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

as $\cos(\Delta t)e^{-\gamma t}$. Both Δ and γ depend on T. MQC can be said to go over into incoherent switching when $\gamma \simeq \Delta$. Usually, $d\gamma/dT > 0$, and though exceptions are known for weak ohmic and certain superohmic environments, we know of no evidence for such an environment having been adduced in ferritin. Even if the peak in $S(\nu)$ is assumed to be swamped by background noise at an intermediate temperature of, say, 500 mK, incoherent switching should still be going on, and it is hard to see how the moment can be thermally blocked.

If one nevertheless accepts that blocking and tunneling can happen at the same time, one is led to unreasonable material parameter values. Blocking requires a high energy barrier U, and MQC then requires a correspondingly high attempt frequency ν_0. ($\nu_0 = \nu_{AFMR}$, the antiferromagnetic resonance frequency.) The formulas in the report (*1*) can be rewritten as

$$U > kT_B \ln(\nu_0 a_t \tau_b) \quad (1)$$

$$\nu_{res} < 4\nu_0 \left(\frac{2U}{\pi h \nu_0}\right)^{1/2} \exp\left(-\frac{4U}{h\nu_0}\right). \quad (2)$$

In Eq. 1, τ_b is the time scale [stated as "seconds" in the report (*1*)] on which blocking is seen, and a_t is a frictional prefactor of order unity. In Eq. 2, the prefactor has been added, and it is an inequality because the effects of transverse anisotropy and nonzero net moment have been left out. Taking $a_t\tau_b = 1$ sec, and the observed values of T_B and ν_{res}, Eqs. 1 and 2 together yield conservative lower bounds for U and ν_0. For Fe loading 1000, with $T_B = 10$ K, and $\nu_{res} = 200$ MHz, we get $\nu_0 > 2.2$ THz, and $U/k > 280$ K. For Fe loading 3000, with $T_B = 17$ K, and $\nu_{res} = 5$ MHz, we get $\nu_0 > 2.7$ THz, and $U/k > 490$ K.

The bound value of 2.7 THz is unexpectedly high for an AFMR frequency and should be compared with the known $\nu_{AFMR} = 11.5$ GHz for α-Fe_2O_3, whose structure is similar to ferritin's with additional Fe^{3+} ions. The bounds also imply values for the anisotropy and exchange fields: $H_a = 0.3$ T and $H_e = 1.5 \times 10^4$ T. The last value is particularly implausible.

A graver difficulty with the statement by the authors of (*1*), and (*2*) that they have seen that. MQC arises from the size of the observed signal (*4*, *5*). For the fully loaded protein (*2*) with 4500 Fe^{3+}'s, $\nu_{res} = 1$ MHz, at T = 29.5 mK. Mössbauer data yield a 50 T hyperfine field, implying a Larmor frequency of $\nu_n = 68$ MHz for a ^{57}Fe nuclear spin. Thus, a single ^{57}Fe would render the two states in question nondegenerate by 68 MHz, and give a relative MQC amplitude of $1/68^2$, practically zero. Simultaneous flip of the Fe electronic and nuclear moments would preserve degeneracy, but the amplitude for this is found to be negligible (*4*–*6*). Thus, out of the 38,000 ferritin particles in the experiment, MQC can be seen only in those with staggered nuclear spin polarization $p_n = 0$. This fraction is found to be 3.4%, from the 2.25% natural abundance of ^{57}Fe, and the known ratio $h\nu_n/kT$. The peak power absorption can be readily calculated for one of the $p_n = 0$ particles, since T, the width of the resonance (50 kHz), the net moment per ferritin (217 μ_B), and the ac driving field (10^{-5} G) are all measured directly (*2*). It is found that one can feed at most 2.4×10^{-25} W into an MQC resonance (*4*). The actual absorption is 10^{-21} W, at least 4000 times larger. Resonance experiments often absorb *less* than the maximum possible power; how one could absorb *more* than is allowed is unclear. The law of energy conservation forbids it.

