Relaxation and Landau-Zener experiments down to 100 mK in 

**Ferritin**

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**Abstract**

Temperature-independent magnetic viscosity in ferritin has been observed from $\sim 2$ 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, $\alpha = \frac{dH}{dt}$, ranging from $10^{-5}$ to $10^{-3}$ T/s, and at different temperatures, from 150 mK up to the blocking temperature. We propose a new $T\ln(\Delta H_{eff}/\tau_{0}\alpha)$ scaling law for the Landau-Zener probability in a system distributed in volumes, where $\Delta H_{eff}$ is the effective width of the zero field resonance.
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. Monodomain magnetic particles of nanometer size contain thousands of magnetic atoms strongly interconnected by exchange interaction. As a result of the exchange interaction, all the atomic spins align parallel or antiparallel between them, resulting in a ferro, or ferri-antiferromagnetic ordering respectively. 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 kelvin regime, showed different phenomena interpreted as quantum tunneling of the ferritin magnetic moment [3–10]. These phenomena can be differentiated as follows: The first was the temperature-independent relaxation of the magnetization below 2.3 K observed in the magnetic viscosity measurements [4]. Secondly, a non-monotonic behaviour of the blocking temperature, $T_B$, on the magnetic field [2,5,6,8–10], contrasting with the monotonic classical expectation. Thirdly, a maximum at zero field in the magnetic field derivative of the magnetization extracted from the hysteresis cycles over 4 K [2,5–8]. And finally, a rapid increase of the magnetic viscosity as the magnetic field approaches to zero at temperatures higher than 3 K [3,9]. More recently, there have been done $^{57}$Fe Mössbauer spectroscopy measurements on an artificial ferritin sample down to 50 mK showing non-incoherent tunnel fluctuations 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. The observation of tunneling only at zero field lies in the fact that ferritin has a broad distribution of energy barriers due to the distribution of volumes of the particles ($f(U = KV)$, where $K$ is the anisotropy constant), and their anisotropy axes are randomly oriented. In the other hand, the temperature-independent viscosity below the
crossover temperature, \( T_c = 2.3 \) K, indicates that, below this temperature, the quantum magnetic relaxation of ferritin occurs through the lowest states.

In this paper we present new 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 to the magnitude of the splitting playing the main role in the quantum relaxation. This is the same method used by Wernsdorfer et al. to determine the quantum splittings of \( \text{Fe}_8 \) 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. The fully packed ferritin contains 4500 \( Fe^{3+} \) ions. A small magnetic moment of the particle arises from the non-compensation 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 non-compensated spin, \( s \), is below 100. This number corresponds to 15 non-compensated \( Fe^{3+} \) ions extracted from magnetic susceptibility measurements [4], in agreement with the theoretical expectation for the square root of the number of ions at the surface of the particle, \( N_s \sim (4500)^{2/3} \), which gives \( (4500)^{1/3} \sim 16 \). This non-compensated spin looks in one of two directions along the anisotropy axis of the particle. In our experiments we have used a \textit{Fluka Biochemical} diluted natural ferritin sample. The distribution of volumes of the sample, \( f(V)dV \), is plotted in the inset of figure 1 (extracted from reference [9]). The center volume is \( V_0 \sim 150 \text{ nm}^3 \). The low moment of the antiferromagnetic particles makes the interactions between different particles to be negligible, as one can see in the inverse susceptibility in the superparamagnetic regime that extrapolates to zero at \( T \rightarrow 0 \) [8].

Low temperature magnetic relaxation measurements were done in an \textit{Oxford Instruments} \(^3\text{He}-\text{He} \) dilution cryostat in the following manner: The sample is cooled until the measure
temperature and then a magnetic field of 1 T is applied during 10 minutes. After that, the field is switched off and the magnetization is measured during 3 hours. 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 major part of the relaxation to be zero with a precision of ±1 Oe. The measurements were done at different temperatures ranging from 100 mK up to 1.5 K in the dilution cryostat and repeated in the same manner in a Quantum Design MPMS magnetometer at temperatures 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

