Search for incoherent tunnel fluctuations of the magnetisation in nanoparticles of artificial ferritin.

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The magnetic behaviour of nanoparticles of antiferromagnetic artificial ferritin, with a mean Fe loading of 410 atoms per core, has been investigated by \(^{57}\text{Fe}\) Mössbauer absorption spectroscopy down to very low temperature (34 mK). In previous experiments of frequency-dependent magnetic susceptibility \(\chi(\omega)\) and magnetic noise \(S(\omega)\) performed at 25 mK in similar samples, it was claimed that a resonance at a frequency of about \(10^8\) Hz, due to a macroscopic quantum coherent state, had been observed. However, our search of incoherent tunnel fluctuations around \(10^8\) Hz using \(^{57}\text{Fe}\) Mössbauer spectroscopy, whose “window” of measurement of fluctuation frequencies lies in this frequency range, was unsuccessful. This casts a doubt about the previous observation of macroscopic quantum coherence in ferritin.

It was recently shown that in small ferromagnetic (FM) particles, a macroscopically large number of spins coupled by a strong exchange interaction can coherently tunnel through the energy barrier created by magnetic anisotropy. Similar, and even stronger, quantum effects should exist in the antiferromagnetic (AF) particles where tunneling of the Néel vector must result in a quantum superposition of AF sublattices. Two different situations must be distinguished: on one side, macroscopic quantum tunneling (MQT) where the magnetisation incoherently tunnels through the energy barrier, and on the other side, macroscopic quantum coherence (MQC) where the magnetisation coherently oscillates between the classically degenerate directions. Because of the AF ordering and the small size of the cores, ferritin has been thought to be a good candidate for the observation of these quantum effects. The observation of a low temperature resonance around \(10^8\) Hz in the absorption spectrum of artificial ferritin with an Fe loading of 1000 atoms per core was interpreted as due to the tunnel splitting of a macroscopic coherent state.

For particles with a mesoscopic number of spins, the incoherent MQT fluctuation rate has the same magnitude as the frequency equivalent of the MQC tunnel splitting. Then, instead of trying to detect the MQC state, one can search for MQT fluctuations with a similar frequency. In this work, we use \(^{57}\text{Fe}\) Mössbauer absorption spectroscopy, which has a “window” for measurement of electronic fluctuation frequencies centered at \(10^8\) Hz, to search for incoherent tunnel fluctuations in a ferritin sample with a Fe mean loading of 410 atoms per core, down to a temperature of 34 mK. The mean Fe content of our particles is lower than that of the smallest particles (1000 Fe atoms per core) where the resonance was found, but the presence of a small, but sizeable, unscreened magnetic field in our experiment can be thought to preclude the establishment of an eventual MQC state. However, a check of the existence of incoherent fluctuations around a frequency \(10^8\) Hz in ferritin at 34 mK can shed light on the existence of a MQC state with a tunnel splitting of similar frequency at the same low temperature.

Details about natural and artificial ferritin can be found in Ref. (1). Our artificial ferritin sample was prepared from ferrous Mohr salt with iron 95\% enriched in \(^{57}\text{Fe}\) in order to obtain a good signal to noise ratio in the Mössbauer spectra. The mean iron content of 410 Fe atoms per core was checked by atomic adsorption analysis, and the protein concentration in the solution (10 mg/ml) was determined by the Lowry method. The mean distance between particles in the sample is about 70 nm. The size histogram, established from transmission electron microscopy (TEM) pictures, is centered at a diameter value \(d_0=4\) nm and has a lognormal mean square deviation \(\sigma=0.18\). The peak in the Zero Field Cooled (ZFC) branch of the magnetic susceptibility occurs at \(T_m=7.5\) K. Our particles have very similar mean size and ZFC peak temperature as those referred to as 500 Fe atoms per core in Ref. (1) \((d_0=3.9\) nm and \(T_m=7.5\) K).

