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Magnetization tunneling in Mn$_{12}$ and Mn$_4$ single-molecule magnets

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The quantum mechanical tunneling of the direction of magnetization is discussed for several examples of single-molecule magnets (SMMs). SMMs are molecules that function as nanomagnets. Magnetization tunneling is described for two crystallographically different forms of [Mn$_4$O$_{12}$(O$_2$CC$_6$H$_4$p-Me)$_6$(H$_2$O)$_4$]·solvate. The two Mn$_{12}$ complexes are isomers, differing both in the positioning of the H$_2$O and carboxylate ligands and also in the orientations of the Jahn-Teller elongation at the Mn$^{III}$ ions. The magnetization vs magnetic field hysteresis loops are quite different for the two isomeric Mn$_{12}$ complexes. Frequency-dependent ac magnetic susceptibility and dc magnetization decay data are presented to characterize the magnetization relaxation rate vs temperature responses of two mixed-valence Mn$_4$ complexes. In both cases the Arrhenius plot of the logarithm of the magnetization relaxation rate vs the inverse absolute temperature shows a temperature-dependent region as well as a temperature-independent region.

I. INTRODUCTION

It was discovered in 1993 that

$$\text{[Mn}_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]\cdot4H_2O\cdot2\text{MeCOOH}$$

functions as a nanoscale magnet$^1$.\textsuperscript{2} Such a molecule has been called$^3$ a single-molecule magnet (SMM). There has been considerable interest in the magnetic properties of complex $^1$,\textsuperscript{4} which has an $S=10$ ground state split by axial zero-field splitting ($DS^2$, where $D=-0.5$ cm$^{-1}$). In 1996, it was reported$^5,6$ that complex $^1$ exhibits quantum mechanical tunneling of the direction of magnetization. The number of known single-molecule magnets is limited. Polynuclear metal complexes with the composition Mn$^{IV}$_{1}Mn$^{III}$_{8},$ Mn$^{IV}$_{4}Mn$^{III}$_{4}Mn$^{II}$_{4},$ Mn$^{IV}$_{1}Mn$^{III}$_{1},$ Mn$^{IV}$_{2}Mn$^{II}$_{2},$ $\gamma_{4}^{III},$ Fe$^{III},$ and Fe$^{II}$, have been identified as SMM's.

Each SMM functions as a superparamagnet as a result of having a large-spin ground state with appreciable magnetoanisotropy. At temperatures below the “blocking temperature” the magnetic moment of a SMM changes sluggishly from “spin up” to “spin down.” It is important to emphasize that the SMM phenomenon arises from the behavior of individual isolated molecules.

A SMM has a potential-energy barrier for reversal of its magnetic moment. It has been found that, in addition to thermal activation of each SMM over the barrier, the reversal of the direction of magnetization also occurs via quantum mechanical tunneling through the barrier.$^7$ In this paper we will discuss some recent observations on SMM's that are manifestations of magnetization tunneling.

II. EXPERIMENTAL RESULTS

The occurrence of magnetization tunneling is discussed for two Mn$^{IV}$_{1}Mn$^{III}$_{8} and two Mn$^{II}$_{2}Mn$^{II}$_{2} complexes. The complexes have the following formulas:

$$\text{[Mn}_{12}O_{12}(O_2CC_6H_4p-Me)_{16}(H_2O)_4]\cdot(HO_2CC_6H_4p-Me),}$$

$$\text{[Mn}_{12}O_{12}(O_2CC_6H_4p-Me)_{16}(H_2O)_4]\cdot3H_2O,}$$

$$\text{[Mn}_4(OAc)_{2}(pdmH)(H_2O)_4](ClO_4)_{2},$$

$$\text{[Mn}_4(hmp)_6Br_2(H_2O)_2]Br_2\cdot4H_2O.$$
Magnetization hysteresis loops were also measured for the oriented eicosane cube of complex 2 at the temperatures of 1.72, 2.20, 2.00, 1.90, and 1.80 K (the 1.90 K data are shown in Fig. 1). The hysteresis loops for complex 2 look quite different than those for complex 3. When the external field is reduced from +2.5 T to zero, the magnetization falls off dramatically. The coercive fields are considerably less for complex 2 than for complex 3. These two p-methylbenzoate Mn12 complexes experience quite different kinetic barriers for reversal of magnetization. It must be emphasized that the sweep rate for all the loops was 25 Oe/s.

