

COMPLEX DYNAMICS OF MESOSCOPIC MAGNETS

For many years physicists thought small structures would be nearly ideal systems in which to explore and manipulate magnetic interactions. On a small enough length scale the interactions between individual atomic spins cause their magnetic moments to align in the ordered pattern of a *single domain*, without the complication of domain walls separating regions of varying orientation. For particle sizes at or below that of a single domain, many theoretical models of dynamical behavior predict simple, stable magnets with controllable classical properties. However, as with advances in semiconductor physics, the process of miniaturizing magnetic materials has unexpectedly revealed fascinating new classical and quantum mechanical phenomena. Even the simplest magnetic system, the isolated single-domain particle, exhibits a wealth of exotic behavior that pushes us to the limits of our present understanding of the fundamentals of magnetism.

The study of small magnetic systems presents several challenges. First, there is the problem of how to fabricate small magnets while controlling the particle dimensions and the variance of size from particle to particle. In addition to traditional subtractive lithographic techniques, there has been much interest recently in new additive techniques based on scanning tunneling microscopy, biomineralization and chemical synthesis.

Second, there is the challenge of measuring the magnetic properties of the small particle. Ideally one would like to study an individual, isolated particle to avoid effects resulting from variations in the particle sizes and inter-particle interactions. However, measuring the magnetization of a single nanometer-scale particle requires highly sensitive measurement techniques, beyond the limits of traditional magnetometers. Among recent advances are improvements in Lorentz microscopy, magnetic force microscopy, Hall-effect magnetometers based on semiconductor heterostructures, and integrated dc SQUIDS. With a well-designed sample and experiment, one can explore a

The study of ever smaller magnets is pushing us to the limits of our understanding of magnetism, providing new headaches for the technologist and new opportunities for the researcher investigating magnetism at the atomic level.

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range of mesoscopic magnetic phenomena, from the classical to the quantum limit.

Third, there is the challenge of understanding the phenomena. The study of single-domain magnets has accelerated the development of new theoretical approaches to magnetic dynamics. New attention is being paid both to the detailed effects of disorder and to how quantum mechanical effects influence

the properties of these small systems.

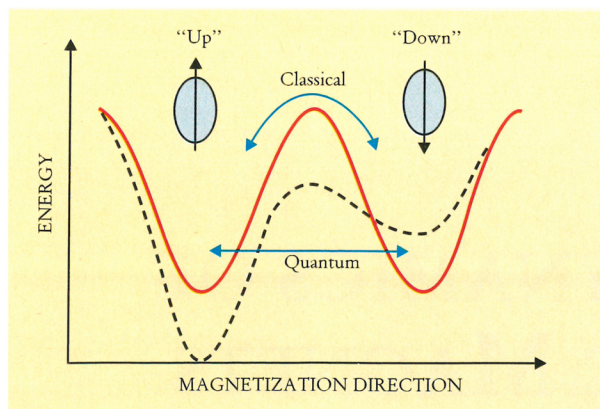
The behavior of individual magnetic domains has already become important in magnetic technology. In the article by E. Dan Dahlberg and Jian-Gang Zhu, the figure on page 38 shows a scanning electron micrograph of "bits" recorded at 1-micron intervals in a CoNi recording alloy. Structures arising from the individual magnetic domains at the 50-nm scale include ripples, vortices and feather-like patterns. At this detailed level the magnetic structure deviates significantly from a simple bit recording pattern: Strong interactions between the domains cause the magnetization vectors to splay significantly away from the desired direction inside each bit, and they also make the transition from one bit to another somewhat ragged and unpredictable. Both of these effects cause "media noise," which is one of the fundamental limits on present-day magnetic storage. These issues are important in present recording technology with densities of around 100 megabits per square inch, and they will be critical to the future development of high-density storage now targeted to be on the order of 10 gigabits per square inch. At that density a single bit is expected to be 1 micron wide and only 70 nm long! (The film thickness will be about 30 nm.)

