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On magnetic relaxation in antiferromagnetic horse-spleen ferritin proteins

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Abstract. We report low-temperature magnetic relaxation measurements of nanometre-scale antiferromagnetic horse-spleen ferritin particles. It is argued that the magnetic relaxation signal is due to the excess uncompensated spins. Our key observation is the non-thermal character of the relaxation below 2 K. The observed features are in agreement with theoretical suggestions on quantum tunnelling of the Néel vector between easy directions.

1. Introduction

Ferritin is an iron-storage protein which has an iron-containing core surrounded by protein [1]. The core consists of iron oxyhydroxide with some additional phosphate. In a full ferritin molecule the core contains about 4500 Fe^{3+} atoms and is spherical with a diameter of about 80 Å. However, a sample of ferritin normally contains a range of core sites. Horse-spleen ferritin has been structurally characterized by dark-field TEM [2], x-ray diffraction [3] and electron diffraction [4].

The core material exhibits antiferromagnetic ordering and in a bulk material this shows a sextet Mössbauer spectrum at temperatures up to the ordering temperature or Néel temperature. When such a material is in the form of small particles, as in the present case, the Mössbauer spectrum becomes a superparamagnetic relaxation spectrum [5]. Mössbauer studies of iron-rich horse spleen ferritin show, at 4.1 K, a well defined magnetic sextet which, as temperature is raised, changes into a doublet at 50 K [6].

The antiferromagnetic order below the Néel temperature is characterized by the Néel vector of unit length

$$l = (M_1 - M_2)/2M_0$$

where M_1 and M_2 are the magnetizations of the two sublattices, have a fixed length M_0 and, in the absence of the magnetic field, are opposite to each other, i.e. $M_1 = -M_2$. Therefore the low-temperature magnetization of nanometre-scale antiferromagnetic particles under the influence of a low magnetic field is mostly due to uncompensated surface spins, their dynamic depending on l.

2. Experimental details

The sample used in these experiments was commercial ferritin from horse spleen (Merck index, 11, 3984). The protein concentration was 50 mg ml^{-1} and we used 0.369 ml of this solution containing 1.2×10^{16} protein molecules. The magnetic measurements were carried out on a SHE SQUID magnetometer.

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3. Results and discussion

The temperature dependences of the magnetizations on zero-field cooling and on field cooling (FC) recorded between 4 and 270 K in a magnetic field of 100 Oe are shown in figure 1. The result shows that the magnetization of the protein sample increases with decreasing temperature until the onset of irreversibility, which is attained at 25 K. At lower temperatures the ZFC magnetization begins to decrease whereas the FC magnetization continues to increase.

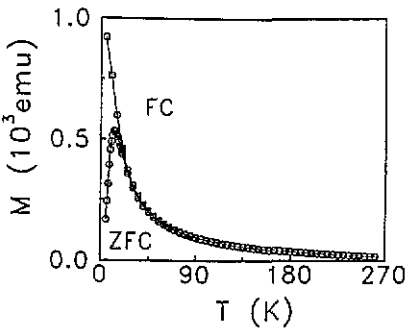

Figure 1. ZFC and FC magnetization curves for the protein with an applied field $H = 100$ Oe.

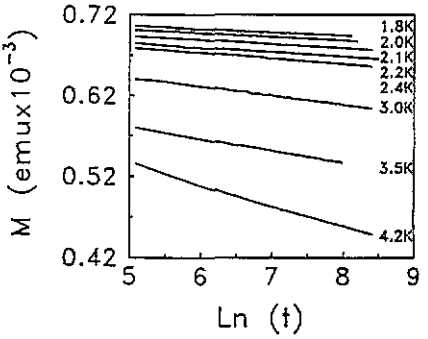

Figure 2. Time dependences for the thermoremanence magnetization of the sample ($H_1 = 100$ Oe; $H_2 = -100$ Oe).

For temperatures $T \geqslant 30$ K a Curie–Weiss law is obeyed with the computer-fitted equation $\chi = 7.44 \times 10^{-5}/(T - 3.4)$ emu cm^{-3} Oe^{-1}. Assuming that at 30 K most of the magnetic signal comes from the uncompensated excess spins, we have estimated that there are 15 uncompensated Fe^{3+} spins per protein molecule. Koenig *et al* [7] found about 12 uncompensated spins per molecule on the outside of the ferritin molecule which dominates water proton longitudinal relaxation in solution at room temperature.

The low-temperature ($T < 20$ K) behaviour is similar to that which characterizes the blocking process of ferromagnetic and ferrimagnetic small particles where the net magnetic moment of each crystallite is substantially greater than in the antiferromagnetic case. In the case where the anisotropy energy E_k for the Néel vector l of the particles dominates, there will be appreciable relaxation between the energy minima when $k_B T$ becomes comparable with E_k. This process is known as superparamagnetic relaxation ($T > 30$ K). At the limit of high anisotropy ($E_k \simeq 30 k_B T$), this leads to a longer relaxation time for the transition from the lower-energy minima to the higher-energy minima than vice versa, owing to the difference in the barrier height. This situation corresponds to the blocking of the Néel vector at T_B. The dynamic of the magnetic moment M of the excess uncompensated spins simply follows l as a 'slave' degree of freedom. Therefore, T_B also corresponds to the blocking of M. In Mössbauer spectroscopy the blocking temperature is the temperature at which the relaxation time coincides with the Mössbauer resolution time $\tau_M \simeq 2.5 \times 10^{-9}$ s. Our observation of a blocking temperature at 13 K agrees with the reported Mössbauer blocking temperature of about 50 K [6].

