Macroscopic quantum spin-flip in Ising nanoparticles

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Macroscopic quantum tunneling (MQT) of magnetization in small particles of a strongly anisotropic magnetic material is analyzed. Non-Kramers ions, which at low temperatures exhibit Ising magnetization, are studied. It is shown that the dynamic interaction of the magnetization with the quadrupole moment of an ion produces continuous reversal from M to $-M$ and results in a nonzero MQT probability.

1. In the last few years the problem of macroscopic quantum tunneling of magnetization in small ferromagnetic particles has been actively studied both theoretically and experimentally.[1–5] The study of such particles is of interest, in particular, in the context of new ideas associated with Feynman computers and quantum electronic circuits.[6] Theoretical works along this line start with the assumption that the modulus of the magnetization vector is conserved, $|M|=\text{const}$, during the motion. This strong condition can be justified for "weakly anisotropic" magnetic materials, in which the "relativistic" effects are weak compared with the exchange interaction. However, in many magnetic materials (rare-earths, actinides, compounds with Co^{2+}, etc.) this condition is not satisfied. We note that many magnetic objects, in which magnetic macroscopic quantum tunneling has been studied experimentally,[7–9] are strongly anisotropic magnetic materials. Moreover, strongly anisotropic ferromagnetic materials are of most interest for applications, in particular, for maximum magnetic storage.

In this letter we consider the quantum tunneling of magnetization in the limiting (Ising) case, in which the magnetization of the system can assume values determined on some straight line (axis) in three-dimensional space. Specifically, we consider a magnetic material whose magnetic ions are non-Kramers ions which have in the ground state two singlet levels separated from the excited states by a rather wide energy interval. It is well known that such ions are, to a high degree of accuracy, Ising ions (see, for example, Ref. 10). According to the existing theory, a necessary condition for MQT is the existence of a continuous trajectory for reversal of the magnetization.[1–4] At first glance, such a trajectory does not exist in the Ising case. We will show that because of the interaction of the magnetization with the quadrupole moment of an ion, such a trajectory does exist in the Ising case.

2. We represent the starting Hamiltonian of the system in the form

$$\hat{H}=\hat{H}_{\rm CF}-\frac{1}{2}\sum_{i\neq j} I_{ij}S_iS_j, \tag{1}$$

where $\hat{H}_{\rm CF}$ is the Hamiltonian of the crystal field, the second term represents the ion–ion exchange interaction, and S_i are the spin operators of the ith ion. Let us assume that the ground state of the ion in the crystal field consists of two closely spaced singlets with real wave functions $|A\rangle$ and $|B\rangle$, which are split by an energy $\Delta \ll E_i$, where E_i is the distance to the excited levels. Projecting the initial Hamiltonian onto the states $|1\rangle=(|A\rangle+i|B\rangle)/\sqrt{2}$ and $|2\rangle=(|A\rangle-i|B\rangle)/\sqrt{2}$, we obtain the following effective Hamiltonian[10] of the system under study:

$$\hat{H}_{\text{eff}}=-\frac{1}{2}\Delta\sum_i \hat{\sigma}_{ix}-\frac{1}{2}\sum_{i\neq j}\lambda_{ij}\hat{\sigma}_{iz}\hat{\sigma}_{jz}, \tag{2}$$

where $\hat{\sigma}_x$ and $\hat{\sigma}_z$ are Pauli matrices, $\lambda_{ij}=I_{ij}[m(g_J-1)/g_J\mu_B]^2 g_J$ is the Landé factor, μ_B is the Bohr magneton, $m=g_J\mu_B\langle 1|J|1\rangle$, and J is the total angular momentum operator of an ion. We note that the magnetic moment of an ion is then $\mathbf{M}=(0,0,M)$, where $M=m\langle\hat{\sigma}_z\rangle$, and the averages $\langle\hat{\sigma}_x\rangle$ and $\langle\hat{\sigma}_y\rangle$ are determined by the components of the quadrupole moment of the ion.

