Does Macroscopic Quantum Coherence Occur in Ferritin?

S. Gider *et al.* (*1*) studied classical and quantum magnetic phenomena in natural and artificial ferritin proteins. If the magnetic moment of the ferritin molecules is blocked below 5 K, as Gider *et al.* show in figures 1 and 2 of their report (*1*), then the observed resonance at 24.3 mK, shown in figure 3 of their report, cannot be attributed to quantum oscillations of the magnetic moment between two equilibrium orientations, as stated by Gider *et al.* To clarify this point one should consider the time-dependent magnetism of a single domain particle.

In the absence of a magnetic field, the energy of a single domain particle is minimized when its magnetic moment aligns with the anisotropy axis of the particle with the two opposite orientations being equivalent. These two orientations are separated by an energy barrier, U, where $U = KV$, where V is the volume of the particle and K the magnetic anisotropy constant characteristic of the material. The overbarrier transition at temperature T is

$$\Gamma(T) = \omega \exp(-U/KT)$$

where ω is the attempt frequency on the order of 1 GHz and KT is the thermal energy. If the thermal energy is larger than the barrier height, the magnetic moment oscillates rapidly between the two orientations, which corresponds to superparamagnetic behavior. As T is lowered, the overbarrier transition rate decreases exponentially and the magnetic moment becomes frozen in a particular direction. The T at which the lifetime of a certain orientation is of the order of the experimental window time, t_0, is called the blocking temperature, T_B, where

$$KT_B = \frac{U}{\ln(\omega t_0)}$$

One should expect, therefore, a linear scaling of the T_B with both the volume of the particle and the inverse of the logarithm of the experimental resolution time t_0. This scaling has been observed in many systems including ferritin particles (*1*, *2*).

To observe quantum resonance, that is, back and forth quantum underbarrier transitions between the two opposite orientations of the magnetic moment, it is necessary that all particles have the same size and shape. Then the barrier separating the two equivalent orientations is the same for all particles. However, a size distribution within only 3%, which is difficult to obtain experimentally, would destroy the resonance as a consequence of the exponential dependence of the transition rate on the volume of the particle.

Gider *et al.* state that their particles were grouped by volume and that the required narrow distribution was achieved within each group, but data to this effect was not presented. According to figure 2 of the report (*1*), particles of all size groups are blocked below 5 K; that is, no transitions between different orientations of the magnetic moment occur on the time scale of the magnetization experiment, from minutes to hours. The resonance frequencies for the same size groups in a millikelvin (mK) experiment [figure 3 of (*1*)] range from megahertz to gigahertz, which suggests that in a mK regime, particles whose magnetic moments are blocked at 5 K exhibit quantum tunneling of their magnetic moments at a rate exceeding 1 million transitions per second. This is certainly inconsistent with figures 1 and 2 of the report. Particles cannot tunnel and be blocked at the same time. Quantum transitions at the observed rate should completely destroy the blocking at any T.

The observations of Gider *et al.* should not be confused with the simultaneous observation of blocking and tunneling in natural ferritin obtained by measurements of magnetization relaxation (*3*), which does not require identical particles. Natural ferritin has a wide distribution of magnetic cores ranging from 30 to 80 Å (*2*–*4*). In relaxation experiments, one first magnetizes the system, then reverses the field and follows the time evolution of the magnetization, which consists of two stages. The first stage corresponds to the rapid rotation of the local magnetization where barriers are removed by the field. This rapid stage stops when barriers start to develop. The slow stage, which is experimentally detected, is caused by thermal overbarrier or quantum underbarrier transitions. Starting with zero barriers, the system automatically reaches a barrier for which the lifetime of metastable states equals the observation time of the experiment. A time logarithmic law is the most common dependence experimentally observed for the time evolution of the magnetization of such systems. The T dependence of the experimental curves normalized to the initial value of the magnetization, the so called magnetic viscosity, reflects the change in the mechanism responsible for the relaxation process. The magnetic viscosity depends on T in the regime of thermal activation and levels off to a T-independent constant value in the regime of quantum relaxation. This has been observed in many different materials (*5*) and in natural ferritin protein molecules (*3*), in qualitative agreement with theory (*6*). In these systems tunneling occurs only in the smallest particles, which is reflected by the fact that a small part of the total magnetization is relaxing. For that reason, the blocking observed in zero field cooled magnetization is not in disagreement with the tunneling interpretation because the blocking is the result of the presence of large particles. On the contrary, in systems studied by Gider *et al.* the three statements about (i) very narrow distribution, (ii) blocking in the K regime, and (iii) quantum resonance in the mK regime, are mutually inconsistent.

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S. Gider *et al.* (*1*) and D. D. Awschalom *et al.* (*2*) state that they have seen macroscopic quantum coherence (MQC) in ferritin. In other words, all Fe^{3+} moments in the antiferromagnetic core of the protein tunnel between opposite directions in perfect unison. Because superpositions of macroscopically different states decohere rapidly in general, for MQC to occur in ferritin would be highly singular. We find the interpretation of the data internally inconsistent and implausible.

In the report by Gider *et al.* (*1*), the blocking temperature, T_B, and the noise spectrum, $S(\nu)$, are measured for several iron loadings. T_B varies from 5 to 15 K, and $S(\nu)$ is measured at $T \lesssim 200$ mK. The peak frequency ν_{res} in $S(\nu)$ is ascribed to MQC on the ground that it falls exponentially with particle volume or iron loading. However, it is unlikely that switching of the magnetic moment M can be thermally blocked below 5 K and reappear through quantum tunneling below 200 mK (*3*). When MQC occurs, the autocorrelation function of M is approximately expressible

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