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

where \( M_{\text{eq}}(H, T) \) is the equilibrium magnetization of the system at fixed temperature and field, which is \( M_{\text{eq}}(H, T) = 0 \) in our case, and \( M_{\text{ini}}(H, T) \) is the initial magnetization. In our experiments \( M_{\text{ini}}(H, T) \) was taken from the extrapolation at small time 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 figure 1. The viscosity shows a maximum at \( T_B \sim 10 \text{ K} \). This is the blocking temperature, defined as

\[ T_B = \frac{KV}{\ln(t_m/\tau_0)}, \]  

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 figure 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, \( \exp(-KV/K_B T) \). The maximum observed in the viscosity at \( T_B \) corresponds to the unfreezing of the particles having the center volume, \( V_0 \), of the volume distribution. If we look at the volume distribution of figure 1, the blocking temperature may correspond to the particles with a volume around 150 nm\(^3\). For these particles, using eq. (2), with \( \tau_0 \sim 10^{-8} \) s, \( t_m = 10^4 \) s and \( K = 2.5 \times 10^{-5} \) erg/cm\(^3\), we obtain \( T_B \sim 10 \) 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 \( \sim 2 \) K the viscosity becomes independent on temperature down to 100 mK. This temperature, at which the system crosses from thermal to quantum relaxation regime is called crossover temperature, \( T_c \) [4]. The new data showed 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 \( T_c \sim (2\epsilon_{an}\epsilon_{ex})^{1/2}/2\pi \) [6]. 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.

ZFC magnetization measurements have been done from 100 mK up to 25 K. The measurements were done as follows: First the system is cooled from room temperature down to 100 mK in the absence of magnetic field. Due to the random orientation of the anisotropy axes of the particles the total magnetization is zero. Then a small magnetic field, \( H = 200 \) Oe, is applied and the magnetization is measured as the temperature is increased. The result is shown in figure 2. In this figure we can observe the maximum corresponding to the blocking temperature of the sample, \( T_B \sim 13 \) K, in agreement with eq. (2) using \( t_m = 10 \) s. A significant fact that one can observe in this figure is the increase of the magnetization
as the temperature goes to zero below $\sim 0.5$ K. The behaviour of the magnetization in this temperature range is $1/T$, indicating that there is a superparamagnetic contribution to the total magnetization. To understand this let us see the expected behaviour for a sample with a broad distribution of barriers in the thermal regime. After the field is applied at the lowest temperature, the smallest particles, having the smallest barriers, become free to rotate their magnetic moments out of the anisotropy axis and align them with respect to the applied field, contributing to the net magnetization of the sample. As the temperature increases, bigger and bigger particles can jump across the anisotropy barrier and the total magnetization increases. When the major part of the magnetic moments of the particles are free, over $T_B$, the system behaves paramagnetically following the $1/T$ Curie behaviour. This is opposed to the observed decrease of $M(T)$ at low temperature. Two different facts can explain this paradox: (a) thermal superparamagnetic behaviour of a second distribution of particles of smaller size or (b) quantum superparamagnetic behaviour of the smallest particles of the mono-distributed sample. The first explanation does not agree with the distribution showed in figure 1, where there is not a significant number of particles below 50 nm$^3$. Applying eq. (2) we obtain that a significant number of particles smaller than 5 nm$^3$ is needed to obtain $T_B < 0.1$ K. The ac-susceptibility measurements (window time of $10^{-3}$ s) and Mössbauer spectroscopy ($10^{-8}$ s) show that there are not significant particles of this size behaving superparamagnetically at low temperature. The second explanation, quantum superparamagnetism, explains better the $1/T$ behaviour at low temperature. This is the quantum behaviour of the particles for which $T_B$ is smaller than $T_c$. That is, these particles do not feel the anisotropy barrier because they can rotate their magnetic moments by quantum tunneling even if the temperature is not enough to jump across the barrier. The quantum tunneling rate is determined by the WKB exponent, $B \sim KV/K_BT_c$, in the following manner, $\Gamma \sim exp(-B)$. This means that the particles having smallest size have the higher probability to tunnel across the barrier.

The most direct way to measure the quantum tunneling splitting, $\Delta$, is by using the Landau-Zener model, which gives the tunnel probability, $P$, when a resonance is crossed.
at a given sweeping rate, $\alpha$:

$$P = 1 - \exp\left[-\frac{h\Delta^2}{2g\mu_BS\alpha}\right], \quad (3)$$

where $h$ is the Plank’s constant and $S$ is the spin of a particle. Due to the distribution of volumes in ferritin there are 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 that different particles have different tunnel probability at a given sweeping rate depending in both volume and orientation 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 $\alpha$ in terms of the Landau-Zener probability as follows:

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

where $M_i$, $M_f$ and $M_{eq}$ are the initial, final and equilibrium magnetizations, respectively.

