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Long-Range Order in the One-Dimensional Cobalt(II)−Radical Coordination Polymer Magnet Probed by Muon-Spin Rotation and Relaxation

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A long-range-ordered state of CoBPNN was characterized by μSR. The temperature at the depolarization rate divergence (40 K) is defined as a magnetic transition temperature (T_N). The phase is unique below T_N, but gradual freezing of the domain-wall motion finally leads to the magnetically hard character.

There have been a number of low-dimensional complexes containing nitronyl nitroxide (NN) radicals[1] with metal hfac salts, in pursuit of metal−radical hybrid magnets.[2] The Co and NN spins in one-dimensionally arrayed NN−$Co(hfac)_2$ systems are antiferromagnetically correlated to form a ground ferrimagnetic chain.[2−4] The first single-chain magnet (SCM) [$Co(hfac)_2$·AnNN] was discovered by Gatteschi et al.[3] (Scheme 1 with R = CH_3). We have reported the record coercivity (H_C = 52 kOe at 6 K) in [$Co(hfac)_2$·BPNN] (abbreviated as CoBPNN hereafter, R = *n*-C_4H_9) and empirically depicted the phase diagram of CoBPNN: a hard magnet in $T \leq 10$ K and a soft magnet in 10 K < $T \leq 45$ K.[4] The alternating-current (ac) magnetic susceptibility of CoBPNN showed a distinct frequency dependence just above 10 K. We have suggested that magnetic domain walls swiftly move in the soft magnet phase and freeze in the hard magnet phase. However, the ground state of CoBPNN has not yet been well investigated.[5] There seem to be problems at present: how can we characterize a magnetically ordered state and determine the magnetic phase transition temperature?

The muon-spin rotation/relaxation (μSR) technique is available to solve these problems. The muon has a half-spin with a large gyromagnetic ratio ($\gamma_\mu = 2\pi \times 13.55$ MHz/kOe), and μSR is a highly sensitive and powerful microscopic probe to investigate the ground state of magnetic materials within its characteristic time window (10^{-6}−10^{-11} s).[6] Zero-field (ZF)-μSR measurements have been successfully used for a number of organic ferromagnets[7−9] as well as molecule-based magnets.[10−12] An experimental approach using μSR on SCMs has rarely been reported so far.[12]

The μSR measurements on CoBPNN were carried out at the RIKEN-RAL Muon Facility in the U.K. A pulsed positive surface muon (μ) beam with a momentum of 27 MeV/c was used. The experimental diagram has been illustrated elsewhere.[6]

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. The muon spin is completely polarized in a beam direction. Positrons were detected by forward and backward counters. The asymmetry is defined as $A(t) = [N_F(t) - \alpha N_B(t)]/[N_F(t) + \alpha N_B(t)]$ where N_F and N_B are the number of the decay positrons counted by the forward and backward counters, respectively, and α is a geometrical factor to set the baseline of $A(t)$ as 0. The data were analyzed by the *Wimda* program.[13]

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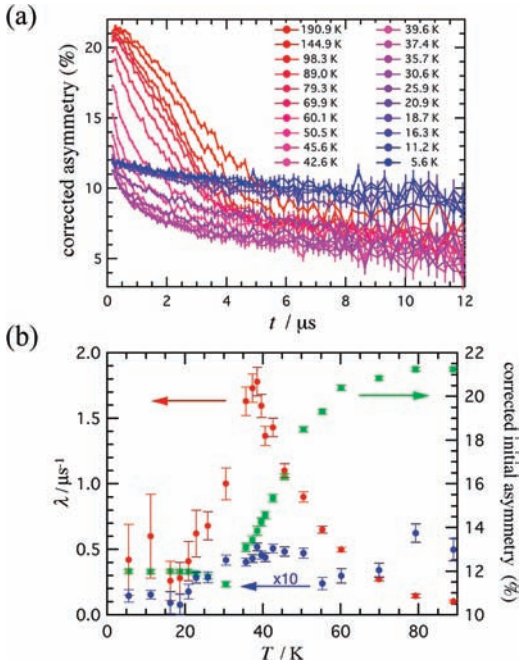

Figure 1. (a) Temperature dependence of the ZF-μSR time spectra on CoBPNN in a temperature range from 190.9 K (red) to 5.6 K (blue). (b) Temperature dependence for the relaxation rate constants λ_{fast} (red) and λ_{slow} (blue) and the total initial asymmetry $A(0)$ (green).