Might all of these problems be avoided if we used *individual* magnetic domains to store each bit? Will the physics of isolated particles provide a simple and uncomplicated storage technology, free of the difficulties encountered in present-day media? The answer seems to be no: As we study the behavior of individual magnetic particles more deeply, we continue to find surprises that will be a headache for the technologist but provide opportunities for investigating magnetism at the near-atomic level.

The Stoner-Wohlfarth model

The illusory hope of simplicity in the single-domain regime was largely provided by a particularly successful (and still very useful) model of magnetic dynamics of small magnetic

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AN ELLIPSOIDAL MAGNETIC PARTICLE in the absence of an external magnetic field has two stable states—"up," with its magnetization parallel to its long, or "easy," axis, and "down," with the magnetization antiparallel. The particle may flip its orientation either by attaining enough thermal energy to surmount the barrier between the states (classical trajectory) or by quantum tunneling through it (quantum trajectory). When an external field is applied, the potential becomes "canted" (dashed curve) and one of the states eventually becomes metastable. **FIGURE 1**

particles, proposed over 50 years ago by Edmund Stoner and Erich Wohlfarth.¹ The Stoner–Wohlfarth model is based on the following premises:

▷ In a particle much smaller than the domain-wall width, the spins will be strictly aligned throughout the particle, or they will be strictly alternating in a Néel antiferromagnet.

▷ The particle will always be oriented such that the magnetic energy E is at a stable or metastable minimum. (See figure 1.) If, as the external magnetic field $\mathbf{H}$ is varied, a minimum becomes unstable (at the coercive field H_c ; see figure 2), then the particle orientation switches immediately, going "downhill" to the nearest available minimum. A simple modification of this premise, which was provided very early by Louis Néel and William Brown,² states that the escape from a metastable state at finite temperature is governed by an Arrhenius thermal activation rate, which is proportional to $\exp(-E/k_B T)$.

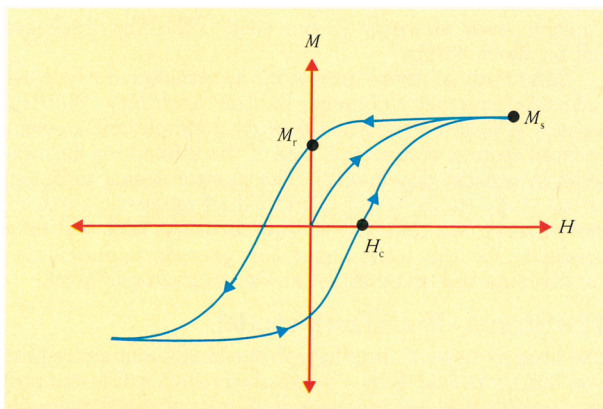
▷ The magnetic energy of the particle will be a function only of the collective orientation of the spins, and is determined by a combination of the external magnetic field, the demagnetizing energy (the magnetic dipole energy of the magnetic fields created by the spins) and the magnetocrystalline anisotropy (the energy arising from the spin–orbit interaction between the spins and the orbital motion of the electrons in the crystal lattice). A consequence of this premise is that the particle's magnetic energy has a simple, linear dependence on its volume.

The SW model provides an elegant and simple explanation for a variety of classical magnetic phenomena, such as the shape (the "squareness") of hysteresis loops and the effect of particle shape and size on magnetic dynamics.³ If it were a perfect description of magnetic particle dynamics, it would provide for a very simple route to

