Field-tuned Tunneling in [Fe(C 5 Me 5) 2] [Mn 12 O 12 (O 2 CC 6 F 5) 16 (H 2 O) 4] Studied by AC Magnetic Susceptibility

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The field dependence of ac magnetic susceptibility of an anionic single-molecule magnet [Fe(C$_5$Me$_5$)$_2$][Mn$_{12}$O$_{12}$(O$_2$CC$_6$F$_5$)$_{16}$(H$_2$O)$_4$] is reported. When the field was applied to perpendicular to the easy axis of the [Mn$_{12}$]$^-$ anion, a decrease of relaxation time was observed at $H = 0$ and 0.45 T. The effect of the transverse field is discussed.

Keywords: single-molecule magnet; anionic Mn$_{12}$-complex; ac magnetic susceptibility; field-tuned quantum tunneling.

INTRODUCTION

The magnetization relaxation behavior of Mn$_{12}$-acetate [Mn$_{12}$O$_{12}$(OAc)$_{16}$(H$_2$O)$_4$] (**1**), which is the first molecule shown to be a single-molecule magnet (SMM), under the magnetic field has been thoroughly investigated by Luis et. al.[1] and Novak et. al.[2] They

observed two minimums of the relaxation time τ at the longitudinal fields, which are ascribed to the enhanced magnetization relaxation by quantum tunneling. On the other hand, the effect of transverse field on the relaxation time is not clear. Paulsen et. al.[3] reported the relaxation time is independent on the angle θ between the applied field and the magnetization easy axis of [Mn$_{12}$], while Luis et. al.[1] reported the contrary results.

During the course of our study on the several [Mn$_{12}$]$^-$ anions, we found that the field-oriented crystalline sample of [Fe(C$_5$Me$_5$)$_2$][Mn$_{12}$O$_{12}$(O$_2$CC$_6$F$_5$)$_{16}$(H$_2$O)$_4$] (**2**) at around 310 K shows the easy axis of the [Mn$_{12}$]$^-$ anion being perpendicular to the applied field.[4] This is due to the dominant contribution of the magnetic anisotropy of decamethylferrocenium cation compared to that of the [Mn$_{12}$]$^-$ anion at this temperature and due to the orthogonal arrangement of their magnetization easy axes in the crystal. By using this sample, we can easily measure the effects of transverse field on magnetization property of [Mn$_{12}$] complex. Here, we report the ac magnetic susceptibility of **2** under various transverse fields.

EXPERIMENTAL SECTION

The preparation, characterization and structure of [Fe(C$_5$Me$_5$)$_2$][Mn$_{12}$O$_{12}$(O$_2$CC$_6$F$_5$)$_{16}$(H$_2$O)$_4$] (**2**) were described elsewhere.[4] The ground spin state of the [Mn$_{12}$]$^-$ anion in **2** is $S = 21/2$. The X-ray single-crystal analysis showed that **2**•2H$_2$O crystallizes in an orthorhombic cell with a quasi-NaCl type structure. The magnetization easy axis of the [Mn$_{12}$]$^-$ anion is parallel to the c-axis whereas the

principal axis ($g_\parallel$) of the decamethylferrocenium cation is lying on the a-b plane.

Alternating current (ac) susceptibility measurements under the magnetic field were carried out on a Quantum Design MPMS2 SQUID magnetometer equipped with a 1 T. The magnitude of ac field was fixed to 0.1 mT, oscillating at frequencies of 5, 75, 250, and 997 Hz. Sample alignment in eicosane was performed while keeping the sample in a 1.0 T field at a temperature above the melting point (308-312 K) of eicosane for 15 min, after which the temperature was gradually decreased below the melting point to solidify the eicosane in order to constrain the sample. As described elsewhere, the sample prepared in this way showed the magnetization easy axis of the [Mn$_{12}$] anion to be perpendicular to the applied field, due the orthogonal arrangement of magnetization easy axes of the anion and the cation.

RESULTS AND DISCUSSION

AC Magnetic Susceptibility Under Transverse Field. It is well known that an SMM shows a frequency-dependent out-of-phase ac susceptibility signal (χ''_M). Figure 1(a) shows χ''_M-T plots of the field-aligned sample of **2** under various fields at 997 Hz ac frequency. The χ''_M peak temperatures are plotted versus external field for the field-aligned and random-oriented samples in Figure 1(b). The decrease of the peak temperature of the field-aligned sample with 1-1.5 K over the entire field range indicates the transverse field accelerates the magnetization relaxation. As increasing the field, the peak firstly moved to higher temperature and shows broad maximum of 4.81 K at 0.125 T

