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Muon-spin-relaxation study of the ground state of the two-dimensional $S=1$ *kagomé* antiferromagnet [2-(3-*N*-methyl-pyridium)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl 3-*N*-oxide]BF_4

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Zero- and longitudinal-field positive muon spin relaxation (μ^+SR) measurements were carried out from 300 K to 30 mK to study a ground state of m-MPYNN$\cdot$ BF_4 which is known to be a two-dimensional *kagomé* antiferromagnet with $S=1$ by ac-susceptibility measurements. An implanted muon is expected to make a hydrogen bonding state with F^- ions in the crystal. Muon-spin depolarization by a dynamically fluctuating component of an internal field was still observed at 30 mK. This fluctuating component is suggested to be caused by an intradimer ferromagnetic interaction of $2J_0/k_B=23.3$ K between radicals. No clear long-range magnetic ordering of the dimer spins was observed down to 30 mK, suggesting that the ground state of m-MPYNN$\cdot$ BF_4 was nonmagnetic. [S0163-1829(98)05625-2]

Ground states of a two-dimensional (2D) *kagomé* magnet, in which magnetic moments on *kagomé* lattices are coupled through an antiferromagnetic interaction, are of interest from the viewpoint of a frustrated system. Theoretical calculations showed that a 2D *kagomé* antiferromagnet (AFM) had the largest frustration, in the sense that an Ising system had the largest zero-temperature entropy.[1] A Heisenberg *kagomé* AFM with a large quantum spin number can take a multiple 120° spin configuration. This configuration appears not only in a coplanar state but also in an *Origami* state.[2,3] Some *kagomé* AFM with $S=\frac{3}{2}$ and $\frac{5}{2}$ have been studied,[4–8] and revealed that a long range magnetic transition with static magnetic moments occurred at a far lower temperature than exchange interaction temperature. In particular, muon spin relaxation (μSR) showed the maintenance of strong spin fluctuations even at a ground state, suggesting the possibility of quantum effects.[5]

Quantum-spin states of the frustrated 2D AFM have been studied in connection with a 1D quantum AFM. A resonating valence bond state was proposed for a triangular AFM with $S=\frac{1}{2}$ from an analogy with the 1D Heisenberg magnet.[9] One can also expect a 2D spin-gap state with a nonmagnetic ground state from the analogy with the 1D quantum AFM-like Spin-Peierls system.[10] 2D solid ^{3}He formed on a graphite is an actual example of the $S=\frac{1}{2}$ Heisenberg AFM.[11,12] Although magnetic short-range ordering was observed, a

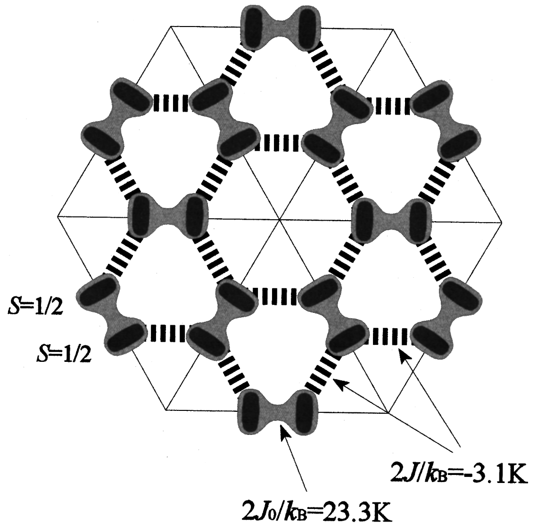

FIG. 1. Model of a crystal structure of m-MPYNN molecule and *kagomé* structure of m-MPYNN$\cdot$ BF$_4$. Two m-MPYNN molecules form a dimer state with $S=1$ by a ferromagnetic intermolecular interaction $2J_0$. The dimer couples with the neighboring dimer by an antiferromagnetic interaction $2J$.

spin-gap state, or a gapless state of the same ground state, has not yet been clarified.