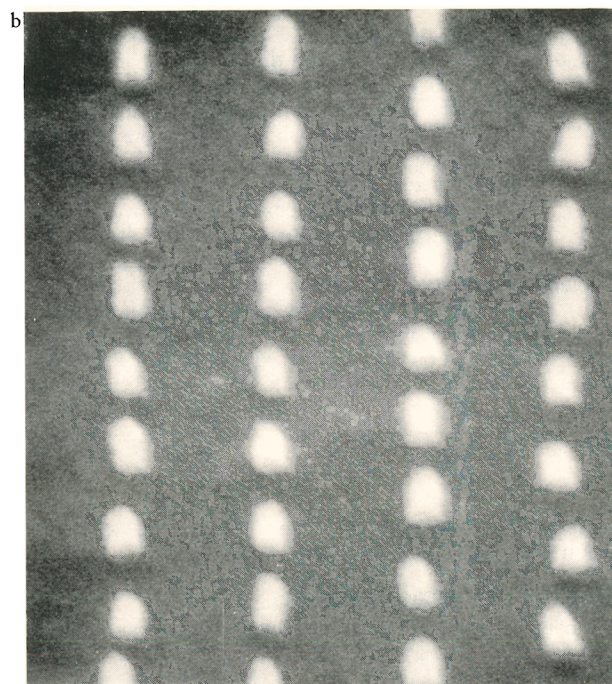
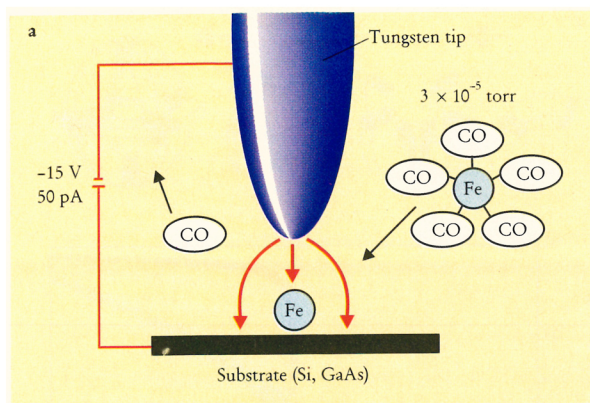
storing a bit in an isolated magnetic particle.

Unfortunately, while the SW model has provided a correct overall picture, it has been found inadequate for explaining many details in experimental systems. Figure 3a, shows how arrays of almost identical, well-separated, Fe magnets of roughly ellipsoidal shape were prepared using a scanning tunneling microscope as a chemical-vapor deposition system.⁴ As the magnet aspect ratio—the ratio of the height of an individual magnet to its diameter—increased, the coercive fields (as determined from magnetic hysteresis loops like those in figure 3c) were found also to increase and eventually to reach an asymptote. The SW theory also predicts such a trend, but at significantly higher coercive fields. In general, the SW and Néel–Brown theories are known to overestimate the coercive field, because the first premise above allows these theories to consider only "coherent" rotations, excluding alternative paths by which the magnetization may reverse. Some recent theories have attempted to account for various "incoherent" rotation modes and thermal activation, for example, involving the motion of domain walls across the particle.⁵ These calculations show that this effect might explain the lower-than-expected asymptote for H_c .

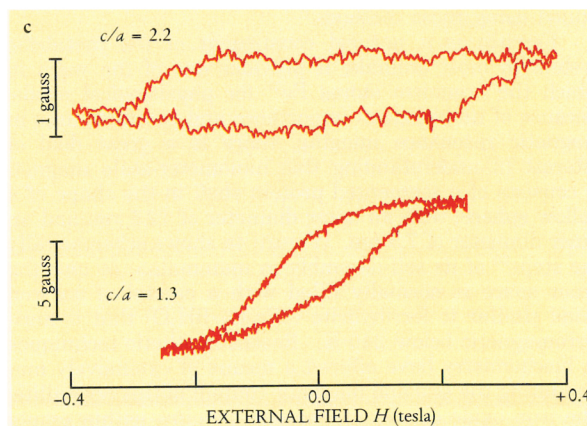
In experimental systems similar to the magnetic arrays just described, both the SW theory and its modifications to include domain-wall reversal fail because of violations of the second premise of the SW model. Recent experiments probed the statistics of magnetization reversal in individual ellipsoidal, single-domain $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) particles by repeatedly sensing their state with a magnetic force microscope.⁶ It was found that while the *static* SW predictions for H_c as a function of angle were reasonable in many cases, the *dynamic* predictions associated with