then moved to lower temperature at higher field with a plateau at around
0.45 T. Similar behaviors were observed at other ac frequencies. On the
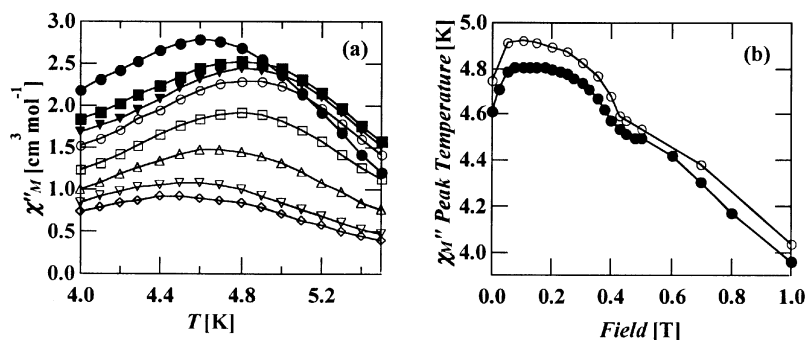

Figure 1. (a) Plots of temperature dependence of ac out-of-phase (χ''_M)
signals at 997 Hz ac frequency for the field-aligned microcrystalline
sample of **2** under various transverse dc fields of 0 (●), 0.05 (■), 0.1
(▼), 0.15 (○), 0.25 (□), 0.35 (△), 0.45 (▽), and 0.5 (◇) T. (b) Plots
of χ''_M peak temperature versus external field for the field-aligned (●)
and random-oriented (○) sample of **2**. The ac frequency was 997 Hz.

basis of the Arrhenius's plots, the effective energy barrier ΔE and pre-
exponential factor τ_0 can be estimated by the following equation:[5]

$$\tau = \tau_0 \exp(\frac{\Delta E}{k_B T}) \qquad (1)$$

where k_B is the Boltzmann constant, τ is the relaxation time evaluated
from $1/(2\pi v)$ where v is the ac frequency, and T is the χ''_M peak
temperature. The estimated τ_0 are ranging from 1.3×10^{-9} s to 2.8×10^{-9}
s, which can be regarded as a constant after Luis et. al.[1] We fixed it to
the averaged value of 2.1×10^{-9} s and estimated ΔE at each field, which
were plotted in Figure 2 as a function of the transverse field. We can see
a sharp minimum at $H = 0$ T and a plateau at $H = 0.45$ T. These values

are corresponding to the field values of 0 and 0.42 T where magnetization steps were observed in the hysteresis loop.[4] For the Mn$_{12}$-Ac (**1**) under the longitudinal field two sharp minimums were observed at 0 and 0.41 T.[1] These minimums are ascribed to the
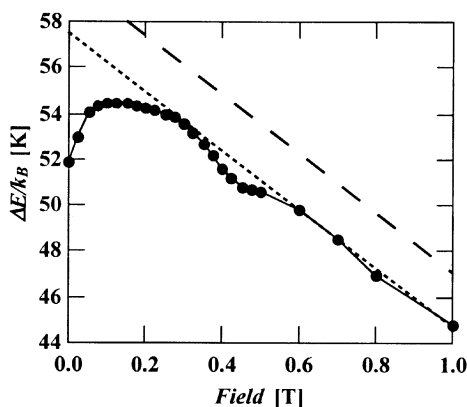

Figure 2. Plot of the energy barrier $\Delta E/k_B$ versus transverse magnetic field for **2**. The energy barriers were estimated from eq.(1) assuming a constant τ_0 of 2.1×10^{-9} s. See the text for the explanation of the dotted and broken lines.

enhanced shortening of the relaxation time by quantum tunneling of magnetization. The main difference between the results of **1**[1] and **2** is the sharpness of the second drop at around $H = 0.45$ T. The suppressed quantum tunneling is probably due to the alignment of the magnetization easy axis of the [Mn$_{12}$]$^-$ anion in **2** being perpendicular to the external field. Two lines in Figure 2 represent the classical overbarrier activation energy $\Delta E / k_B = -10g\mu_B H - 110D$ with $g = 1.91$ and $D = -0.52$ K for the dotted line, and with $g = 1.92$ and $D = -0.55$ K for the broken line, where μ_B is the Bohr magneton. The former parameters were obtained by the best fit for the linear part of the

experimental data whereas the later was adopted from the variable-field dc magnetization analysis using a random-oriented sample.[4] Although the discrepancy between them indicates the effects of the sample orientation, there was no drastic change anticipated from the theoretical works.[1] The reason is probably the insufficient alignment of microcrystals. In the magnetization relaxation experiments the slower relaxation process hides the faster relaxation process. Further studies using a single crystal are awaited.

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