To study this matter, it is important to clarify whether or not magnetic transitions exist, and to confirm a nonmagnetic ground state. In this paper, we report results of zero-field (ZF) and longitudinal-field (LF) μSR on a single crystal of the 2D $S=1$ *kagomé* AFM m-MPYNN$\cdot$ BF$_4$, which has been proposed to show a spin-gap state by an ac-susceptibility measurement.[13] We carried out μSR down to 30 mK, and observed no clear static ordering of magnetic moments.

The organic AFM m-MPYNN$\cdot$ BF$_4$ [2-(3-N-methylpyridium)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl 3-N-oxide], comprises magnetic layers of an α-nitronyl nitroxide cation allyl radical (m-MPYNN) with $S=\frac{1}{2}$.[14] Figure 1 shows a model of a crystal structure of m-MPYNN$\cdot$BF$_4$ constructed by the m-MPYNN unit molecules. The radical spin has an isotropic g value of 2.006 like other allyl radical spins. Two m-MPYNN molecules make a dimer state by an intradimer ferromagnetic interaction $2J_0$. The dimers form a *kagomé* lattice through an interdimer AF interaction $2J$. Both $2J_0$ and $2J$ were obtained by the susceptibility measurement to be 23.3 and -3.1 K, respectively.[15] The *kagomé* lattices form a 2D layer structure. One-third of BF$_4$ molecules are located at interstitial spaces of the *kagomé* lattice, and two-thirds of the BF$_4$ molecules sit in between layers. Because of the strong ferromagnetic intradimer interaction, m-MPYNN$\cdot$ BF$_4$ can be regarded as the 2D *kagomé* AFM with $S=1$ below the temperature of $2J_0/k_B$.[15]

A heat-capacity measurement on m-MPYNN$\cdot$ BF$_4$ suggested a short-range ordering of the dimer spins below 1.4 K. This temperature is half of the exchange interaction temperature of $2|J|k_B=3.1$ K.[13] The susceptibility showed a peak at 240 mK, and almost zero at 30 mK along each crystal axis.[13] This susceptibility behavior is completely different from the spin-glass behavior,[16] but quite similar to that observed in the 1D Heisenberg AFM, which shows a spin-gap state. Therefore, the $S=1$ m-MPYNN$\cdot$ BF$_4$ is suggested to show a 2D spin-gap state with a nonmagnetic ground state.[13]

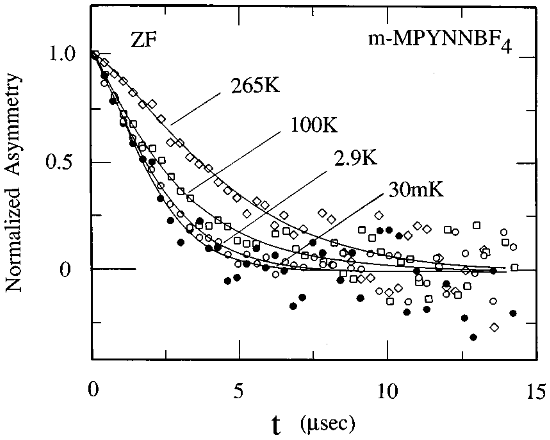

FIG. 2. ZF-μ^+SR time spectrum of a single crystal of m-MPYNN$\cdot$ BF$_4$ obtained at 265 K, 100 K, 2.9 K, and 30 mK. Solid lines are best fit results by using a function of $A_0e^{-(\lambda t)^\beta}$. A_0 at each temperature is normalized to be 1.

Positive muon spin relaxation (μ^+SR) is a good microscopic probe to sense such a magnetic state of the system. A muon spin is completely polarized along a beam direction even in the ZF condition, and depolarized after the stop at a potential-minimum position in the crystal of m-MPYNN$\cdot$ BF$_4$ interacting with a local field at a muon site.[17] A long- or short-range ordering of the dimer spins can be recognized as a change of the depolarization behavior of the muon spin, because a static or dynamically fluctuating component of the internal field which is accompanied by the magnetic transition affects strongly the muon-spin polarization.[17,18]

The preparation procedures of m-MPYNN$\cdot$ BF$_4$ have been described elsewhere.[14] Because a typical size of a piece of the crystal was about $2\times2\times2$ mm^3, we prepared more than 30 pieces for the μ^+SR measurement. The samples were mounted on a high-purity (5N) Ag sample holder like a mosaic, and fixed by an Apiezon-N grease. The alignment of the crystal axes was not considered. The sample area was about 30 mm in diameter, which was comparable to a muon beam spot size at a sample position.