The rate of thermal transition is given by the Boltzman factor $\tau - \tau_0 \exp(-U/k_B T)$, where U is the anisotropy barrier height $U = KV$, K is the anisotropy constant and V is the volume of the magnetic core of the protein ($\frac{4}{3}\pi \times 40^3$ Å^3) and $\tau_0 \simeq 10^{-10}$–10^{-11} s. Around

the temperature T_B at which $\tau \simeq 30$ s, the initial ZFC magntization is expected to peak. Hence taking into account that, in our sample, $T_B = 13$ K, and that the average volume for the particles is $V = 2.68 \times 10^5$ Å^3, it is possible to estimate the average magnetic anisotropy constant for the magnetic core of this protein. We found that $K = 2 \times 10^5$ erg cm^3, which is in good agreement with previous estimations using Mössbauer data [6] and also agrees with the magnetic anisotropy of α-Fe_2O_3 [8].

The following procedure was used in the relaxation experiments: the sample was cooled from 270 K to a well defined temperature in the presence of a 100 Oe field. Then the field was rapidly changed from 100 Oe to −100 Oe. The variation in the magnetization M with time was then followed for a few hours. The magnetic field resolution for the relaxation experiments was 0.1 Oe and the temperature accuracy was $\Delta T/T = 0.1\%$. Details of this procedure have been published elsewhere [9, 10].

Figure 2 shows the variation in M as a function of $\ln t$ at different temperatures. The coefficient of $\ln t$, the magnetic viscosity S, is plotted versus temperature in figure 3.

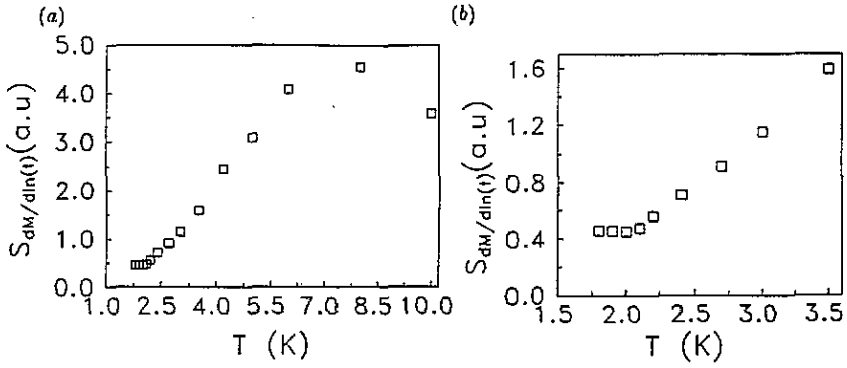

Figure 3. Temperature dependence of the magnetic viscosity $S(T)$: (*a*) temperature range 1.8–10 K; (*b*) temperature range 1.8–3.5 K.

The observed logarithmic law, $M \sim \ln t$, indicates, as expected from ZFC data, that there is a broad distribution of energy barriers which are mostly related to the different magnetic core sizes of protein particles.

$S(T)$ presents a maximum at $T \simeq T_B$, and above T_B the time interval for which $M - \ln t$ is reduced. All this agrees well with the interpretation of T_B as the temperature separating the superparamagnetic and blocked regime. At lower temperatures, $S(T)$ varies approximately linearly with temperature which corresponds to thermal activation processes with a distribution of energy barriers. At these temperatures the magnetization vector M of the excess uncompensated spins has enough thermal energy to overcome the barrier separating the different orientations of M. This temperature behaviour does not extrapolate to zero at $T = 0$. The proportionality between S and T is expected to occur only at temperatures $T \ll T_B$. Below 2 K we find a plateau for S, indicating the existence of relaxation processes which are not thermally activated. This is our central observation for which the only plausible interpretation is the occurrence of quantum tunnelling of the magnetization between the energy barriers.

The theory [12] predicts that the crossover temperature between the thermal and quantum regimes is $T_c = (\mu_B/k_B)\sqrt{K/\chi_\perp}$. Introducing the values of $K = 2 \times 10^5$ erg cm^{-3} and $\chi_\perp = 5 \times 10^{-5}$ determined experimentally, we find that $T_c \simeq 4$ K. Below T_c the rate Γ_Q, of quantum underbarrier transition is given by $\Gamma_Q = \nu \exp(-B)$, B being the WKB exponent

and $\nu = 10^{10}$–10^{11} s^{-1}. Therefore, B must be small ($B \leqslant 30$) for quantum transitions to be observed on a reasonable scale. Using the theoretical expression for $B = V\hbar\sqrt{K\chi_\perp}/\mu_B$, we can estimate the volume V for the magnetic core tunnelling, giving $B \leqslant 30$. We have found that $V \leqslant 8 \times 10^4$ Å^3, corresponding to particles with a radius smaller than 40 Å. For particles with a larger radius the quantum tunnelling rate Γ_Q is much smaller than the thermal transition rate Γ_T and consequently it is not possible to observe quantum underbarrier transitions even at $T < T_c$.

The existence of very recent results on Monte Carlo simulations of a magnetic system consisting of non-interacting single-somain particles with different size distribution functions should be noted [11]. The results show $S(T)$ dependences very similar to our experimental findings above the crossover temperature. The low-temperature regime for the magnetic viscosity found in these simulations never extrapolates to a positive non-zero value and it seems to decrease at very low temperatures depending on the size distribution function used.

The data of Awschalom *et al* [13] indicate the occurrence of macroscopic quantum tunnelling of the Néel vector with the crossover temperature $T_c \simeq 0.2$ K. The latter was derived from the fact that 0.2 K was the temperature below which the resonance in the absorption of the AC field occurred. This resonance may correspond to a quantum transition driving the particles between $\pm l$ states. The observation of the resonance was attributed to the very narrow distribution of particle sizes.

Acknowledgments

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