The integral over $\theta$ 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 where 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 $\alpha$, 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 figure 3. In order to make the nomenclature shorter we will use $P_{\Delta M}$ (probability to change the magnetization) instead the expression given in eq. (4). One can see that, at a given temperature, $P_{\Delta M}$ increases when $\alpha$ decreases. That is, as the zero field resonance
is crossed slower the probability to change the magnetization of the sample is higher. With the same dependence in $\alpha$, the probability becomes higher for higher temperatures. The bahaviour of $P_{\Delta M}$ on $1/\alpha$ is perfectly logarithmic. This dependence reminds the behaviour of the time magnetic relaxation observed in this sample and, in general, in any sample with barriers 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 it in time magnetic relaxations. That is, $S_{LZ}$ can be expressed as

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

(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 figure 4. From the comparison of this result with the magnetic viscosity extracted from time magnetic relaxations (figure 1), the agreement between the results of both methods is clearly observed. $S_{LZ}$ has a maximum at 10 K, which, using eq. (2), corresponds to the blocking temperature with an effective time, $\Delta H/\alpha$, of $10^4$ s, this 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 that 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 new scaling law proposed following.

To look for evidences of thermal or quantum relaxation from time magnetic relaxation experiments it is usually used a $T \ln(t/\tau_0)$ plot. 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, $\tau_0$, is adequately chosen. This analysis permits to extract evidences of quantum tunneling when the magnetic relaxation departs from the master curve below a characteristic temperature. This temperature corresponds to the crossover temperature, $T_c$,.
explained before. Independently, it is possible to find the barriers distribution function from the derivative of the master curve. We show in figure 4 (black lines and right axis) 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. Below $\sim 2$ K all the curves are parallel, showing the temperature independence of the quantum relaxation.

We propose a new scaling law, equivalent to the $T \ln(t/\tau_0)$ plot in time magnetic relaxations, for the total change of magnetization of a volume distributed sample in a Landau-Zener process using a $T \ln(t_{\text{eff}}/\tau_0)$ plot, where $t_{\text{eff}} = \Delta H_{\text{eff}}/\alpha$. In figure 4 (open circles and left axis) is shown the $T \ln(t_{\text{eff}}/\tau_0)$ plot of $P_{\Delta M}^{\text{rot}} = 1 - P_{\Delta M}$, in order to compare with the magnetic relaxation master curve. The scaling is obtained with $\tau_0 = 10^{-8}$ s and $\Delta H_{\text{eff}} = 5$ Oe. It is observed that the data collapse into a master curve for temperatures higher than $\sim 5$ K. The value of the effective resonance width, $\Delta H_{\text{eff}} = 5$ Oe, is two orders of magnitude smaller than the width of the zero resonance observed in the magnetic hysteresis loops at the same temperatures, $\Delta H \sim 1000$ Oe [2-8] and associated to thermally assisted resonant quantum tunneling [6,8,9]. The same phenomena was previously observed in molecular clusters [12][13]. In principle, the width of this resonance is associated to 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 to 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 to be 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 $\Delta H_{\text{eff}}$ 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 $\Delta H_{\text{eff}}$ with the quantum
splitting of the effective blocking level, $\Delta_{eff}$, 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 $\sim 1$ MHz resonance found by Awschalom et al. and attributed to the quantum splitting of the ground state of ferritin particles.

In conclusion, we have obtained temperature-independent magnetic relaxation from both magnetic viscosity measurements and Landau-Zener viscosity down to 100 mK. We have proposed a new scaling law for the probability to change the magnetization in a Landau-Zener process in a sample with barriers distribution. The excellent agreement between the two studied methods (time magnetic relaxation and Landau-Zener process) permits to establish that quantum tunneling is the process governing magnetic relaxation in ferritin at low temperatures. From the comparison of these two methods one can extract additional information about the magnitude of the effective quantum splitting playing the main role in the low-temperature magnetic relaxation of a sample distributed in volume.

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FIGURE CAPTIONS

Figure 1: Magnetic viscosity as a function of temperature of ferritin sample extracted from time magnetic relaxations at zero field. The inset shows the distribution of volumes of the sample (extracted from [3]).