HYSTERESIS LOOP. An initially unmagnetized magnetic particle exhibits a hysteresis loop in its magnetization $\mathbf{M}$ as an external magnetic field $\mathbf{H}$ is increased from zero to a maximum value, reversed through zero to a minimum value, and subsequently returned to zero. Characteristic features of hysteresis curves include the saturation magnetization M_s , the sample's maximum magnetization; the remanent magnetization M_r , the magnetization that persists in the sample when the external field is zero; and the coercive field H_c , the external field necessary to return the magnetization to zero. **FIGURE 2**



MICROSCOPIC MAGNET ARRAYS. **a:** A scanning tunneling microscope served as a chemical-vapor deposition system by decomposing $\text{Fe}(\text{CO})_5$ and depositing the iron as arrays of almost identical, well-separated, roughly ellipsoidal Fe magnets with minor radii as small as 10 nm and heights between 10 and 1000 nm. The magnets were grown on a semiconductor structure that functioned as an extremely sensitive magnetometer by detecting changes to the Hall effect due to the field of the Fe magnets in a two-dimensional electron gas. **b:** Scanning electron microscope image of such an array of magnets. The magnets here are 30 nm in diameter, 66 nm high and spaced 100 nm apart. **c:** Magnetic hysteresis loops measured at 5 K by this technique for arrays of about 500 particles show that increasing the aspect ratio—the ratio of the height c of the particles to their diameter a —causes the coercive field to increase until it reaches an asymptote. The Stoner-Wohlfarth and Néel-Brown theories predict such a trend, but at much higher coercive field. (Adapted from ref. 4.) **FIGURE 3**



the probability distribution in time of the spontaneous reversal of the particle magnetization were incorrect. The rate of reversal is inconsistent with an exponential activation rate over any individual energy barrier. The best explanation is that the transition state is structured, probably with greater spatial intricacy than a simple domain-wall picture.

Because of their large surface-to-volume ratios, small magnetic particles can have properties quite different from those of bulk materials, resulting in a violation of the third premise of the SW model. Small $\gamma\text{-Fe}_2\text{O}_3$ particles (on the order of 6 nm in diameter), for example, have a noncollinear spin arrangement⁷ that researchers have systematically studied by binding the surface spins to other molecules. Other evidence for nontrivial spatial dependence of the magnetic structure of nominally single-domain particles comes from studies of the coercive field of acicular, or needle-like, $\gamma\text{-Fe}_2\text{O}_3$ particles, such as those used in magnetic tape recording,⁸ typically of 600 nm length with a 6:1 aspect ratio. A simple surface treatment of these particles with a variety of reagents, including sodium polyphosphates, can produce variations in coercivity of up to 50%. Molecular orbital calculations support the idea that phosphate ions bind to the surface of a particle; this surface charge tunes the oxidation state of the near-surface Fe ions so as to maximize their spin-orbit energy, thus maximizing their contribution to the magnetic anisotropy. Locally this treatment can make the anisotropy

100 times larger at surface sites than in the bulk material, effectively “pinning” the magnetic vector at the surface. Simulations suggest⁸ that the transition state of the reversing particle involves first overturning of the spins in the bulk, then “dragging” along the surface spins. This result reveals a serious breakdown of the third SW assumption—that the anisotropy energy depends simply on the volume.