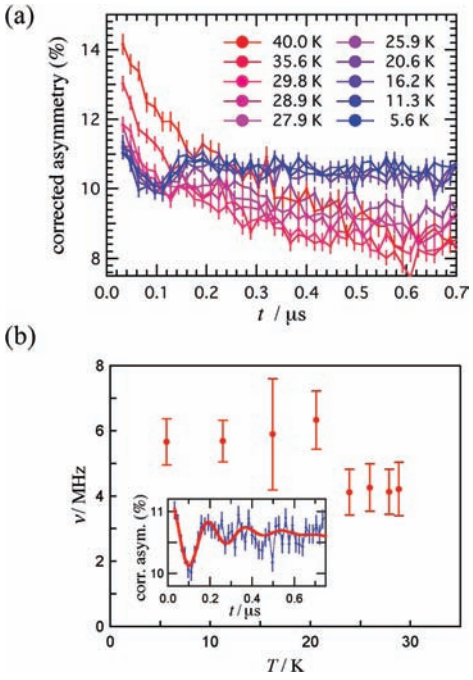

Figure 2. (a) Temperature dependence of the ZF-μSR time spectra on CoBPNN in a temperature range from 40 K (red) to 5 K (blue). (b) Frequency of the muon-spin precession as a function of the temperature. Inset: calculation curve with an oscillation of 5.65 MHz for the time spectrum measured at 5.6 K.

Scheme 1

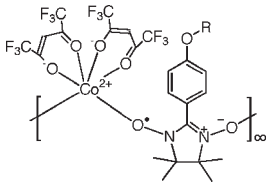

Figure 1a shows ZF-μSR time spectra measured at various temperatures from 200 K down to 5.6 K. Above ca. 60 K, Gaussian-like depolarization behavior was observed. This behavior is usual for the presence of a random static internal field due to the Co and BPNN nuclear moments in a paramagnetic phase.[12,14] With decreasing temperature, the time spectra changed to exhibit a Lorentzian shape, and a decrease of the initial asymmetry [$A(0)$] was observed (red to reddish-purple lines in Figure 1a). Below ca. 30 K, the depolarized time spectrum was recovered with an extremely slow exponential depolarization (blue lines).

We analyzed time spectra measured below 90 K based on a phenomenological function,[12,15] $A(t) = A_{fast}(0)\exp(-\lambda_{fast}t) + A_{slow}(0)\exp(-\lambda_{slow}t)$. For the data points in 55 K $\leq T \leq$ 90 K, a small contribution of the Kubo−Toyabe function[14] was added. The relaxation rates, λ_{fast} and λ_{slow}, and the total initial asymmetry $A(0)$ [$= A_{fast}(0) + A_{slow}(0)$] are plotted as a function of the temperature (Figure 1b). The divergence of λ_{fast} was found at 40 K. Simultaneously, the decrease of $A(0)$ was observed around 40 K. Actually, a loss of the initial asymmetry implies that the muon spin would depolarize faster than the time resolution of the detection system (20 ns).

The divergence of the muon-spin depolarization rate means the appearance of the critical slowing-down behavior of magnetic moments, from the Co and BPNN spins in the present system. In addition, both the decrease of $A(0)$ and the recovery of the depolarized time spectrum are typical of the μSR on a static magnetically ordered state. The same behavior was observed in another SCM in which a static magnetically ordered state appeared.[12] Thus, the magnetic transition temperature, T_N, is defined to be 40 K in CoBPNN.[16] The almost flat depolarization behavior at the measured base temperature indicates that the Co and BPNN spins are completely static and frozen from the viewpoint of the μSR time scale.

Figure 2a shows ZF-μSR time spectra of CoBPNN at low temperatures within an early time region of less than 0.7 μs. Below 28 K, the wiggling of the time spectra was observed, indicating the appearance of the coherent muon-spin Larmor precession (rotation) and accordingly the presence of an appreciable internal magnetic field due to spontaneous magnetization. Because each muon experiences the electronic dipolar field regulated by the r^{-3} law in a three-dimensional manner, the coherency implies that the specimen is in a long-range-ordered state. If the interchain coupling were missing, despite the short-range spin alignment within a chain, a spatially random arrangement of the spins in two other directions would cause randomly oriented dipolar fields. The μSR technique is a sensitive probe for both short- and long-range magnetic orderings. We can conclude a ferromagnetic ground state with respect to the assembly of the ferrimagnetic chains, combining the result on the saturation

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(16) An apparent magnetic phase transition temperature of CoBPNN was reported to be 45 K,[4] which corresponds to 40 K in this study. The present value is more reliable because of the complete absence of an applied field.

