Communication

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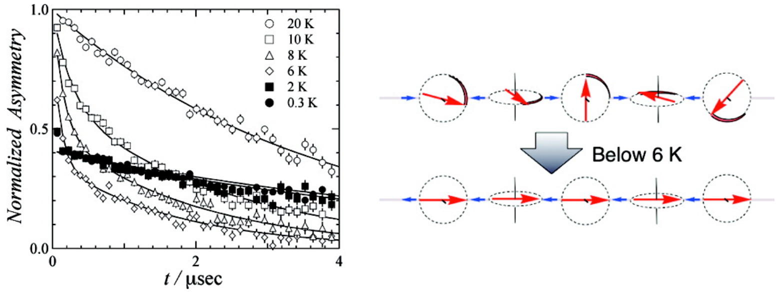

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Direct Observation of the Ground-Spin Alignment of Fe(II)−Fe(III) Single-Chain Magnet by Muon-Spin Relaxation

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Nanosized magnets, including single molecule magnets (SMMs)[1−3] and single-chain magnets (SCMs),[4] are remarkable compounds which show unique physical properties never previously observed in conventional permanent magnets. The attention of numerous nanoscientists is currently directed toward the construction and the behavior of such nanomagnets. SMMs and SCMs have well-defined structures and exhibit well-characterized easy-axis magnetic anisotropy ($D < 0$), forming a "double-well potential" which prevents reversal of the molecular magnetization. SCMs are strategically constructed nanomagnets based on the alignment of spin-carrier components possessing easy-axis anisotropy which exhibit Glauber's dynamics.[5] Recently, we reported a novel type of SCM using spin-carrier components possessing hard-axis anisotropy (or easy-plane anisotropy, $D > 0$), *catena*-$[\mathrm{Fe^{II}(ClO_4)_2\{Fe^{III}(bpca)_2\}}]\mathrm{ClO_4}$ (**1** shown in Figure 1), which is formed by an alternate arrangement of high-spin $\mathrm{Fe^{II}}$ and low-spin $\mathrm{Fe^{III}}$ in the chain complex.[6] The SCM character of **1** is derived from a twisted arrangement of easy-planes of $\mathrm{Fe^{II}}$ along the chain axis which generates easy-axis anisotropy along the chain axis.

We have reported short-range spin ordering of **1** in a zero-magnetic field, which was confirmed by temperature-dependent Mössbauer spectroscopy.[6] Broadening of the Mössbauer signals due to paramagnetic relaxation[7] occurred below 7 K and two sets of sextet signals appeared at 3.7 K, where the spin reversal slows down below the Mössbauer time scale of 10^{-7} s. Muon spin relaxation (μSR) is a unique experimental method to sense the fluctuations of weak magnetic fields formed within the characteristic time window of 10^{-6}−10^{-11} s. Since the muon has a half spin with a large gyromagnetic ratio ($\gamma_\mu = 2\pi \times 13.55$ MHz/kOe) which is 4 times larger than that of a proton, μSR is a highly sensitive and powerful probe of solid-state magnetic materials.[2,3,8−10] The growth of spin ordering of Fe(II) spins can be probed even in the zero-field (ZF) condition by making use of the self-polarization of muon spin. μSR was once employed for investigating ordinal SCM systems,[2] and the results were briefly discussed. In this paper, we report details of the short-range spin ordering of **1** in ZF by means of μSR measurements as well as the character of the incoming static internal magnetic field from the results of μSR dependence on the longitudinal-field (LF).

ZF- and LF-μSR measurements were carried out at the RIKEN-RAL Muon Facility in the U.K. A pulsed positive surface-muon beam with a momentum of 27 MeV/c was used. Forward and backward counters were located on the upstream and downstream sides in the beam direction that was parallel to the initial muon-spin and LF direction. Muons injected into the sample lose their energy and come to rest at the minimum of the Coulomb potential. The stopped muons decay with a lifetime of 2.2 μs and emit positrons preferentially along the spin direction. These positrons are detected to obtain the asymmetry parameter $A(t)$, defined as $A(t) = [F(t) - \alpha B(t)]/[F(t) + \alpha B(t)]$, with $F(t)$ and $B(t)$ denoting the numbers of positrons counted by the forward and backward counters at a time t. The α is a calibration factor reflecting relative counting efficiencies of the forward and backward counters. Then, $A(t)$ describes the degree of polarization of the muon spin. The direction of the initial muon-spin depolarization is along the beam line, and LF was applied parallel to this direction.

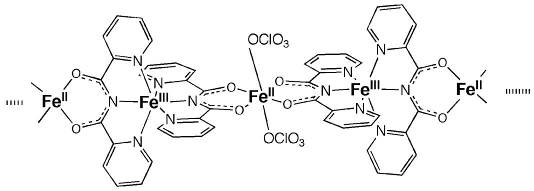

Figure 1. Structure of the single-chain magnet **1** constructed with an alternate arrangement of high-spin Fe(II) and low spin Fe(III).