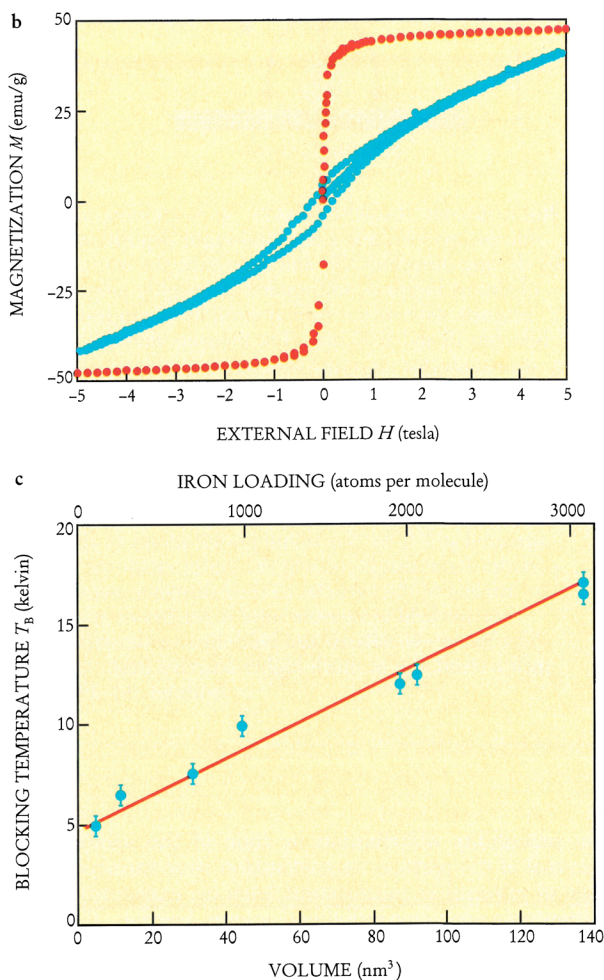
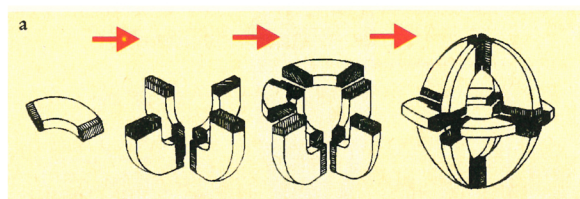
The foregoing discussion might suggest that the principal problem with the simplified SW picture is that we expect it to work well for any single-domain particles, even rather “large” ones (more than 50 nm). But these large single-domain particles have rather complex nonequilibrium or transitional states. In contrast to larger particles with complicated domain patterns, one might think that the pure SW behavior would emerge in “small” magnetic particles, in which spatial structure is likely to remain more uniform. As discussed below, a series of studies on considerably smaller particles (on the order of 10 nm) indicate that to some degree this expected behavior does emerge. Investigations in this size range have been less extensive, largely because at this scale traditional synthe-

MOLECULAR MAGNETS can be assembled inside the cavity of apoferritin—a protein shell that isolates the magnet and allows the experimenter to control its characteristics.

a: The individual protein strands of the apoferritin shell self-assemble into a sphere because the balance of hydrophobic and hydrophilic forces causes the strands to bond together at 90° angles. (Adapted from ref. 10.)

b: Magnetic hysteresis loops for artificially engineered antiferromagnetic (blue) and ferrimagnetic (red) ferritin at 5 K. For ease of comparison, M values for antiferromagnetic ferritin were multiplied by a factor of 10.

c: Measured blocking temperatures T_B for a series of artificial antiferromagnetic proteins show that T_B is linearly dependent on the magnetic volume of the proteins and therefore on their iron loading, as predicted by the Néel-Brown theory. **FIGURE 4**



sis methods from materials science cease to be capable of producing uniform, reproducible structures.

Making nanoscale magnets

A variety of nontraditional synthesis techniques, largely adapted from biology and chemistry, show great promise for making nanoscale magnets. Natural and artificial ferritin proteins are fascinating examples of systems obtained using these methods.⁹

Ferritin is a natural constituent of the metabolic system in most animals; it provides one of the ways in which the organism stores Fe^{3+} for physiological needs. Because of its biological importance and potential uses in magnetic resonance imaging, there is a great deal of interest in understanding this nanometer-scale magnet. It consists of a segmented protein shell in the shape of a hollow sphere, with an outer diameter of 12.5 nm and an inner diameter of 7.5 nm. (Figure 4a shows schematically the steps¹⁰ of its self-assembly in mammals.) *In vivo* the inner space is normally filled with a crystal of an iron oxide similar to ferrihydrite ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$) that is antiferromagnetic below 240 K. Recent synthetic techniques in biochemistry have offered a means of extensively manipulating the size and magnetic content of this crystallite. The iron oxide can be synthesized *in vitro* within empty protein shells (called apoferritin) and the reaction controlled to give particles with desired iron loading from a few to a few thousand ferric ions per protein (the maximum is about 4500). Apoferritin can also serve as a vessel for the synthesis of other materials, such as magnetite (Fe_3O_4), maghemite, MnOOH and UO_3 . Magnetite and maghemite are ferrimagnetic, and thus we have a system where we can vary both the size and the nature of magnetic interactions.

