Relaxation and Landau-Zener experiments down to 100 mK in ferritin

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Temperature-independent magnetic viscosity in ferritin has been observed from ~2 K down to 100 mK, proving that quantum tunneling plays the main role in these particles at low temperature. Magnetic relaxation has also been studied using the Landau-Zener method, making the system crossing zero resonant field at different rates $\alpha = dH/dt$ ranging from 10^{-5} to 10^{-3} T/s and at different temperatures from 150 mK up to the blocking temperature. We propose a $T \ln(\Delta H_{eff}/\tau_0 \alpha)$ scaling law for the Landau-Zener probability in a system distributed in volumes, where ΔH_{eff} is the effective width of the zero-field resonance.

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Over the past decade there have been experimentally observed a large number of quantum phenomena in the dynamics of the magnetic moment of mesoscopic systems like monodomain magnetic particles. One particular system has had much attention since Awschalom and co-workers announced the observation of a resonance near 1 MHz that interpreted in terms of quantum coherence of the magnetic moment[1,2]: the system is composed by antiferromagnetic particles which grow inside the cage of the horse spleen ferritin proteins.[3]

Next experimental studies of the dynamics of the magnetization of ferritin particles, carried out at the kelvin regime, showed different phenomena interpreted as quantum tunneling of the ferritin magnetic moment.[3–10] More recently, there have been done ^{57}Fe Mössbauer spectroscopy measurements on an artificial ferritin sample down to 50 mK which show that incoherent tunnel fluctuations do not appear around 10^8 Hz.[11] Attending to the recent observation of resonant quantum tunneling of the spin observed in molecular clusters like Mn_{12}-acetate,[12,13] one can conclude that all these phenomena observed in ferritin particles in the kelvin range can be attributed to thermally activated resonant quantum tunneling of the magnetic moment at zero field.

In this paper we present magnetic data which extend the quantum relaxation measurements to the millikelvin regime. At the same time, in order to estimate the value of the quantum splittings of ferritin particles, we have done measurements of the change of magnetization when the system crosses zero magnetic field at different rates of the field sweep and we analyze the results in terms of the Landau-Zener probability associated with the magnitude of the splitting playing the main role in the quantum relaxation. This is the same method used by Wernsdorfer and Sessoli to determine the quantum splittings of Fe_8 molecular clusters.[14]

Ferritin is an iron storage protein. It has a spherical cage of about 8 nm in diameter in whose interior grows mineral ferrihydrite combined with a phosphate. Its core is equivalent to a small antiferromagnetic particle. The size of the core in natural ferritin ranges from 3 to 7.5 nm. Fully packed ferritin contains 4500 Fe^{3+} ions. A small magnetic moment of the particle arises from the noncompensation of collinear spin sublattices due to the finite size and irregular shape of the core. The spin of the sublattice, *S*, is of the order of 5000, while the noncompensated spin *s* is below 100. In our experiments we have used a Fluka Biochemical diluted natural ferritin sample, containing 10^{16} molecules per cm^3. The distribution of volumes of the sample, $f(V)dV$, is plotted in the inset of Fig. 1 [extracted from the fit of *M* versus $T \ln(t/\tau_o)$ shown in Fig. 2, using a γ function, $f(V) = V^{\beta} \exp(-V/V_0)$, with $\beta = 5$, in the form referenced in Ref. 9]. $f(V)$ has a maximum at $V_m \sim 108$ nm^3. The coupling among the different particles is negligible due to the small magnetic moment of each antiferromagnetic particle and the weak dipole-dipole interaction between them.[6,9]

Low-temperature magnetic relaxation measurements were done in an Oxford Instruments ^{3}He-^{4}He dilution cryostat and in a Quantum Design MPMS magnetometer in the following manner: The sample is cooled until the measure temperature and then a magnetic field of 1 T is applied during 10 min. After that, the field is switched off and the magnetization is measured during 3 h. In order to avoid remanent fields in the superconducting magnet and to obtain the relaxation measurements as close as possible to zero field a demagnetizing cycle is immediately applied after switching off the field. The demagnetizing cycle was previously tested in a pure Pb diamagnetic sample. This method makes the field along the