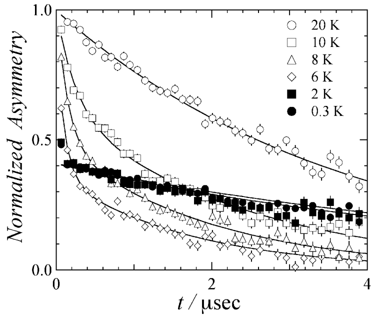

Figure 2. Zero-field μSR time spectra of the complex **1** at various temperatures. The corrected asymmetry from the sample was normalized by the value obtained at 20 K. Solid lines are the best fit results using single- or double-exponential functions described in the main text.

Figure 2 shows the ZF-μSR time spectra at various temperatures down to 0.3 K. The muon spin depolarizes monotonically with time at 20 K. The time spectrum changes with decreasing temperature and shows exponential-type depolarization behavior down to about 10 K. A loss of the initial asymmetry at $t = 0$ starts to be observed below 10 K, suggesting the appearance of strong internal fields at the muon site, and the muon spin depolarizes fast by the strong fields within the resolution time of the detection system. The muon-spin polarization is almost lost at a longer time region than about 2 μs. This depolarized time spectrum in the longer time region partially recovers and becomes nearly flat below 2 K.

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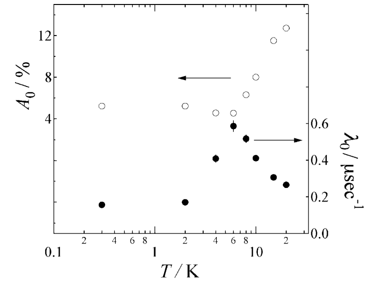

Figure 3. Temperature dependence of the initial asymmetry of the slow depolarizing component (A_0) and the depolarization rate (λ_0).

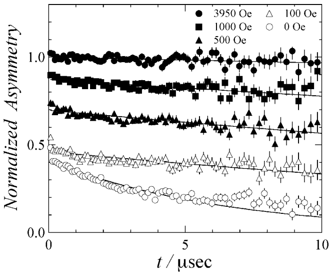

Figure 4. Variation of LF-μSR time spectra with the longitudinal field of the complex **1** at 0.3 K. Solid lines are the best-fit results using the single-exponential function (see text).

The two-exponential function, $A_0 \exp(-\lambda_0 t) + A_1 \exp(-\lambda_1 t)$, was simply used to describe time spectra, where A_0, A_1 and λ_0, λ_1 are the initial asymmetries and depolarization rates of the slow and fast depolarizing components, respectively. Figure 3 summarizes the results of the analysis. A_0 decreases with decreasing temperature and reaches a minimum at 6 K, and then shows a constant value below 2 K. λ_0 is enhanced with decreasing temperature and exhibits divergence at 6 K. This observation of the divergence of the muon-spin depolarization rate means that the critical slowing-down behavior of the internal field at the muon site appears around 6 K, which is caused by Fe spins. Both the decrease in the initial asymmetry and existence of the critical slowing-down behavior are typical characteristics of the appearance of a static magnetically ordered state.[11]

LF was applied to confirm whether the ground state of Fe spins is dynamic or static at 0.3 K (Figure 4). The normalized asymmetry recovered with increasing LF and the time spectrum was almost quenched by an LF of 1000 Oe. In addition, the time spectrum in LF of more than 100 Oe was nearly flat showing that there is almost no muon-spin depolarization due to dynamically fluctuating internal fields at the muon site. These results indicate that the Fe(II)-spin fluctuations are almost suppressed at 0.3 K. Taking into account the results of ZF-μSR, it is concluded that the observed magnetically ordered state appearing below 6 K is static. Following the previous way,[12] the magnetic transition temperature was determined to be 6 K, which is consistent with that determined by Mössbauer spectroscopy.

When a muon is located in a uniform magnetic field, all muons precess with the same Larmor precession frequency to give a periodic precession of the asymmetry. The lack of coherent muon-spin precession in the magnetically ordered state below 6 K indicates that muons probably locate in a widely distributed magnetic field. This result supports the picture of short-range ordered Fe(II) ions observed by Mössbauer spectra in the same temperature range. Because of short-range ordering of Fe(II) ions, the muon-spin polarization decays owing to distributed precession frequencies, and the amplitude of the asymmetry decreases with time.

The initial asymmetry below 2.0 K is close to one-third the total asymmetry at 20 K (Figure 2). The saturated A_0 below 2.0 K is regarded as the so-called one-third tail of the static Kubo−Toyabe function,[12] and this proves that almost all Fe spins are statically ordered, showing the full magnetic volume fraction. The averaged internal field at the muon site was also estimated to be 406 ± 30 Oe.

In conclusion, the growth of short-range spin ordering in Fe(II)−Fe(III) SCM **1** was observed by μSR. The observed phenomena are very close to those observed for spin-glasses, and a similar analytical method can be applied to reveal the details of spin ordering. The uniaxial anisotropy arising from the twisted arrangement of easy-plane anisotropy resulted in a slow reversal of the spin even in a zero-external field below 6 K within the μSR characteristic time window.

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Supporting Information Available: Mössbauer spectra of complex **1** and experimental details of μSR measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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