The \(^{57}\text{Fe}\) Mössbauer absorption spectroscopy experiments were performed in zero field at 34 mK and in the temperature range 4.2 K – 40 K. The 34 mK spectrum was recorded with a spectrometer coupled to a \(^3\text{He}–^4\text{He}\) dilution refrigerator. The sample holder is a copper cell with 0.5 mm thick plexiglass windows, which can contain about \(1\) ml of solution. For the 34 mK spectrum, the particles were diluted by a factor 3 to reduce interaction effects. Thermalisation is achieved by gluing thin sheets of pure Al (for the spectra at and above 4.2 K) or of pure Cu (for the spectra in the dilution refrigerator) onto the plexiglass windows. The thin metal sheets are in contact with the bulk copper of the sample holder, thus realising an isothermal box insuring a good thermalisation of the frozen solution. In the dilution refrigerator, the sample holder is thermally coupled to the mixing cham-
ber through a cold silver finger. For the 34 mK spectrum, the magnetic field at the sample place, created mainly by the magnets in the Mössbauer driving unit, was screened, resulting in a maximum field of 0.15 G.

The magnetic structure of the ferritin cores is expected to be of AF type, with a Néel temperature of a few hundred Kelvins. In the simplest picture of Néel’s model, an AF lattice consists of two FM sublattices, which have opposite magnetisations $M_1$ and $M_2$ with the same magnitude $M_0$. The AF ordering can be characterized by the unit Néel vector:

$$ l = \frac{M_1 - M_2}{2M_0}. \quad (1) $$

At a given temperature $T$, the Néel vector fluctuates by crossing the energy barrier created by the magnetic anisotropy: this is the superparamagnetic relaxation. For an axial anisotropy and for a given particle volume $V$, the thermally activated fluctuation frequency for the reversal of the Néel vector of a particle is given by $\tau$:

$$ \frac{1}{\tau} = \frac{1}{\tau_0} \exp(-\frac{KV}{k_BT}), \quad (2) $$

where $K$ is the magnetic anisotropy energy per unit volume and $\tau_0$ a microscopic relaxation time with magnitude $10^{-9}$-$10^{-11}$ s. When the thermal energy is much smaller than the barrier height, the Néel vector is classically forbidden from crossing the anisotropy energy barrier, but it can tunnel through it. In zero magnetic field and in the limit of weak dissipation, a macroscopic coherent state can be established where all the Fe$^{3+}$ moments in the AF sublattices tunnel between opposite directions in perfect unison. The system then presents a tunnel splitting $\Delta$ separating the antisymmetric and symmetric states built up from the “up” and “down” configurations of the Néel vector $l$. In the presence of a magnetic field such that the Zeeman splitting is larger than the tunnel splitting, the quantum coherent state is destroyed, but incoherent tunnel fluctuations with frequency $\Gamma$ can take place, with reversal of the $l$ vector (MQT). For a given particle volume $V$, $\Delta$ and $\Gamma$ can be expressed, in the WKB approximation, as $l$:

$$ \Delta \simeq \Delta_0 \exp[-\frac{S(V)}{2}] \text{ and } \Gamma \simeq \Gamma_0 \exp[-S(V)], \quad (3) $$

where $\Delta_0$ is a microscopic frequency and $S(V)$ is the WKB action, proportional to $V$. Expressing the action in the AF case yields a resonance frequency $\Delta$ in the MQC state $l$:

$$ \Delta = \Delta_0 \exp\left(\frac{V}{\mu_B} \sqrt{\frac{\chi_\perp K}{\chi^*}}\right), \quad (4) $$

where $\chi_\perp$ is the AF transverse susceptibility. The crossover temperature $T^*$ between the thermally activated regime and the quantum regime, estimated as the temperature where the rate of the thermal fluctuations is equal to that of the MQT, then writes $l$:

$$ T^* = \frac{\mu_B}{k_B} \sqrt{\frac{K}{\chi_\perp}}. \quad (5) $$

Estimations of $T^*$ using standard values for $K$ ($10^6$ ergs/cm$^3$) and $\chi_\perp$ ($10^{-4}$ emu/cm$^3$) show that it must be in the range 0.1 – 1 K $l$.