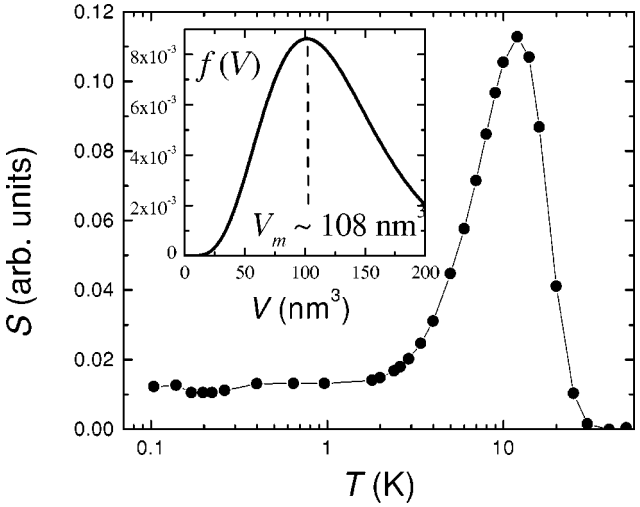

FIG. 1. Magnetic viscosity as a function of temperature of a ferritin sample extracted from time magnetic relaxations at zero field. The inset shows the distribution of volumes of the sample (extracted from Ref. 9).

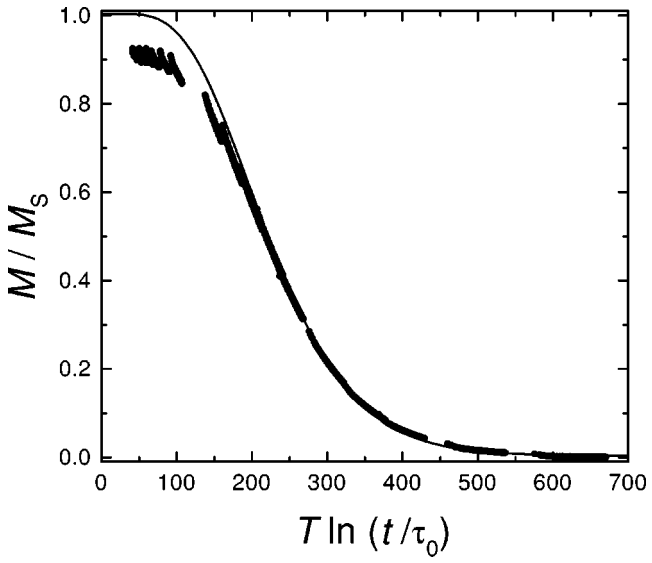

FIG. 2. $T\ln(t/\tau_0)$ plot of the magnetization extracted from time magnetic relaxations at zero-field (black points). The solid line is the thermal relaxation master curve.

major part of the relaxation to be zero with a precision of ± 2 Oe. The measurements were done at different temperatures ranging from 100 mK up to 25 K. The logarithmic on-time dependence of the magnetic relaxation is clearly observed over the whole measure. In a sample with a distribution of energy barriers, the quantitative magnitude which measures the relaxation time is the magnetic viscosity defined as[15]

$$S=\frac{1}{[M_{ini}(H,T)-M_{eq}(H,T)]}\frac{dM(H,T,t)}{d\ln(t)}, \qquad (1)$$

where $M_{eq}(H,T)$ is the equilbrium magnetization of the system at fixed temperature and field, which is $M_{eq}(H,T)=0$ in our case, and $M_{ini}(H,T)$ is the initial magnetization. In our experiments $M_{ini}(H,T)$ was taken from the extrapolation at small times of each magnetic relaxation curve. It is known that after switching off the field the system rapidly runs to a critical state in a time much more shorter than the times involved in the slow relaxation process occurring after the system reaches this critical state and relaxes to the final equilibrium state.[15] The observed dependence of the magnetic viscosity with temperature is shown in Fig. 1. The viscosity shows a maximum at $T_m \sim 10$ K. The temperature at which $S(T)$ changes its curvature sign is known as blocking temperature, $T_B \sim 8$ K, defined as