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Response: Tejada and Garg focus on the latter part of the report by Gider *et al.* (*1*), which described the low-temperature magnetic dynamics of synthetic ferritin particles. They question the interpretation for which we have been offering evidence for the last 5 years that MQC is responsible for important features of the mK dynamics in ferritin. The quantum tunneling model, while not perfect in all respects, has successfully explained and predicted a host of independent experimental observations of the temperature, magnetic field, size, and dilution dependence of the magnetic noise and ac susceptibility of ferritin in the mK regime.

Tejada states that there is an inconsistency between the observation in our report (*1*) of blocking in the regime of a few K and tunneling in the mK regime, and he implies that our frequency-dependent susceptibility measurements in the mK regime (*1*–*4*) are inconsistent with his relaxation measurements in the K regime (*5*). Consideration of the separate experimental conditions in each set of measurements reveals crucial differences that remove apparent inconsistencies. Blocking temperatures are typically obtained using dc magnetization measurements in the presence of a magnetic field on the order of 10 mT (*1*, *5*, *6*). As noted in the report (*1*), there is a shift of the blocking temperature with field, which additional measurements show to change from ~10 K to ~13 K in fields from 10 mT to 100 mT, respectively. In contrast, our measurements of frequency-dependent ac susceptibility (*1*–*4*) were performed with a magnetic field on the order of nT and with temperatures as low as 30 mK—a difference of seven orders of magnitude in field and three orders of magnitude in temperature. An attempt to extrapolate from 10 mT to 1 nT and from 10 K to 30 mK is questionable. Although the dynamics would most likely change over such a large range, it is not possible to conclude from measurements at 10 mT and 10 K whether the particles are blocked in the classical sense at 1 nT and 30 mK.

The measurements of the amplitude of the ac susceptibility (*4*) demonstrate that coherent tunneling (MQC) vanishes for fields exceeding ~100 nT. Similarly, if the sample is not diluted at least by a factor of 1000, the dipolar couplings among the ferritin particles will completely suppress coherent tunneling (*2*) (quite apart from differences in the effective magnetic anisotropies). Thus the experimental condition under which the blocking temperature is measured (high fields and low dilution) is such that the two-level system is detuned and no coherent tunneling can take place under these conditions, even if the observation temperature is lowered far below the blocking temperature. Thus, the fact that the blocking temperature is much higher than the cross-over temperature that is observed in the ac susceptibility data (in low fields and high dilution) is compatible with the MQC interpretation and does not constitute any apparent contradiction, as suggested by Tejada. The situation would be different if the blocking temperature were measured under the same condition as the ac susceptibility, where we would expect that the blocking is reduced or even absent.

Tejada does not correctly address the differences in the nature of the particle size distributions in our samples and the significance of those differences for both the classical and quantum measurements. We do not claim that our systems are constituted by identical particles. Table 1 in the report (*1*) lists the means and variances for our distributions, and later Gider *et al.* state (*1*), "there is a distribution of anisotropy barriers due to the distribution in particle

sizes." We are aware that the shape of the zero field-coiled curves depends on the distribution, which is explained in our report, when we draw a distinction between the ferritin and spin glasses. Thus it is not unexpected that we obtained the same blocking temperature for the natural ferritin as does Tejada (*5*). Furthermore, there is no inconsistency with observation of tunneling in the mK regime with the distribution of particle sizes: The distribution can only affect the width of the resonance peak; the central frequency will still be reflective of the mean particle size (*2–4, 7*). While the particle sizes have a distribution, they are very narrow: This is confirmed by our observation of two distinct resonance peaks when two of the artificial samples are mixed. Importantly, concentration of the samples in our tunneling measurements (*1–4*) are at least 100 to 1000 times more dilute than the concentration of commercially available natural ferritin, which was undiluted in the experiments of Tejada (*5*). While we do not observe an effect of the dilution in blocking at higher temperatures and fields (10 K and 10 mT), we see an effect in the tunneling regime where dipolar fields become significant (*1, 4, 7*). It would be interesting to see a detailed study of the effect of dilution on relaxation measurements such as those done by Tejada (*5*).

