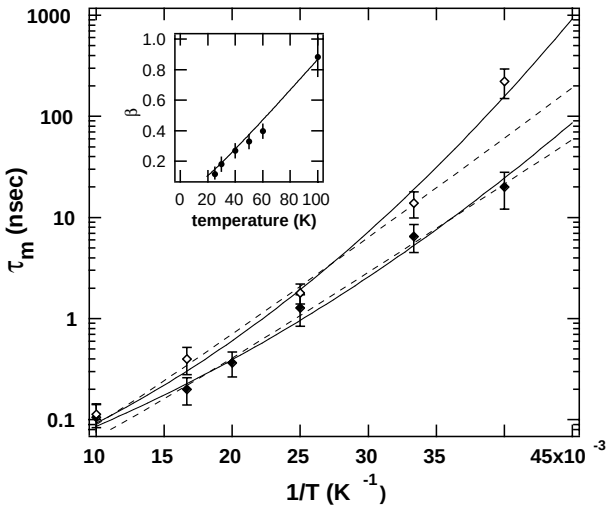

FIG. 3. Mean longitudinal relaxation time τ_m vs $1/T$ for $q = 0.07$ Å^{-1} (solid symbols) and $q = 0.035$ Å^{-1} (open symbols). The dashed lines are the fit using the expression proposed by Néel and Brown. The solid lines correspond to a fit using the phenomenological form $\tau_0 \exp(\kappa/T + a^2/T^2)$ for each q value. The data for $q = 0.15$ Å^{-1} are not shown since the low counting rates at this q permitted only a qualitative examination of the relaxation. The inset shows the coefficient β for $q = 0.07$ Å^{-1} as a function of temperature. The line corresponds to β as deduced from the fitted values for κ and a.

zero-temperature offset emphasizing the breakdown of the Arrhenius behavior at low temperature. To within the accuracy of these data, one could describe the T dependence of $\tau_m(T)$ by a Vogel-Fulcher-like expression, implying a freezing transition at finite temperature. However, susceptibility measurements of T_B on the same system do not see any signature of such freezing at low temperature. Therefore, we prefer to use the approach based on interacting superparamagnetic particles having no finite temperature transition, where the energy barrier is renormalized due to the local field arising from neighboring particles [7]. In this case, β can be phenomenologically described by $T/(\kappa + a^2/T)$, where the term a^2/T models the effect of a local field [9]. For $q = 0.07$ Å^{-1}, we find $\kappa = 97 \pm 30$ K and $a = 43 \pm 20$ K, whereas for $q = 0.035$ Å^{-1}, we fix κ at 97 K and obtain $a = 55 \pm 26$ K. These fits are shown as solid lines in Fig. 3, but we emphasize that this is a fit with purely phenomenological parameters. The coefficient τ_0 can be deduced from the fitted values for τ_m and β and is essentially constant in temperature but with a relatively large uncertainty ($\tau_0 = 0.02 \pm 0.01$ nsec). It should be noted that through the form of Eq. (1), in the absence of a specific model, one cannot simultaneously deduce a temperature dependence of τ_0 and β.

A fit of τ_m vs T with the expression proposed by Néel and Brown for isolated particles, where τ_0 varies as $\sqrt{T}$ does not agree with the data as well as the correlated particle approach (see Fig. 3). This is quite apparent when examining the q dependence of the relaxation. Fluctuations sensitive to interparticle correlations will become q dependent if such correlations appear. Comparing the τ_m for $q = 0.07$ and 0.035 Å^{-1} clearly shows a slowing down of the fluctuations with decreasing q (Fig. 3). This is something that a model with purely noninteracting particles cannot reproduce. The enhancement of the freezing behavior with decreasing T is also more evident at $q = 0.035$ Å^{-1} than at $q = 0.07$ Å^{-1}. We do not show the behavior of τ_t and R. Their behavior is consistent with that found in Ref. [9] and confirms that τ_t is only weakly q dependent whose weight R diminishes with decreasing q.

The following picture thus emerges from the analysis of this experiment: For $T \gtrsim 100$ K, there is essentially a single weakly q and V dependent relaxation component due primarily to isotropic single-particle fluctuations. Below 100 K, the temperature is less than the magnetic anisotropy energy barrier and the relaxation splits into two components: fluctuations transverse to the easy axis remain weakly q dependent whereas the longitudinal relaxation is sensitive to interparticle correlations. These correlations affect the dynamics below 40 K, where one observes a more pronounced freezing (both in q and T) than from noninteracting particles. This also coincides with the pronounced broadening and loss of spectral weight of the transverse component [9].

The dynamics of *antiferromagnetic* (AF) α-Fe_2O_3 particles using triple-axis neutron scattering was recently reported [17]. Because of the much smaller whole-particle magnetization in this system, the fluctuation rate is much faster, allowing one to use the triple-axis technique, which has a much lower energy resolution than NSE. The experiment found that the dynamics of AF α-Fe_2O_3 is consistent with the Néel and Brown theory [1,2]. However, if this system also develops superspin correlations, the limited energy resolution of this technique would not have permitted one to detect any effect on the dynamics. Furthermore, it is clear from our experiment that the particle-size distribution must be taken into account in any in-depth analysis. This also suggests that it is important to study the dynamics in monodomain systems without a particle-size distribution in order to improve our understanding of magnetic nanoparticle dynamics.

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