$$T_B=\frac{KV}{K_B\ln(t_m/\tau_0)}, \qquad (2)$$

which for viscosity measurements, with a characteristic measuring time t_m of hours, corresponds to the unfreezing of the magnetic moment of a particle of volume V which changes its orientation jumping over the energy barrier. In a sample distributed in size (see inset of Fig. 1) there is a distribution of energy barriers, $f(U=KV)$. The rate at which individual moments of the particles jump across the anisotropy barrier depends on temperature through the Arrhenius exponential factor, $\exp(-KV/K_BT)$. The blocking temperature in the viscosity at $T_B \sim 8$ K corresponds to the unfreezing of the particles having the volume V_m of the maximum of the volume distribution function. If we look at the volume distribution of Fig. 1, the blocking temperature may correspond to the particles with a volume around 110 nm^3. For these particles, using Eq. (2), with $\tau_0 \sim 10^{-8}$ s, $t_m=10^4$ s, and $K=2.5\times10^{-5}$ erg/cm^3, we obtain $T_B \sim 8$ K, in good agreement with the experimental result. As the temperature decreases, the magnetic viscosity goes to zero, as expected for thermal relaxation in a system with barriers distribution. However, below ~ 2 K the viscosity becomes independent of temperature down to 100 mK. This temperature, at which the system crosses from the thermal to quantum relaxation regime, is called the crossover temperature T_c.[4] The data shown in this paper extend the observation of the plateau of the magnetic viscosity down to a few millikelvin. This takes high relevance assuming the fact that below T_c the system relaxes exclusively through the lowest levels of the magnetic structure by quantum tunneling. This temperature does not depend on the volume of the particles. The expression expected from theory which determines this temperature for antiferromagnetic monodomain particles is $T_c \sim (2\epsilon_{an}\epsilon_{ex})^{1/2}/2\pi$.[16] Taking $\epsilon_{an} \sim 0.1$ K, (anisotropy energy per spin) and $\epsilon_{ex} \sim 10^3$ K (exchange energy per atom),[6] we obtain $T_c \sim 2$ K, in good agreement with the experimental value.

Zero-field cooling (ZFC) magnetization measurements have been done from 100 mK up to 25 K. The ZFC magnetization curve has a maximum at $T_m \sim 13$ K, in agreement with previous measurements.[4–10] The ZFC blocking temperature is $T_B \sim 10$ K, in agreement with the value extracted from Eq. (2) using $t_m=10$ s. The monotonic increase of the ZFC magnetization in the temperature range in which the viscosity plateau is observed supports the interpretation of the relaxation dynamics in terms of quantum tunneling, because there is no barrier distribution (e.g., minor particles, surface spins, etc.) which can simultaneously explain these two facts in terms of thermal relaxation.[15]

To look for evidence of thermal or quantum relaxation from time magnetic relaxation experiments a $T\ln(t/\tau_0)$ plot is usually used. In the thermal relaxation regime the dependence of the magnetization on $T\ln(t/\tau_0)$ scales in a master curve if the characteristic relaxation time τ_0 is adequately chosen. We show in Fig. 2 (black points) the $T\ln(t/\tau_0)$ plot corresponding to the time magnetic relaxations of the ferritin sample. The scaling is reached using $\tau_0=10^{-8}$ s. One can see that the relaxation curves depart from the master curve at temperatures below 5 K, indicating the presence of quantum tunneling as the temperature arrives near the crossover temperature. The thermal relaxation master curve is represented by the solid line. To calculate the magnetization master curve we have integrated the magnetic moment ($\mu \propto V^{1/3}$) of each particle over the whole sample, using a γ function for the volume distribution (inset of Fig. 1).

The most direct way to measure the quantum tunneling splitting Δ is by using the Landau-Zener model,[17] which gives the tunnel probability P when a resonance is crossed at a given sweeping rate α:

$$P = 1 - \exp\left[- \frac{h\Delta^2}{2g\mu_B S\alpha} \right], \tag{3}$$

where h is Planck's constant and S is the spin of a particle. Due to the distribution of volumes in ferritin there is a distribution of spin values, $S(V)$, and a distribution of quantum splittings, $\Delta(V)$. Also, the random orientation of the anisotropy axis of the particles in the sample introduces a distribution of sweeping rates, $\alpha(\theta)$, on the angle between the applied field and the anisotropy axis of each particle. This makes it such that different particles have different tunnel probability at a given sweeping rate depending in both volume and orientation with respect to the applied magnetic field. Taking into account the mentioned conditions, we can express the change of magnetization of the whole sample as the zero resonant field is crossed from H_i to H_f at a given α in terms of the Landau-Zener probability as follows:

$$\frac{M_f - M_i}{M_{eq} - M_i} = 2\pi \int_0^{\pi/2} \sin(\theta) d\theta \times \int_V S[V] P[\Delta(V), S(V), \alpha(\theta)] f[V] dV, \tag{4}$$

where M_i, M_f, and M_{eq} are the initial, final, and equilibrium magnetizations, respectively. The integral over θ has been chosen to take into account the random orientation of the anisotropy axes of the particles respect to the applied field. The form of $\alpha(\theta)$ for one particle is then $\cos(\theta)\alpha$.