Figure 2: ZFC-FC magnetization versus temperature in ferritin recorded at $H = 200$ Oe. The inset amplifies the low temperature zone. $1/T$ quantum superparamagnetism behaviour is observed below 0.5 K.

Figure 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 clearly logarithmic.

Figure 4: $T\ln(t_{eff}/\tau_0)$ plot for both time magnetic relaxations, $t_{eff} = t$ (black lines, right axis), and Landau-Zener relaxations, $t_{eff} = \Delta H_{eff}/\alpha$ (open circles, left axis). The values of $\tau_0$ and $\Delta H_{eff}$ used to obtain the scaling are $10^{-8}$ s and 5 Oe, respectively. The inset shows the temperature dependence of the Landau-Zener viscosity.
REFERENCES

[1] D. D. Awschalom, J. F. Smith, G. Grinstein, D. P. DiVincenzo, and D. Loss, Phys. Rev. Lett. 68, 3092 (1992).

[2] S. Gider, D. D. Awschalom, T. Douglas, S. Mann, and M. Chaparala, Science 268, 77 (1995).

[3] S. Gider, D. D. Awschalom, T. Douglas, K. Wong, S. Mann, and G. Cain, J. Appl. Phys., 79, 5324 (1996).

[4] J. Tejada and X. X. Zhang, J. Phys.: Condens. Matter 6, 263 (1994).

[5] J. R. Friedman, U. Voscoboynik, and M. P. Sarachik, Phys. Rev. B 6, 10793 (1997).

[6] J. Tejada, X. X. Zhang, E. del Barco, J. M. Hernandez, and E. M. Chudnovsky, Phys. Rev. Lett. 79, 1754 (1997).

[7] Salah A. Makhlouf, T. Parker and A. E. Berkowitz, Phys. Rev. B55 R14717 (1997).

[8] E. del Barco, F. Luis, J. Tejada, X. X. Zhang, J. Bartolome, J. M. Hernandez, and E. M. Chudnovsky, J. Appl. Phys. 83, 6934 (1998).

[9] F. Luis, E. del Barco, J. M. Hernandez, E. Remiro, J. Bartolome, and J. Tejada, Phys. Rev. B59, 11837 (1999).

[10] R. Sappey, E. Vincent, N. Hadacek, F. Chaput, J. P. Boilot, and D. Zins, Phys. Rev. B56, 1451 (1997).

[11] P. Bonville, and C. Gilles, Physica B304, 237 (2001).

[12] J. R. Friedman, M. P. Sarachik, J. Tejada, and R. Ziolo, Phys. Rev. Lett. 76, 3830 (1996).

[13] J. M. Hernandez, X. X. Zhang, F. Luis, J. Bartolome, J. Tejada, and R. F. Ziolo, Europhys. Lett. 35, 301 (1996).
[14] W. Wernsdorfer, and R. Sessoli, Science 284, 133 (1999).

[15] E. M. Chudnovsky, and J. Tejada, 'Macroscopic Quantum Tunneling of the magnetic moment', Cambridge University Press (1998).

[16] B. Barbara and E. M. Chudnovsky, Phys. Lett. A145, 205 (1990).

[17] S. H. Kilcoyne and R. Cywinski, J. Magn. Magn. Mat. 140-144, 1466 (1995).

[18] C. Zener, Proc. R. Soc. London A 137, 696 (1932); S. Miyashita, J. Phys. Soc. Jpn, 64, 3207 (1995); V. V. Dobrovistki and A. K. Zvezdin, Europhys. Lett. 38, 377 (1997); L. Gunter, ibid. 39, 1 (1997); G. Rose and P. C. E. Stamp, J. Low Temp. Phys. 113, 1153 (1998).
Figure 1: Duran et al.

\[ S(\text{a. u.}) \]

\[ V(\text{nm}^3) \]

\[ f(V) \]

\[ V_0 = 150 \text{ nm}^3 \]
Figure 2: Duran et al.
$P_{\Delta M} = (M_f - M_i)/(M_{eq} - M_i)$
$$t_{\text{eff}} = \Delta H_{\text{eff}} / \alpha$$

$$T \ln \left( \frac{t_{\text{eff}}}{\tau_0} \right)$$

Figure 4: Duran et al.