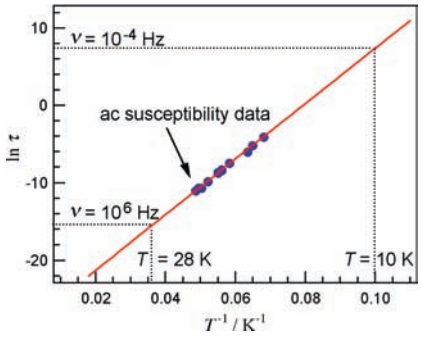

Figure 3. Arrhenius plot of the time constant ($\tau = 1/\lambda$) against T^{-1} from the data of the ac susceptibility for CoBPNN. The solid line stands for the best fit of the ac susceptibility data with $E_a/k_B = 350$ K.

magnetization of CoBPNN.[4] The small amplitude and strong damping of the muon-spin oscillation are most likely related to the size of a magnetic domain.

The frequencies of the muon-spin precession were extracted from numerical fitting, together with Fourier analysis, to give 5.65 ± 0.28 and 0.365 ± 0.034 MHz at 5.6 K. These values can be reduced to the internal magnetic fields (B_{int}) of 420 and 27 G, respectively, from the relation $\nu = (\gamma_\mu/2\pi)B_{int}$. This finding indicates that there are at least two muon trap sites in the crystal lattice. The frequency and amplitude seem practically constant up to 28 K; in other words, the long-range-ordered state does not change very much and disappears around 28 K (Figure 2b). The critical temperature was 10 K between the soft and hard magnets,[4] but no anomaly was found around there in the μSR experiments.

Attention must be paid to the characteristic time scale of the μSR technique, as is typically indicated by the muon-spin rotation of CoBPNN with a frequency on the order of megahertz. The analysis according to the Arrhenius equation, $\ln(2\pi\nu) = -\ln(\tau_0) - E_a/k_BT$, gave $E_a/k_B = 350 \pm 6$ K and $\tau_0 = 6.8\times10^{-13}$ s obtained from ac susceptibility measurements with a frequency of $10 - 10^4$ Hz.[4] The temperature at which the dynamic process is sufficiently slow as $\nu = 10^{-4}$ Hz (i.e., τ becomes hours) is 10 K from the extrapolation of this equation, which corresponds to the critical temperature for the hard magnet phase (Figure 3). Similarly, assuming that the dynamic process is as fast as $\nu = 1$ MHz, the freezing temperature is estimated to rise to 28 K. This calculation perfectly agrees with the present μSR observation. Thus, the characteristic temperatures of 10 and 28 K are not magnetic transition temperatures but are due to the time scale of experimental tools to see the stabilization of the hard magnet state.

Taking into account the present μSR results together with our previous experiments,[4] the magnetically ordered

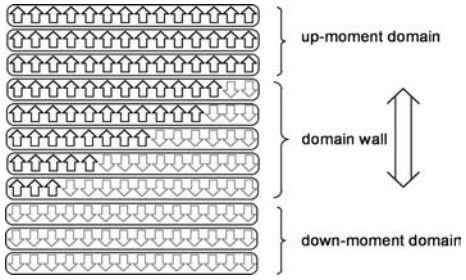

Figure 4. Model for magnetic domain-wall motion. The wall moves upward or downward, accompanied by magnetization reversal of each chain when a kink slides in the chain direction. Only the cobalt spins in the ferrimagnetic cobalt(II)−radical chains are drawn for clarity.

state of CoBPNN can be interpreted as follows. On cooling from 40 K, which can be defined as an intrinsic T_N, CoBPNN enters into the quasi-static magnetically ordered state, and the magnetic hardness gradually grows in a unique phase. Although the spins tend to form the long-range-ordered state, moving domain walls disturb the alignment of the spins. When the dynamics of the domain walls become slower than the time scale of 10^{-6} s below 28 K, muons start to sense the appearance of the quasi-static long-range-ordered state. On further cooling, the dynamics of domain walls become more static to be observable in the ac magnetic susceptibility, and the hard magnet state is finally settled down below 10 K.

Thermal activation allows a kink between two opposite magnetizations to move along the chain.[17] The magnetic domain walls would have a fairly large volume, and magnetization reversal of each chain takes place cooperatively within a wall width, giving rise to a macroscopic wall motion with a large activation energy (Figure 4). It seems essential that the magnetic easy axis of CoBPNN lies perpendicular to the chain direction[4] to afford the interchain dipolar ferromagnetic coupling, which is more appreciable than those of other SCMs. The large E_a is effective for the large H_C owing to the freezing domain-wall motion. The presence of sizable interchain coupling also leads to a relatively high T_N. Classical dipolar coupling is versatile for the development of high-T_N (T_C) and high-H_C magnets.

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