3. We assume that the macroscopic quantum spin-flip process is coherent when the spins of the atoms are parallel to one another. The dynamic behavior of the two-level system (2) will then be described by the quantum-mechanical equations of motion for the effective spin:

$$i\hbar d_t S_{\text{eff}}=[S_{\text{eff}},\hat{H}], \tag{3}$$

where $S_{\text{eff}}=(1/2)\vec{\sigma}$, and $\hbar$ is Planck's constant. Averaging Eq. (3) over the coherent quantum state

$$|\tau\rangle=\frac{\sqrt{1+n_z}}{2}\left|\frac{1}{2}\right\rangle+\frac{\sqrt{1+n_z}}{2}e^{-i\varphi}\left|-\frac{1}{2}\right\rangle,$$

where $\mathbf{n}=(\sqrt{1-n_z^2}\cos\varphi,\ \sqrt{1-n_z^2}\sin\varphi,\ n_z)$ is the unit vector which determines the orientation of S_{eff} in space, we obtain

$$d_t n=-\gamma\left[\mathbf{n}\times\frac{\delta E}{\delta n}\right], \tag{4}$$

where $\gamma=2/\hbar$, $E=\langle\hat{H}\rangle=-\frac{1}{2}N\Delta n_x-N\lambda n_z^2$ is the energy of the system at $T=0$, and N is the total number of ions in the particle. In terms of the variables n_z and φ, Eq. (4) has the form

$$d_t\varphi-=-2\gamma\lambda n_z+\frac{\Delta\gamma n_z}{2\sqrt{1-n_z^2}}\cos\ \varphi, \tag{5a}$$

$$-d_t n_z=\Delta\gamma\sqrt{1-n_z^2}\sin\ \varphi. \tag{5b}$$

Equation (5) are associated with the Lagrangian

$$L=\frac{1}{\gamma}N\dot{\varphi}n_z+N\lambda n_z^2+\frac{1}{2}N\Delta\sqrt{1-n_z^2}\cos\ \varphi. \tag{6}$$

The system (5) has the first integral $d_t H=0$, where

$$H=-N\lambda\left[n_z^2+\frac{\Delta}{2\lambda}\sqrt{1-n_z^2}\cos\ \varphi\right]=\text{const}. \tag{7}$$

4. The positions of stable equilibrium of the system described by the Lagrangian (4) correspond to the points $\varphi=0$ and $n_z=\pm\sigma_0=\sqrt{1-(\Delta/4\lambda)^2}$, between which tunneling occurs. The probability of tunneling between equilibrium states is determined, in the quasiclassical approximation, by the expression[11] $P\sim\omega\exp(-B)$, where ω is the oscillation frequency near the equilibrium position, $B=2S_E/\hbar$ is Gamow's constant, and $S_E=i\int Ldt$ is the action calculated on the tunneling trajectory.

The oscillation frequency near the equilibrium positions $n_z\sim\sigma_0$ is found by the standard method by analyzing the linearized equations of the system (5) described by Lagrangian (6). It is $\omega=2\gamma\lambda\sigma_0$. In order to find the tunneling trajectory and the corresponding contribution to the action, we must change in the integral of motion (7) to the imaginary time $\gamma=it$. Taking into consideration the value of the integral (7) at the equilibrium points of the system $n_z=\pm\sigma_0$, we obtain from Eqs. (5b) and (7), after algebraic transformations, the equation

$$d_\tau n_z=\lambda\gamma(\sigma_0^2-n_z^2). \tag{8}$$

Integrating this equation with the initial conditions $n_z(\tau=\pm\infty)=\pm\sigma_0$ gives the instanton solution $n_z=\sigma_0\tanh(\lambda\gamma\tau)$. The change in the angle φ is then given by the integral of motion (7). Substituting $d\tau=dn_z/d_\tau n_z$ for the integration variable in the expression for the action, we find, after corresponding substitutions and simple transformations, that the desired constant is

$$B=N\sum_{-\sigma_0}^{+\sigma_0}2n_z^2\left[1-\frac{\sqrt{4(1-\sigma_0^2)(1-n_z^2)+(\sigma_0^2-n_z^2)}}{2(1-n_z^2)}\right]dn_z=N\left(\ln\frac{1+\sigma_0}{1-\sigma_0}-2\sigma_0\right). \tag{9}$$

It is evident that $B\simeq2N\sigma_0^3/3$ as $\sigma_0\to0$, and also $B\to\infty$ as $\sigma_0\to1$.

