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The relaxation times in tetranuclear manganese complex with $S = 8$

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Abstract

Magnetization relaxation of $[Mn_4(hpdm)_6(OAc)_2](ClO_4)_2$ with $S = 8$ ground state has been investigated with AC susceptibility and DC magnetization measurements below 4 K. The temperature dependence of the relaxation time follows the Arrhenius law with activation energy $E = 17$ K above 1 K. At lower temperatures, the relaxation deviates from the thermal activation formula and becomes temperature independent below 0.5 K with $\tau_{\rm sat} \sim 10^4$ s. These observations are attributed to magnetic quantum tunneling.

Keywords: Macroscopic quantum tunneling; Magnetism

Quantum spin dynamics in mesoscopic magnets has received much attention over the recent years [1]. The molecular clusters, which behave like nanomagnets at low temperature, are a particularly appealing class of materials for these investigations. Several molecular clusters have been reported to show evidence of quantum tunneling of the magnetization over an anisotropic energy barrier. The best examples are Mn12ac and Fe8, both of which have a net spin $S = 10$, showing temperature-independent relaxation times at low temperatures [2,3]. Recently, $Mn_4O_3Cl(O_2CCH_3)_3(dbm)_3$, which has a net spin of $S = \frac{9}{2}$ was also reported to show such a quantum tunneling effect [4]. Here we report low-temperature magnetic properties of a new cluster, $[Mn_4(hpdm)_6(OAc)_2](ClO_4)_2$. It has a net spin of $S = 8$ [5], intermediate between the above clusters, and shows a clear evidence of quantum tunneling of magnetization.

A polycrystalline sample was stuck on a quartz glass with a small amount of N-grease. It was immersed in liquid ^{4}He which was cooled by way of a sintered powder heat exchanger with a ^{3}He–^{4}He dilution refrigerator. The AC susceptibilities, χ_{AC}, were measured with a superconducting quantum interference device (SQUID) magnetometer. The data were taken in zero DC field and in less than 1 Oe AC field at the frequency of 1–1000 Hz. The values of χ_{AC} are normalized in such a way as the plots of χ_{AC} are smoothly connected to those of the high-temperature data [5].

Typical results of the AC susceptibility are shown in Fig. 1 for different frequencies. Out-of-phase AC susceptibility (χ''_{AC}) is seen in the temperature range of 1–2.5 K. The temperature dependence of the relaxation time τ can be obtained from the frequency and the temperature corresponding to the maximum in χ''_{AC}, where $\tau = 1/[2\pi\nu_{AC}$ (= frequency of the AC field)]. The τ values are plotted as $\ln(\tau)$ versus $1/T$ in Fig. 2. The relaxation follows $\tau = \tau_0 \exp(\Delta E/k_B T)$ with an energy barrier (ΔE) of 17 K and $\tau_0 = 3.4 \times 10^{-8}$ s, above 1 K. This is to be compared with the barrier height given by $|DS^2| = 22.4$ K, which is calculated by taking the ground state as $S = 8$ with the D value of -0.35 K obtained from magnetizaion data [5]. The reasonable agreement can be explained in terms of a multistep Orbach process [6].

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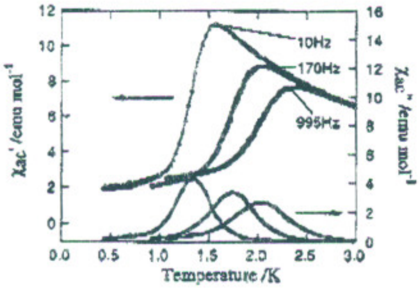

Fig. 1. Temperature dependence of the AC magnetic susceptibility for the polycrystalline sample at various frequencies.

In order to investigate the magnetic relaxation at lower temperatures, the magnetization measurements in zero DC field were made by using the same SQUID magnetometer. Initially, a small DC field of 3.7 Oe was applied at desired temperatures. After several hours, the magnetic field was reduced to zero and the magnetizaion was recorded as a function of time. The magnetization curves can be well fitted by a stretched exponential [7], $M(t) = M_{in} + [M_{eq} - M_{in}]\exp((\tau/t)^{\beta})$ where τ is relaxation time, M_{in} is the initial magnetization at time $t = 0$ and M_{eq} is the equilibrium magnetization. The temperature-dependent exponent β varies from 0.5 to 1. As shown in Fig. 2, below 0.5 K the relaxation time τ becomes independent of temperature with $\tau_{sat} \sim 10^4$ s. This temperature-independent process should correspond to magnetization tunneling through the anisotropic energy barrier. The observed value of τ_{sat} is intermediate between the reported ones in the other manganese clusters, $\tau_{sat} \sim 10^8$ s of Mn12 with $S = 10$ [8] and $\tau_{sat} \sim 3 \times 10^1$ s of $Mn_4O_3Cl(O_2CCH_3)_3(dbm)_3$ with $S = \frac{9}{2}$ [4]. It is noted that the relaxation time is comparable to $\tau_{sat} \sim 10^4$ s of Fe8 [3] in which an quantum interference

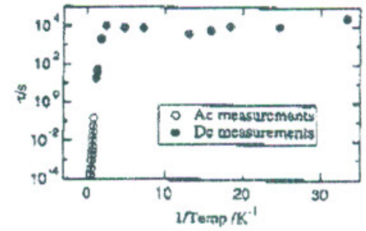

Fig. 2. ln(τ) versus $1/T$. The line is the fit described in the text.

effect was recently observed at low temperatures [9]. Detailed magnetic measurements are in progress, such as a relaxation measurement under high DC fields.

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