Our experiments were done in the following manner: First, a saturating magnetic field was applied at the measure temperature. Then, the field was changed to $H_i = 250$ Oe at the highest sweeping rate and the magnetization was measured giving M_i. Immediately, the field was changed to $H_f = -250$ Oe at a given α, measuring M_f after the process was finished. The procedure was repeated at different sweeping rates, ranging from 10^{-5} T/s up to 10^{-3} T/s and, at different temperatures, from 100 mK up to the blocking temperature. The results are shown in Fig. 3. In order to make the nomenclature shorter we will use $P_{\Delta M}$ (probability to change the magnetization) instead of the expression given in Eq. (4). One can see that, at a given temperature, $P_{\Delta M}$ increases when α decreases. That is, as the zero-field resonance is more slowly crossed the probability to change the magnetization of the sample is higher. With the same dependence in α, the probability becomes higher for higher temperatures. The behavior of $P_{\Delta M}$ on $1/\alpha$ is logarithmic below $T = 20$ K. This dependence recalls the behavior of the time magnetic relaxation observed in this sample and, in general, in any sample with barrier distribution. Indeed, we can find the equivalence between the sweeping rate and time using $t = \Delta H/\alpha$, where $\Delta H = H_i - H_f = 500$ Oe in our experiment. Due to this equivalence, we can define a new parameter S_{LZ} to evaluate the characteristics of the magnetic relaxation in a Landau-Zener process with a barrier-distributed sample in the same manner that the magnetic viscosity does in time magnetic relaxations. That is, S_{LZ} can be expressed as

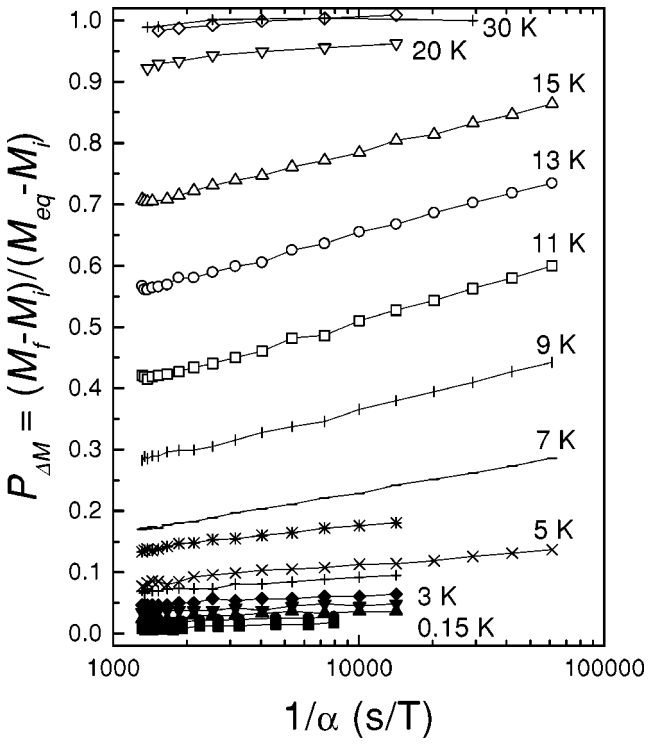

FIG. 3. Probability to change the magnetization as the zero-field resonance is crossed at different sweeping rates of the applied magnetic field and at different temperatures. The dependence with $1/\alpha$ is logarithmic.

$$S_{LZ} = \frac{dP_{\Delta M}}{d\ln(\Delta H/\alpha)}, \tag{5}$$

where $P_{\Delta M} = (M_f - M_i)/(M_{eq} - M_i)$. The temperature dependence of the *Landau-Zener viscosity*, S_{LZ}, is shown in the inset of Fig. 4. From a comparison of this result with the magnetic viscosity extracted from time magnetic relaxations (Fig. 1), the agreement between the results of both methods is clearly observed. S_{LZ} has a maximum at 10 K, and the blocking temperature around 8 K which, using Eq. (2), corresponds to the blocking temperature with an effective time, $\Delta H/\alpha$, of 10^4 s: that is, $\alpha = 10^{-5}$ T/s and $\Delta H = 5 \times 10^{-2}$ T. That is, the Landau-Zener procedure carried out in a sample of particles distributed in volume gives the same information as the magnetic viscosity analysis. However, we can extract new information from this procedure if we analyze the change of magnetization as the zero-field resonance is crossed under a scaling law proposed as follows.