ZF- and LF-μ^+SR were carried out at Meson Science Laboratory in KEK (KEK-MSL) by using a pulsed surface μ^+ beam with an energy of 4 MeV. A top-loading-type dilution refrigerator was used for low temperature measurements down to 30 mK. A conventional gas-flow-type cryostat was used for the temperature region from 2 to 300 K. Forward and backward counters are positioned along the beam line. An asymmetry parameter of the muon spin at time t, $A(t)$, is defined as $[F(t)-B(t)]/[F(t)+B(t)]$, where $F(t)$ and $B(t)$ are muon events counted by the forward and backward counters, respectively.

Figure 2 shows ZF-μ^+SR time spectra obtained at 265 K, 100 K, 2.9 K, and 30 mK. The asymmetry at each temperature is normalized to 1 at $t=0$, to compare the difference of the depolarization behavior. The depolarization behavior cannot be described by either a simple Gaussian function or a Lorentzian function. For convenience's sake, the obtained

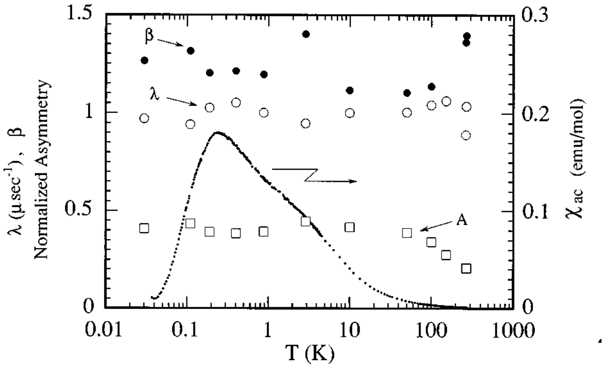

FIG. 3. Temperature dependence of A_0, λ, and β obtained from the best fit of the ZF-μ^+SR time spectra using a power function $A_0 e^{-(\lambda t)^{\beta}}$. A_0 is normalized to be 1 at 50 K. The susceptibility was obtained by Wada *et al.*

ZF-μ^+SR spectra were analyzed by a power function $A_0 e^{-(\lambda t)^{\beta}}$, where A_0 is the initial asymmetry at $t = 0$ and λ is the depolarization rate. The solid lines in Fig. 2 are the best-fit results obtained by using this power function.

Figure 3 shows the temperature dependence of A_0, λ, and β obtained from the best-fit analysis. A_0 is normalized to be 1 at 50 K. The temperature dependence of the susceptibility which was obtained by Wada *et al.*[13] is also shown in the same figure. All parameters show a temperature independence up to about 100 K, showing that static and dynamical properties of the local field at the muon site are temperature independent. This fact is different from other types of *kagomé* magnets,[4–7] in which a strong enhancement of the depolarization rate caused by a critical slowing down behavior of magnetic moments is observed around a magnetic transition temperature. A slight decrease of λ above 150 K is due to the motional narrowing effect, indicating that the muon starts to diffuse through the crystal.

To investigate an origin of the ZF depolarization of the muon spin, the LF was applied along the muon-spin direction at 30 and 700 mK. The system is predicted to be nonmagnetic at 30 mK, but magnetic at 700 mK.[13] Figure 4 shows the LF dependence of the μ^+SR time spectrum obtained at 30 mK. The asymmetry is almost recovered by the LF of 100 G, showing the decoupling behavior of a distributed static internal field. The decoupling behavior can be described by the modulated Kubo-Toyabe function $G_Z(t,\Delta H,\lambda_{\mathrm{LF}},H_{LF})$,[17] A dynamically fluctuating component of the internal field at the muon site is also taken into account as a parameter of λ_{LF}. ΔH is a half-width of the distribution of the static internal field at the muon site. H_{LF} is the LF applied along the muon-spin direction. Solid lines in Fig. 4 are the best-fit results. The obtained ΔH and λ_{LF} are summarized in Table I. Errors in Table I are statistical errors of the fitting. The field distributions at 30 and 700 mK are obtained to be about 10 G on average, and show almost no difference between two temperatures within the experimental error of ±2 G.