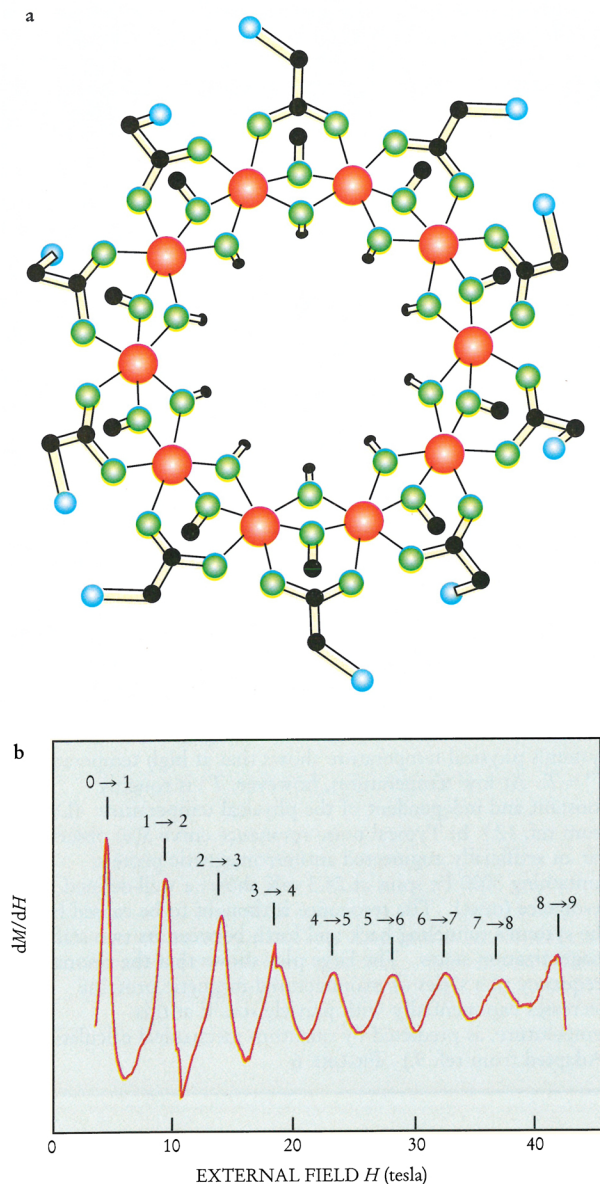
Figure 4b shows the magnetization of the ferrimagnetic ferritin, as compared with that of antiferromagnetic ferritin, demonstrating the dramatic range in the magnetic properties of artificial ferritin. The Néel-Brown theory predicts that T_B —the “blocking temperature,” below which thermally assisted hopping between magnetic orientations becomes frozen out—depends linearly on the Fe loading. Figure 4c shows that measurements on artificial magnets agree with the overall trend, but that some nonideal classical behavior, perhaps akin to the surface pinning effects discussed earlier, must be invoked to produce the dependence of T_B as Fe loading goes to zero. Ferritin deviates from SW behavior in a much more exotic way, which arises from quantum mechanical effects that we will describe below.

Remarkable new techniques in molecular chemistry

are now realizing the possibility of creating true molecular magnets, in which the magnetic ions are added one at a time and the resulting magnet has a precisely defined atomic weight.¹¹ Like ferritin, many of these new magnetic molecules are constructed such that the magnetic cluster is secluded from contact with its external environment by a shell of organic ligands. Figure 5a shows one such magnet, Fe_{10} , dubbed the “ferric wheel” by its inventors because of the ring structure formed by the ten Fe atoms and the bridging organic anions. The magnetization measurements on Fe_{10} shown in figure 5b reveal that this cluster is a perfect molecular antiferromagnet, with an $S = 0$ quantum ground state. The successive transitions from one discrete quantum spin state to the next, evident for magnetic fields up to 42 tesla, closely resemble a sequence of phase transitions in the magnetic order of bulk layered antiferromagnets.