From the hysteresis loop data it is clear that the p-methylbenzoate complex 2 has an appreciably greater rate of magnetization relaxation than does isomeric complex 3. This can be quantified by analyzing the frequency dependencies of the out-of-phase ac susceptibilities. Ac susceptibility data were collected at 8 different frequencies from 1.0 Hz to 1512 Hz for complex 3. From the peaks in the χ″ vs temperature plots values of the magnetization relaxation time Τ were determined at 8 temperatures. These data give a straight line Arrhenius plot of ln(1/Τ) vs the inverse absolute temperature (1/Τ) for complex 3. The data were least-squares fit to the Arrhenius equation to give the parameters of Τ₀ = 7.7×10⁻⁹ s and Uₑff = 64 K. A similar analysis of the frequency dependence of the ac data for complex 2 gives Τ₀ = 2.0×10⁻¹⁰ s and Uₑff = 38 K. The activation energy (Uₑff) for reversal of the direction of the magnetization for complex 2 (Uₑff = 38 K) is considerably less than that (Uₑff = 64 K) for the isomeric complex 3. The Mn₁₂−acetate complex 1 has been reported to have a Uₑff value of 62 K, very close to the value for complex 3.

It is likely that the appreciably faster rate of magnetization tunneling observed for complex 2 compared to the isomeric complex 3 is due to the lower symmetry observed for complex 2. This lowered symmetry would increase the rhombic zero-field splitting [E(S₁²−S₂²)] in the S = 10 ground state of complex 2 leading to an increase in the rate of magnetization tunneling.

Variable-field magnetization data have been fit to determine that complex 4 has an S = 8 ground state with D/kB = −0.358 K. Ac magnetic susceptibility measurements were carried out by cooling the sample with a ³He–⁴He dilution refrigerator in the 0.04–3.5 K range. Eleven different ac frequencies were used in the 1.1–995 Hz range, which gave rates of magnetization reversal at 11 different temperatures. These relaxation data fit well to the Arrhenius equation to give an activation energy for magnetization reversal of Uₑff = 17.3 K with a pre-exponential factor of τ₀ = 2.54×10⁻⁷ s. The thermodynamic barrier can be calculated to be U = 22.4 K. As with other SMMs, it is expected that U > Uₑff, for the reversal of magnetization not only involves a thermal activation over the potential-energy barrier, but also quantum tunneling of the direction of magnetization.

The most definitive data showing that complex 4 does reverse its magnetization direction by quantum tunneling were obtained by means of magnetization decay experiments. In a dc magnetization decay experiment the sample is decreased. At 1.72 K the coercive magnetic field for complex 7 is ≈2 T.

Magnetization hysteresis loops were also measured for the oriented eicosane cube of complex 2 at the temperatures of 1.72, 2.20, 2.00, 1.90, and 1.80 K (the 1.90 K data are shown in Fig. 1). The hysteresis loops for complex 2 look quite different than those for complex 3. When the external field is reduced from +2.5 T to zero, the magnetization falls off dramatically. The coercive fields are considerably less for complex 2 than for complex 3. These two p-methylbenzoate Mn12 complexes experience quite different kinetic barriers for reversal of magnetization. It must be emphasized that the sweep rate for all the loops was 25 Oe/s.

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first cooled and maintained at a low temperature, after which it is subjected to a very small magnetic field. At low temperatures, only a small field is needed to achieve magnetization saturation. The field is then suddenly removed and the magnetization is measured as a function of time. Over time the magnetization decays from some initial value to an equilibrium value, defined as the time when the applied field becomes zero, to an equilibrium value.

Plots of magnetization vs time were measured in the 0.030–0.860 K range. These magnetization decay data were fit to a stretched exponential function. This gave a set of relaxation data in the 0.047–1.195 K range. These magnetization decay data were combined with those obtained at higher temperatures by means of the ac susceptibility. At the higher temperatures the relaxation rate is temperature dependent with an activation energy of 15.8 K. At the lower temperatures we again see a temperature-independent rate of relaxation. This is surely attributable to ground state magnetization tunneling. The temperature-independent magnetization tunneling rate is $1 \times 10^{-4} \text{ s}^{-1}$ for complex 4. Preliminary HFEPR data indicate that complex 5 experiences a larger rhombic zero-field splitting than does complex 4. This would explain the faster rate of tunneling in complex 5. Further experimentation is needed on these interesting tetranuclear manganese SMMs to understand in detail the mechanism of magnetization tunneling in these complexes.

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