Hysteresis Steps Demonstrate Quantum Tunneling of Molecular Spins

Hysteresis is a familiar macroscopic phenomenon in the behavior of magnetic materials: When a sample is subjected to a varying external magnetic field, its magnetization curve does not, in general, retrace its steps as the external field in a fixed direction is swept from a large negative value to a large positive value and then back again. But until the summer of 1995, no one had ever seen quantum steps in a hysteresis loop.

At a conference in November 1995 Jonathan Friedman, from City College in New York, presented hysteresis loops like the ones shown below. He and collaborators from CCNY, the University of Barcelona and Xerox had measured the magnetization curves of an extraordinary material—crystalline Mn_{12} acetate—at temperatures from 1.7 to 3 K. All the hysteresis loops exhibited clear steps. This appeared to be the first direct evidence[1] of a quantum phenomenon much sought after by theorists and experimenters in recent years: the tunneling of a spin through a potential barrier from one orientation to another. Recent reports of similar experiments by Xavier Tejada's group at Barcelona[2] and Bernard Barbara's group at the Louis Néel Laboratory of Magnetism in Grenoble[3] seem to confirm the idea that the spins of individual Mn_{12} acetate molecules are in fact reversing direction by "resonant quantum tunneling" from one potential well to another.

Quantum tunneling is well established in many microscopic phenomena, and even in one macroscopic system—the Josephson junction. But this newly observed spin tunneling breaks some new ground, not least in its technological promise. Mn_{12} acetate is a large, complicated molecule that was first synthesized in 1980. At low temperatures, we now know, the molecule's many constituent electronic spins freeze into an overall state of fixed angular momentum 10 $\hbar$. The spin is carried by the 12 manganese ions, which are bound together by an elaborate pattern of oxygen bonds and acetate groups. Spin 10 is very high for a molecular ground state. Some of the experts even argue that it sits on the boundary between the microscopic realm and the "mesoscopic" spins of order 10^3 $\hbar$ found in small ferromagnetic domains and antiferromagnetic protein cages. The larger the spin, of course, the less restrictive is the orientational quantization of angular momentum. In the classical limit a spin can point in any direction it likes. Therefore it has been suggested that these observations of spin tunneling in Mn_{12} acetate, especially in the dissipative context of hysteretic relaxation, might help elucidate the long-standing problem of how, quite generally, Nature arranges the transition between the quantum and classical realms.

When molecular spins in a crystal tunnel in lockstep under potential barriers, one sees not only a spectacular demonstration of quantum effects, but also the promise of magnetic information storage by individual molecules.

The chemistry does the trick

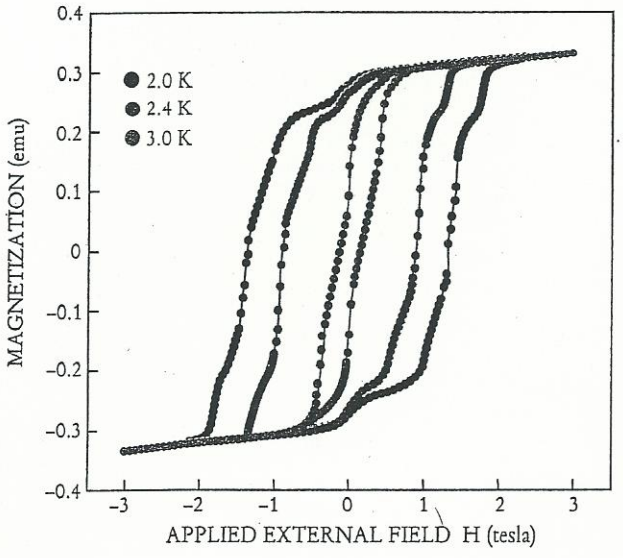
The quantum stepping that the three Mn_{12} acetate hysteresis experiments have recorded is not really a collective phenomenon. The resonant spin tunneling happens separately in each molecule of the crystalline sample. How then do the experimenters come to see such clear macroscopic manifestations of microscopic quantum events? "It's the chemistry that does the trick," explains Myriam Sarachik, leader of the CCNY contingent. "All the Mn_{12} acetate molecules are identical, and they all have the same orientation within the crystal. So when we bring the applied magnetic field to one of the resonance values, they all react the same way, giving us an enormously enhanced signal." In earlier experiments that gave more indirect evidence of tunneling by mesoscopic spins in small magnetic domains and protein cages, the quantum steps were largely washed out by the variation of size and shape among the individual domains.

In addition to its unusually high spin, Mn_{12} acetate has another great advantage for the observation of spin tunneling. Its crystalline form has a very large magnetocrystalline anisotropy parameter D, which means that the energy of the molecule is strongly dependent on the orientation of the spin $\mathbf{S}$ relative to the "easy-magnetization" axis of the crystal. If we label that axis z, the Hamiltonian giving the spin dependence of the energy is written

$$\mathcal{H} = -DS_z^2 - g\mu_B \mathbf{S}\cdot\mathbf{H}$$

where $\mathbf{H}$ is the external magnetic field, applied in the z direction, and $g\mu_B$ is the gyromagnetic ratio of the electron.

The molecule's spin S can have 21 (that is, $2S + 1$) different orientations relative to the crystal axis, labeled by the magnetic quantum number m, which ranges from +10 to −10. In the absence of an applied external field, the energies of the different orienta-



HYSTERESIS LOOPS for crystalline Mn_{12} acetate at three temperatures from 2 to 3 K. Starting from saturated magnetization in either direction along the crystal axis, one sees indications of quantum steps at intervals of about 0.45 tesla, beginning when the applied magnetic field crosses zero toward restoring values in the opposite direction. (Adapted from ref. 1.)