Quantum mechanical effects

The simple dynamical picture of figure 1 suggests that the magnetic orientation of a small particle will remain



MOLECULAR ANTIFERROMAGNET. a: The “ferric wheel” consists of ten Fe^{3+} ions (red) bound into a ring structure, along with chlorine (blue), oxygen (green) and carbon (black). b: Plot of dM/dH versus applied magnetic field for Fe_{10} at 0.65 K resembles a sequence of phase transitions in the magnetic order of bulk layered antiferromagnets. The maxima represent crossovers to states of higher spin multiplicity. (Adapted from ref. 11.) **FIGURE 5**

temperature-independent relaxation behavior at low temperatures has been noted in many other experiments.

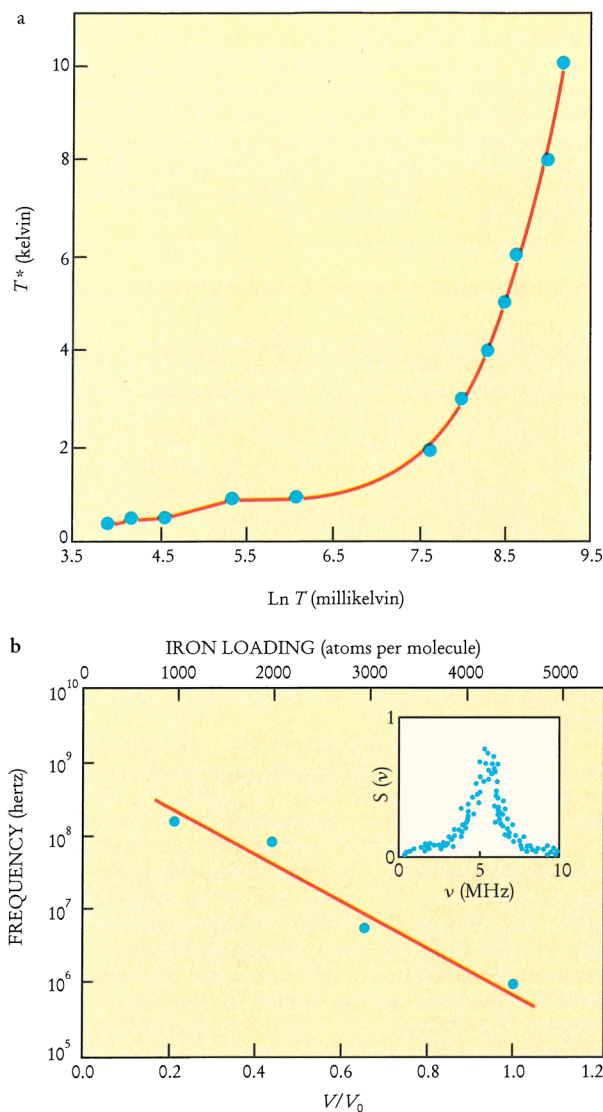
One-dimensional barrier penetration is a misleadingly simple depiction of quantum tunneling of the magnetization; there is no simple Schrödinger equation that describes this process, since it is not an elementary particle that is tunneling, but a collective coordinate: the magnetization direction of a collection of spins. However, the classical micromagnetic theory of magnetic dynamics can be quantized within a path integral formalism.¹³ This treatment predicts that the tunneling rate for antiferromagnetic particles should typically be much larger than the rate for ferromagnetic particles (because of the smaller “effective mass” of the antiferromagnetic particles) and that the tunneling rate is exponentially suppressed as particle size increases.