We propose a scaling law, equivalent to the $T\ln(t/\tau_0)$ plot in time magnetic relaxations (Fig. 2), for the total change of magnetization of a volume-distributed sample in a Landau-Zener process using a $T\ln(t_{eff}/\tau_0)$ plot, where $t_{eff} = \Delta H_{eff}/\alpha$. In Fig. 4 (black points) is shown the $T\ln(t_{eff}/\tau_0)$ plot of $P_{\Delta M}^{not} = 1 - P_{\Delta M}$, in order to compare with the thermal magnetic relaxation master curve (solid line). The scaling is obtained with $\tau_0 = 10^{-8}$ s and $\Delta H_{eff} = 5$ Oe. It is observed that the data collapses onto a master curve for temperatures higher than ~ 5 K. The value of the effective resonance width, $\Delta H_{eff} = 5$ Oe, is two orders of magnitude smaller

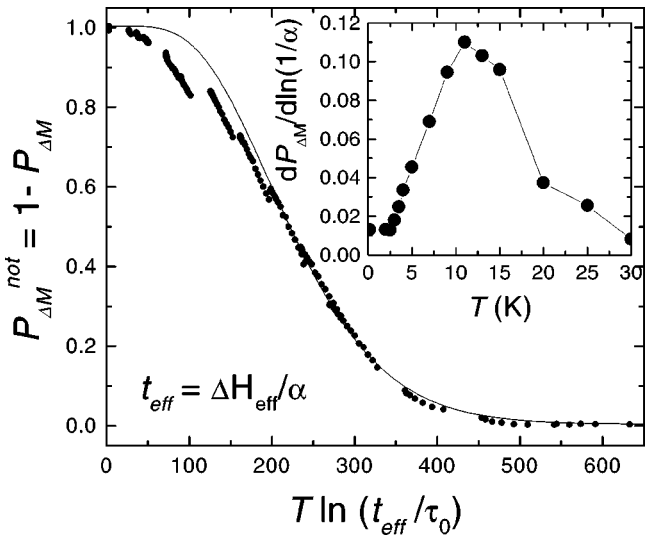

FIG. 4. $T\ln(t_{eff}/\tau_0)$ plot for Landau-Zener relaxations, $t_{eff} = \Delta H_{eff}/\alpha$ (black points). The values of τ_0 and ΔH_{eff} used to obtain the scaling are 10^{-8} s and 5 Oe, respectively. The solid line represents the thermal relaxation master curve. The inset shows the temperature dependence of the *Landau-Zener viscosity*.

than the width of the zero resonance observed in the magnetic hysteresis loops at the same temperatures, $\Delta H \sim 1000$ Oe (Refs. 2 and 5–8) and associated with thermally assisted resonant quantum tunneling.[6,8,9] In principle, the width of this resonance is associated with the quantum splitting of the blocking level, m_B. This is the level through which the quantum tunneling occurs at a given temperature. In ferritin the width of the resonance is associated with the distribution of quantum splittings of the blocking levels due to the different volumes of the particles of the sample. This fact, together with the random orientation of the anisotropy axes respect to the applied magnetic field, makes the width of the zero-field resonance several orders of magnitude higher than the width of the quantum splitting of one of the particles of the sample. However, the scaling law proposed here takes into account the effect of an average particle of the sample. Due to this, the physical meaning of ΔH_{eff} extracted from the master curve can be attributed to the width of the zero-field resonance for an average particle of the sample. That is, we may associate ΔH_{eff} with a quantum splitting of the effective blocking level, Δ_{eff}, of the distribution of particles in ferritin in the following manner: $\Delta_{eff} \sim g\mu_B S \Delta H_{eff}$. Using $S \sim 50$, we obtain $\Delta_{eff} \sim 700$ MHz. Taking into account the uncertainties associated to the random orientation of the anisotropy axes of the particles it seems clear that the obtained value of the quantum splitting of the effective blocking level agrees with the ~ 1 MHz resonance found by Awschalom *et al.*[1] and attributed to the quantum splitting of the ground state of ferritin particles.

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