![FIG. 1. $^{57}$Fe Mössbauer lineshapes in the presence of fluctuations of a hyperfine field of 500 kOe as a function of the relaxation frequency, calculated following Ref. $l$.](image)

It is well known that the electronic fluctuations frequencies can be measured by Mössbauer spectroscopy if they lie within a “relaxation window” centered at the hyperfine Larmor frequency $1/\tau_L = \frac{1}{2\pi} \omega_{hf}$, where $\omega_{hf}$ is the hyperfine energy $l$. For $^{57}$Fe and a magnetic hyperfine field of 500 kOe, $1/\tau_L$ is around $10^8$ Hz. When the Néel vector $l$ fluctuates, the hyperfine field $H_{hf}$ at the nucleus, proportional to the individual Fe$^{3+}$ magnetic moment (and opposite to it in direction), fluctuates at the same rate. The Mössbauer “relaxation window” in the case of a fluctuating hyperfine field extends over two frequency decades, from $5 \times 10^6$ Hz to about $2 \times 10^8$ Hz; it is illustrated in Fig $l$, which shows the evolution of the spectrum as the fluctuation frequency $1/\tau$ increases. When $1/\tau$ is above a few $10^8$ Hz, the magnetic hyperfine structure is smeared out, $1/\tau$ is no longer measurable, and the spectrum is a single line or a two-line quadrupolar spectrum. However, in the presence of a large distribution of relaxation frequencies, as it is the case for an assembly of superparamagnetic particles, one actually only observes the patterns corresponding to two populations...
of particles, those whose Néel vector fluctuates with a frequency higher than $1/\tau_L$ (two-line spectrum), and those with $1/\tau < 1/\tau_L$ (six-line spectrum).

Representative $^{57}$Fe Mössbauer absorption spectra in the artificial ferritin sample with 410 Fe atoms per core are shown in Fig. 2.

Above 4.2 K, the spectra consist of a superposition of a six-line magnetic hyperfine field pattern, with a mean hyperfine field $H_{hf} \approx 490$ kOe, and of a two-line quadrupolar hyperfine field pattern (see spectrum at 20 K in Fig. 2). With increasing temperature, the quadrupolar doublet progressively replaces the six-line magnetic pattern. The thermal dependence of the relative intensity $f_p(T)$ of the quadrupolar sub spectrum is shown in Fig. 3. It can be calculated with the assumption of thermally activated fluctuations according to Néel’s equation (2). At a given temperature, the distribution of anisotropy barriers $KV$ results in a very broad distribution of relaxation times, and a “blocking volume” $V_b(T)$ can be defined such that $\tau = \tau_L$: $V_b(T) = \frac{k_B T}{K} \ln(\tau_L/\tau_0)$. Then the “superparamagnetic fraction” $f_p(T)$ is given by:

$$f_p(T) = \frac{1}{\langle V \rangle} \int_{V_{\text{min}}}^{V_{\text{max}}} V f(V) dV,$$

where $f(V)$ is the volume distribution. The experimentally determined $f_p(T)$ is well reproduced by expression (6), as shown by the solid line in Fig. 3. The fit, where the volume distribution function determined from the TEM size histograms was used, yields $K = 5 \times 10^3$ ergs/cm$^3$, which is a standard value for ferric oxides. Above 4.2 K, the dynamics of the Néel vector is therefore well described by thermally activated fluctuations across an anisotropy barrier with mean value: $\langle KV \rangle = 120$ K. The spectrum at 34 mK, shown at the bottom of Fig. 3, is essentially identical to the spectrum obtained at 4.2 K. Both spectra can be fitted with identical narrow distributions of static hyperfine fields. Such distributions are due to the presence of inhomogeneities in the lattice of the ferritin cores, and result in a spread of hyperfine field values of about 10% on each side of the mean value (500 kOe). They give rise to “inhomogeneous” static broadenings of the Mössbauer lines, which remain unchanged below 4.2 K. Therefore, at 34 mK, all the particles have their Néel vector fluctuating with frequencies below the “relaxation window”, i.e. slower than $5 \times 10^6$ Hz.