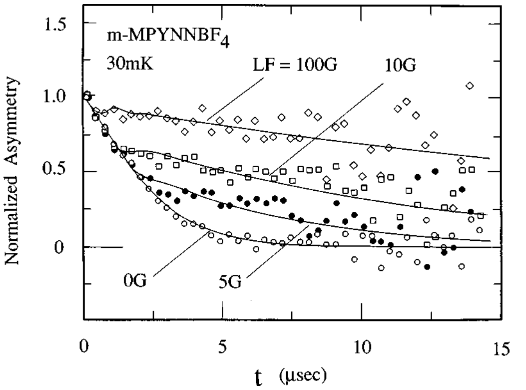

FIG. 4. Longitudinal-field dependence of the μ^+SR time spectrum. A_0 at each temperature is normalized to be 1. The asymmetry is almost decoupled by the field of about 100 G, showing the decoupling behavior of the distributed static internal field made by ^{19}F-nuclear dipoles.

TABLE I. Static-local field distribution at the muon site and dynamical depolarization rate obtained at 30 and 700 mK.

	30 mK		700 mK	
H_{LF} (G)	ΔH (G)	λ_{LF} (μs^{-1})	ΔH (G)	λ_{LF} (μs^{-1})
5	8.1±0.05	0.60±0.04	7.7±0.1	0.59±0.01
10	9.0±0.02	0.40±0.06		
20	8.8±0.6	0.43±0.05		
30	11.4±0.04	0.40±0.02	10.1±0.1	0.50±0.1
60	10.4±0.1	0.93±0.02		
100	11.9±3.6	0.42±0.19	10.0±0.3	0.64±0.03

It is known that the muon implanted into a crystal which contains F$^-$ ions forms a strong FμF state through hydrogen bonding.[19] In this case, the distance between the F$^-$ ion and the muon is similar to a nominal F$^-$ ionic radius of 1.16 Å.[19] Assuming that the distance between the stopped muon and the ^{19}F nucleus in *m*-MPYNN · BF$_4$ is the nominal F$^-$ ionic radius, the dipole field of the ^{19}F nucleus at the muon site is estimated to be about 8.5 G. This value is comparable to the obtained $\Delta H = 10 \pm 2$ G. Although the reason for the missing muon-spin precession, which has been observed in other fluorides,[19] is still unclear, it can be concluded that the implanted muon is expected to stop near the F$^-$ ion, forming hydrogen bonding, and that the static internal field at the muon site originates from the ^{19}F nuclear dipole field.

If an additional field due to a long-range magnetic ordering of the dimer spins appears, the internal field at the muon site is expected to be modified by the additional field. The distance between the center of the nearest dimer spin and the ^{19}F nucleus near to which the muon stops is estimated to be about 4.3 Å. Assuming this distance, the additional dipolar field by the nearest dimer spin is expected to be about 230 G/1μ_B. This value is much larger than the observed internal field at the muon site, so that the nuclear dipole field at the muon site is overcome, and the change of the depolarization behavior of the muon spin is expected.

However, the temperature independence of the internal field distribution at the muon site indicates that such a large additional internal field does not appear. The difference of the internal field distribution between 700 and 30 mK is less than 2 G, even though the experimental errors are taken into account. If we try to explain this small difference of the internal field distribution, assuming the existence of a long-range ordered state of the dimer spins, we have to expect the magnitude of the moment of the dimer spin to be less than 0.01 μ_B at 700 mK. Such a small magnetic moment cannot explain the susceptibility behavior in this temperature region. In addition, the critical slowing down behavior of the dimer spins is missing. These facts mean that a clear long-range magnetically ordered state of the dimer spins with $S=1$, like a spin-glass state which was observed in another *kagomé* AFM,[4–7] does not appear in m-MPYNN$\cdot$ BF$_4$ down to 30 mK. Therefore, taking into account the previous results of the susceptibility measurement,[13] it is concluded that the ground state of m-MPYNN$\cdot$ BF$_4$ is nonmagnetic.