The tunneling frequency is $\delta\omega\sim(\omega/\pi)\exp(-B)$. It is determined by the number N of particles in the cluster and by the spin σ_0. In the case of a strong exchange interaction $\lambda\gg\Delta$, when the spin approaches $\sigma_0=1$, the tunneling probability approaches zero. As the ratio Δ/λ increases and the spin decreases ($\sigma_0\to0$), the tunneling frequency approaches the normal frequency of the oscillator, since the barrier $U_0=E(n_z=0)-E(n_z=\sigma_0)=2N\lambda[1-\sigma_0^2/2-\sqrt{1-\sigma_0^2}]$ decreases to zero.

Quantum tunneling predominates at low temperatures, $T\ll T^*$, when thermally activated processes, whose rate varies with the temperature as $\exp(-U_0/kT)$, are suppressed. The characteristic temperature T^* (the crossover temperature), at which the quantum tunneling probability is equal to the probability of thermally activated spontaneous magnetization reversal, is determined by the condition $B=U_0/kT^*$. We then find

$$T^*=[2N\lambda/kB(\sigma_0)][1-\sigma_0/2-\sqrt{1-\sigma_0^2}].$$

It follows from this expression that $T^*\to0$ as $\sigma_0\to0$, and also when $\sigma_0\to1$.

5. While in the weakly anisotropic case the possibility of continuous reversal of the magnetization M in space, with the vector M remaining constant in magnitude, causes the states $|M\rangle$ and $|-M\rangle$ to be separated by a finite energy barrier and leads to a nonzero tunneling probability, in the Ising case the corresponding probability is formally equal to zero, because a continuous transition trajectory does not exist. We

TABLE I.

Ferrite	T_c, K	Δ, cm^{-1}	$\Delta/4\lambda$	$\omega/2\pi$, Hz	$-\frac{d}{dN}\log\frac{\delta\omega}{\omega}$	T^*, K
$LiTbF_4$	2.87	1.0	0.25	1.2×10^{11}	0.33	0.49
$Tb(OH)_3$	3.7	0.3	0.059	1.5×10^{11}	0.95	0.81

$\delta\omega$—MQT frequency, ω—frequency of characteristic oscillations in the ground states.

have shown that interaction with the quadrupole moment and the excitation of the quadrupole mode in a transition[1)] open up a transition trajectory with continuous reversal of the quadrupole moment in space and a continuous one-dimensional transition of the magnetization $M\to -M$. On this trajectory the corresponding tunneling probability is different from zero.

Good model-based objects for experimental study of MQT in Ising magnetic materials are some rare-earth hydroxides $R(OH)_3$ and rare-earth lithium fluorides $LiRF_4$. The expected characteristic parameters of the phenomenon studied are given in Table I for some of these materials. Another interesting object is the singlet magnetic Pr (or Pr with a small admixture of Nd ions). Many investigations have shown that in this material the ratio $\Delta/4\lambda$ of the exchange constant to the characteristic crystal-field parameter is very close to the threshold value $\Delta/4\lambda=1$ required for inducing a metamagnetic transition, and it can be easily changed in either direction, for example, by slight doping or by special treatment. In this case the factor $\sigma_0^3\sim(1-(\Delta/4\lambda)^2)^{3/2}$ can decrease Gamow's constant significantly.

In the Ising magnetic materials the effect of the magnetic field on macroscopic quantum tunneling of magnetization is very unusual, especially in view of the possibility for the appearance of crossover, i.e., crossing of ground-state levels of the ion in a field and accompanying magnetic phase transitions.[10]

The theoretical model studied in this letter can also be used to analyze macroscopic tunneling effects in some ferroelectric crystals with structural transformations.

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[1)]In this connection, we call attention to the work of Ostrovskiĭ,[12] who studied domain walls in Ising magnets. The quadrupole moment of rare-earth ions has actually been observed in an investigation of linear birefringence of garnets.[13]

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