Several solutions of artificial ferritin, with an iron average loading ranging from 1000 to 4000 Fe atoms per core, were studied in Ref. [6,7]. In these studies, the chemical process used to synthesize the samples was identical to ours. For all the samples, a well-defined resonance was observed below 200 mK, both in the magnetic noise $S(\omega)$ and in the imaginary part $\chi''(\omega)$ of the a.c. susceptibility, which was attributed to the tunnel splitting associated with MQC. The obtained resonance frequency increases rapidly as the particle size decreases and, for the samples with a Fe loading less than 2000 atoms, the resonance frequency at 25 mK is found to be at $10^8$ Hz or higher, which is precisely of the same magnitude as the hyperfine Larmor frequency associated with $^{57}$Fe Mössbauer spectroscopy. Therefore, if a macroscopic coherent state could establish in the 25 – 50 mK range in the ferritin samples with the smallest Fe loading, with a tunnel splitting around or above $10^8$ Hz, then incoherent tunnel fluctuations with a similar frequency should be observed. Their signature in the Mössbauer spectra would be a single line or a two-line quadrupolar pattern (see the simulated spectra at $10^8$ and $10^9$ Hz in Fig. 3), and such a signature is absent from the 34 mK spectrum. Therefore, there are no incoherent tunnel fluctuations of the Néel...
vector at 34 mK with a frequency around $10^8$ Hz in our artificial ferritin sample with 410 Fe atoms per core.

Our $^{57}$Fe Mössbauer experiments were however not performed exactly in the same conditions as the $\chi(\omega)$ experiments of Ref. [6]. First, the magnetic field at the sample location is larger in our experiment (15 $\mu$T vs 1 nT). Such a field creates a Zeeman splitting between the “up” and “down” configurations of the Néel vector of the order of $10^6$ Hz per percent of uncompensated moment; this splitting is smaller than the supposed tunnel splitting of $10^8$ Hz and is neither expected to destroy the MQC state nor to have an influence on existing incoherent tunnel fluctuations. Second, our ferritin sample has been prepared with Fe 95% enriched in the isotope $^{57}$Fe, which has a ground nuclear spin $I=1/2$, and thus a non-zero nuclear magnetic moment, whereas the samples used in Ref. [6] were made from natural Fe, where the abundance of $^{57}$Fe is 2.2%. Actually, all the nuclear spins in the sample (i.e. both the $^{57}$Fe and proton spins) can be expected to have an influence on the tunneling properties. In this respect, there is no great difference as to the total nuclear spin content between our $^{57}$Fe enriched sample and those made with natural Fe. It is generally admitted that a MQC state is much more likely to be destroyed by the coupling to the nuclear spins (both through dissipation and decoherence effects) than MQT. Concerning MQT fluctuations, recent models show that the nuclear spins provide a “spin bath” which is likely to enhance the tunnel relaxation rate rather than deplete it.

Ideally, the check for the existence of tunnel fluctuations by Mössbauer spectroscopy should have been performed in the same conditions as the experiments of Ref. [7], i.e. in a ferritin sample prepared with natural Fe. Unfortunately, such an experiment with small Fe loadings would require impractically long counting times because of the very small signal. However, the presence of nuclear moments is not expected to influence at all the thermally activated fluctuations of the Néel vector. Then, at least down to 4.2 K, the spectra of an artificial ferritin sample with a natural Fe loading of 410 atoms per core would be identical with that of the same sample prepared with $^{57}$Fe, as the crossover temperature to the quantum regime is expected to lie below 4.2 K for AF particle systems. As the fluctuation frequencies at 4.2 K in our sample are below the Mössbauer “relaxation window” (i.e. they are lower than $5 \times 10^6$ Hz), then a spectrum at 34 mK in a ferritin sample with natural Fe loading would (if feasible) also show that all the fluctuation frequencies are below $5 \times 10^6$ Hz. Therefore, one can conclude that incoherent tunnel fluctuations at a frequency $10^8$ Hz are absent at 34 mK in artificial ferritin with a mean Fe loading of 410 atoms per core, implying the absence of MQC of the Néel vector at that temperature.

As a conclusion, our $^{57}$Fe Mössbauer experiments in artificial ferritin with a mean Fe loading of 410 atoms per core down to 34 mK show that, if a MQC state can establish in ferritin cores with low Fe loading, its tunnel splitting cannot be in the $10^8$ Hz range. This casts a doubt on the interpretation, in similar artificial ferritin samples, of a resonance at a frequency $10^8$ Hz as due to a tunnel splitting in a macroscopic coherent state. Indeed, one then would expect incoherent tunnel fluctuations to be detectable at $10^8$ Hz or above, which we do not observe. Our data however do not exclude tunnel fluctuations frequencies slower than $5 \times 10^6$ Hz, as these would not be observable by $^{57}$Fe Mössbauer spectroscopy.

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