While great progress has been made in recent years in the size refinement of our magnetic particles, size alone is not the sole relevant factor in the magnetic dynamics; in particular, narrow size distributions do not always imply narrow magnetic anisotropy distributions. We have found that the concentrated samples (dc magnetization studies) dry in the form of self-supporting films that are themselves magnetically anisotropic (*1*); however, the diluted samples do not form such films, making a direct comparison between the dc blocking experiments and the ac tunneling experiments even more difficult. It is well known from the study of thin magnetic films that strain can greatly alter the direction and magnitude of the magnetic anisotropies of the unstrained system. The dc experiments have nevertheless proved useful in establishing some of the general systematics of the ferritin dynamics (for example, dependence with average iron loading). However, more advances in the experimental art would be required before we will have the capability to control, in every experiment, all the parameters which are relevant to the dynamics in the quantum-coherent regime.

The comment by Garg raises two issues. The first repeats Tejada's objection which we address in detail above. However, we disagree with his interpretation of our results: we did not state that blocking and tunneling can happen in the same experiment. Blocking temperature measurement and the MQC measurement are performed under distinctly different conditions. In particular, we see no basis for Garg's ad hoc assumption that the value of the anisotropy potential, U, deduced from the blocking temperature, T_B, (Garg's equation 1) is the same as the tunneling barrier, U, occurring in the MQC relation (Garg's equation 2). Because typically the attempt frequency ν_0 typically equals $\alpha \sqrt{U}$ the same caveat applies to his use of the same attempt frequencies in his eqs. 1 and 2. Thus, conclusions drawn from combining these two equations are of questionable significance. Garg's equation 2 is based on the additional assumption of the XY-limit of an antiferromagnetic Heisenberg model. Other limits, which cannot be excluded a priori, have significantly different prefactors as large as an additional order of magnitude.

In the second part of his comment, Garg objects to the MQC interpretation based on power absorption and the effect of nuclear spins on MQC. A number of these objections have previously been addressed by us (*3*) and others (*8*). He repeats his earlier arguments that the size of the observed susceptibility signal is too large (by a factor of about 133) when compared with the particle magnetic moments and linewidths that we have reported. (The number 4000 quoted by Garg follows from 133×30, with the factor 30 resulting from nuclear spins; see below.) When he says that the MQC resonance power can be "at most" some value, he implies that his calculation represents some strict upper bound on the power; in fact, it is an estimate subject to many different assumptions and uncertainties (Lorenzian lineshapes, a single relaxation time, and others). When we redo his earlier estimates, and compare them with more reliable calculations based on the thermodynamic sum rule, we find a range of possible discrepancies in the magnitude of the signal, the lower end being as small as a factor of 5 as compared to his stated 133. Although an absolute calibration of power absorption was attempted in our experiments, such calibrations are subject to considerable uncertainty, and no conclusive arguments should be based on absolute power numbers.

Finally, we comment on the role of nuclear spins as advocated by Garg. If one accepts his model calculation [note, however, that the correct relative MQC amplitude equals $1/(68 \cdot 2)$ in contrast to $1/(68)^2$] and his statement that nuclear spins would reduce the peak height by about a factor of 30, this would not be sufficient to invalidate our MQC analysis, as these reductions within experimental uncertainty for the power absorption. While this observation is reason enough to neglect the effect of nuclear spins, his model is not realistic because it does not include dynamical effects. For example, the time scales for tunneling (instanton frequency) and for the superexchange processes can be quite comparable. Thus, his basic assumption of a *static* interaction between nuclear and electronic spins seems unjustified, and his estimates represent (at best) an upper bound on the effect of nuclear spins.

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