Because of its antiferromagnetic structure and small size, ferritin is a good candidate for such quantum tunneling. In zero applied magnetic field, the symmetric double-well potential of figure 1 leads to quantum mechanical behavior in which the magnetization tunnels *coherently* back and forth between the two wells. At temperatures below 200 mK this behavior produces a resonance line in the magnetic susceptibility and noise spectra.¹⁴ Figure 6b shows an experimental measurement of this resonance and its dependence on protein volume. The frequency of the resonance line and its exponential dependence on the number of spins in the particle correspond reasonably well to theoretical predictions.¹³ Experiments have also confirmed that the resonance disappears rapidly when a magnetic field is applied and the symmetry of the double-well potential is broken. This work has stimulated a number of theoretical investigations¹⁵ on the effects of dissipation, including the role of nuclear spins in magnetic quantum tunneling, as well as on the feasibility of seeing quantum effects in larger magnetic structures.

Limitations or opportunities?

It might appear that all of these studies point to limitations and restrictions on the use of small magnetic structures for the storage of information: The switching of magnetic domains depends on a myriad of detailed features of the particles, and quantum effects ultimately limit the length of time that a magnetic bit can remain stable.¹⁶ Nevertheless it seems equally possible that these investigations will provide fundamentally new ways of using magnetic structures in technology. For example, theoretical investigations of magnetic quantum tunneling led to the surprising discovery that a selection rule quite generally forbids quantum tunneling for particles with an odd number of electrons!¹⁷ This derivation led to a new understanding of Kramers’s theorem within a path integral description. Thus limitations imposed by quantum effects may be overcome. Another area for new investigations concerns the use of magnetic systems not for memory but for logic. Some computational problems can be greatly accelerated in a “quantum computer” in which bits and gates are implemented at the level of individual

stable indefinitely below the blocking temperature. However, quantum mechanics tells us that the states in the two potential wells can be coupled by tunneling, leading to strikingly different dynamics. Early suggestions of such effects were observed through relaxation of the magnetization in particulate media. A recent example, shown in figure 6a, involves measurements of $\text{Tb}_{0.5}\text{Ce}_{0.5}\text{Fe}_2$ containing a distribution of magnetic particle sizes centered around 15 nm.¹² Although the reversal of the magnetization in such systems is complicated because of the range of particle sizes and the range of interaction strengths between particles, one can model the decay of magnetization on reversal of the field above $T = 4$ K by an Arrhenius activation over a range of energy barriers. At lower temperatures, however, the magnetic relaxation does not freeze out, but behaves independently of temperature. The authors of this study have suggested that the rotation of the magnetic domains is accomplished by a quantum tunneling process in an asymmetrical potential well like that indicated by the dashed curve in figure 1. Such



QUANTUM EFFECTS. **a:** The Néel-Brown and other classical theories predict that the magnetic relaxation time should depend exponentially on the inverse of the temperature, $1/T$. This prediction agrees well with most experiments above 4 K. Below that temperature, quantum effects become important. For $\text{Tb}_{0.5}\text{Ce}_{0.5}\text{Fe}_2$ particles this plot of T^* , the temperature as determined from the relaxation time assuming the Néel-Brown theory, versus the natural logarithm of the system's physical temperature shows that at high temperatures $T^* = T$. At low temperatures, however, T^* is roughly constant and independent of the physical temperature. (Data from ref. 12.) **b:** Typical noise resonance curve $S(v)$ observed for an artificially engineered antiferromagnetic protein containing 3000 Fe spins at 24.3 mK shows a well-defined resonance (inset). The resonance is thought to be caused by the system's tunneling back and forth between its two stable magnetization states. The large plot shows that the resonance frequency of a series of manufactured magnetic proteins decreases exponentially with particle size V at this temperature, as predicted by quantum mechanical calculations. (Adapted from ref. 9.) **FIGURE 6**

spins, permitting calculations that exploit quantum interference effects within the computer itself.¹⁸ It seems fair to say that the book is not closed on the discovery of fundamental directions for magnetic phenomena at the mesoscopic or microscopic level, nor will it be for some time to come.

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