Although the static and dynamical properties of the dimer spin seem not to change at around 240 mK from the microscopic viewpoint of μSR, the susceptibility measurement shows the large change of the net spin system of m-MPYNN$\cdot$ BF$_4$. A possible explanation for this difference is due to the fact that the dimer spins make a singlet state through the AF interdimer interaction of $2J/k_B$ below 240 mK. This feature looks to support the spin-gap state which was suggested by Wada *et al.*[13] A detailed ZF-μSR measurement with high statistics is carried out to clarify the change of the dimer spin state at around 240 mK. From the present μSR study, a sign of the short-range ordering of the dimer spins, which has been predicted by the heat-capacity measurement, was not clarified.[13]

A nonzero λ_{LF} on the order of 0.5 $\mu\mathrm{s}^{-1}$ is still maintained even at 30 mK, as shown in Table I. The dynamical quantum fluctuation of the dimer spin caused by the intradimer interaction of $2J_0/k_B=23.3$ K can be an origin of this depolarization behavior. Below this temperature, the quantum exchange frequency ν between two radicals in the dimer is estimated to be about 1.5×10^{12} s^{-1} from the relationship of $\nu=2J_0S/\hbar$. In the motional narrowing limit, the depolarization behavior of the muon spin is described as $\lambda_{\mathrm{LF}}=2(\delta H\gamma_\mu)^2/\nu$, where δH is an alternative field amplitude and γ_μ is the gyromagnetic ratio of the muon spin ($2\pi\times13.55$ MHz/kG). If δH is assumed to be about 7 kG, the value of ν of about 0.5 $\mu\mathrm{s}^{-1}$ could be explained.

From a molecular orbital calculation, the shortest distance between the radicals on two singly occupied molecular orbitals (SOMO) and the muon is estimated to be about 2 Å, because the two SOMO's are spread in a wide area on the dimer. If the magnetic moment of the radical spin is assumed to be $1\mu_B$, several kG of the dipolar field can be achieved at the muon site. Based upon this model, the depolarization rate should show a temperature dependence above $2J_0/k_B=23.3$ K, because ν is given as $\nu=k_BT/\hbar$. Detailed ZF-μSR studies on m-MPYNN$\cdot$ BF$_4$ at a higher-temperature region are also in progress to compare qualitatively with this model.

The quantum ground state of the $S=\frac{1}{2}$ Heisenberg *kagomé* AFM has been calculated as a perturbation of a trimer state.[20] Although the trimer state has a spin gap, there is no conclusive answer to the spin-gap state of the *kagomé* AFM. Quantum tunneling between multiple 120° structures gives the spin-gap state.[21] These calculations, however, give no exact solution for the spin-gap state of the $S=1$ Heisenberg *kagomé* AF magnets.

In conclusion, the ZF- and LF-μ^+SR measurements were studied on a single crystal of m-MPYNN$\cdot$ BF$_4$ from 300 K to 30 mK to investigate the quantum magnetism. The temperature-independent depolarization behavior which is due to the distributed static internal field induced by the ^{19}F-nuclear dipoles at the muon site was observed down to 30 mK. The width of the field distribution was 10 ± 2 G. No clear long-range magnetic ordering of the dimer spins was observed. Taking into account the results of the previous susceptibility measurement,[13] the ground state of m-MPYNN$\cdot$ BF$_4$ is concluded to be nonmagnetic. The dynamically fluctuating component of the internal field at the muon site was still observed at 30 mK. This dynamical depolarization behavior can be explained by the exchange fluctuation of the dimer spin with $S=1$, which is caused by an intradimer ferromagnetic exchange interaction of $2J_0/k_B$.

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