PHYSICAL REVIEW B **70**, 220404(R) (2004)

Muon spin relaxation study of the magnetic transition in a two-dimensional distorted triangular lattice β'-$(CH_3)_4P[Pd(dmit)_2]_2$

Seiko Ohira,[1,*] Masafumi Tamura,[2] Reizo Kato,[2] Isao Watanabe,[1] and Masahiko Iwasaki[1]
[1]*Advanced Meson Science Laboratory, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan*
[2]*Condensed Molecular Materials Laboratory, RIKEN, JST-CREST, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan*

(Received 2 July 2004; published 16 December 2004)

The spin dynamics in a molecular spin system on a two-dimensional (2D) distorted triangular lattice, β'-$(CH_3)_4P[Pd(dmit)_2]_2$ (dmit=1,3-dithiol-2-thione-4,5-dithiolate, C_3S_5), has been investigated by virtue of muon spin relaxation (μSR). The muon spin relaxation rate increased with decreasing temperature within a narrow temperature range (<0.8 K) near the antiferromagnetic (AFM) transition temperature, T_N=39.3 K. Muon spin precession signals appeared abruptly at this temperature. The AFM contribution to the μSR signal continuously increased just below T_N as temperature decreased. These peculiar features are discussed in terms of the crossovers specific to this frustrated system.

DOI: 10.1103/PhysRevB.70.220404 PACS number(s): 75.50.Ee, 75.40.Gb, 76.75.+i

The physical properties of the frustrated antiferromagnetic on a two-dimensional (2D) triangular lattice have been a subject of active research. In the case of the spin-1/2 Heisenberg system, in particular, whether quantum spin fluctuation destroys the long-range magnetic ordering to form the resonating valence bond (RVB) state[1] has been under debate.[2] Furthermore, the effects of the spin frustration in 2D organic molecular conductors with an approximately triangular lattice structure have been pointed out from a theoretical point of view.[3–8] On the other hand, experimental information on such frustrated 2D antiferromagnetic (AFM) systems, particularly as regards the finite temperature behavior, is still limited, since the existing substances are quite few.[9–11]

A series of organic compounds β'-$X[Pd(dmit)_2]_2$, where X is the counter cation, such as Me_4P, Me_4Sb, Et_2Me_2P, and Et_2Me_2Sb ($Me=CH_3, Et=C_2H_5$), are formed of 2D layers of the $[Pd(dmit)_2]$ molecules, which are separated from each other by the layers of the cations X^+.[12–15] All of these salts are Mott insulators under ambient pressure. The $[Pd(dmit)_2]$ molecules are strongly dimerized to form spin-1/2 units $[Pd(dmit)_2]_2^-$. The dimers form an approximately triangular lattice arrangement with AFM interactions between the dimers. The salts show some deviation from the regular triangular lattice due to the spatially anisotropic molecular packing. The paramagnetic susceptibilities χ_p of these salts exhibit a temperature dependence characteristic of the 2D spin-1/2 Heisenberg triangular-lattice antiferromagnet.[16] These salts are classified into three types (A, B, and C) by their physical properties, depending systematically on the cations:[16,17] (A) the Me_4P and Me_4As salts, with $T_N \sim 35$ K, (B) the Et_2Me_2P and Me_4Sb salts, with $T_N \sim 18$ K, and (C) the Et_2Me_2Sb salt, which has been reported to show no long-range ordering down to 4.3 K.

It has been pointed out that the deviation from a regular triangular lattice within the layers is the most significant factor for the appearance of the long-range ordering,[15–18] unlike other quasi-2D systems, where the transition temperature may be related to the interlayer couplings. In other words, the spatial anisotropy seems to enhance T_N, by releasing the frustration. If this is the case, type A is the most anisotropic with the highest T_N. We have carried out a muon spin relaxation (μSR) study on the spin dynamics, such as the dimensional crossover from 2D to three-dimensional (3D) accompanying the long-range ordering in this peculiar system. Muon is a microscopic probe that is highly sensitive to magnetic fields. Therefore, the μSR method is useful to detect weak internal magnetic fields and the spin dynamics of organic materials, even in the absence of external fields.[19,20]

In this Rapid Communication, we report the μSR result of a type-A compound, β'-$(CH_3)_4P[Pd(dmit)_2]_2$, above and near T_N. The muon spin relaxation was enhanced within 0.8 K just above T_N, indicating a very sharp AFM transition. Muon spin precession signals appeared at and below T_N, which evidenced the occurrence of the AFM phase. Their amplitudes gradually increased showing coherent spin precessions.

250 mg of polycrystalline sample of β'-$(CH_3)_4P[Pd(dmit)_2]_2$ was prepared by the air oxidation of a solution containing $(Me_4P)_2[Pd(dmit)_2]$ and acetic acid in acetone at 10 °C. The sample was wrapped with silver foil to be a plate shape of $20\times20\times1$ mm^3, and fixed onto the sample holder. A ^{4}He minicryostat was used for a measurement with a wide temperature range. Another ^{4}He cryostat, designed by Oxford Instruments, was used for measurements near T_N, in order to achieve better stability and accuracy of temperature. In this cryostat, the sample packed in the silver foil is cooled by exchange gas, and good homogeneity of temperature is guaranteed.

The experiment was carried out at Port-2 of the RIKEN-RAL Muon Facility in the United Kingdom. A pulsed surface muon (μ^+) beam with a momentum of 27 MeV/c was used. The muon spin is completely polarized along the direction of the momentum. Decay positrons, which are preferentially emitted from μ^+ along the muon spin direction, were detected by counters placed forward and backward of the sample position for the initial muon spin polarization. The asymmetry is described 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 numbers of the decay positrons counted by the forward and backward counters, respectively, and α is a geometrical factor. The environmen-

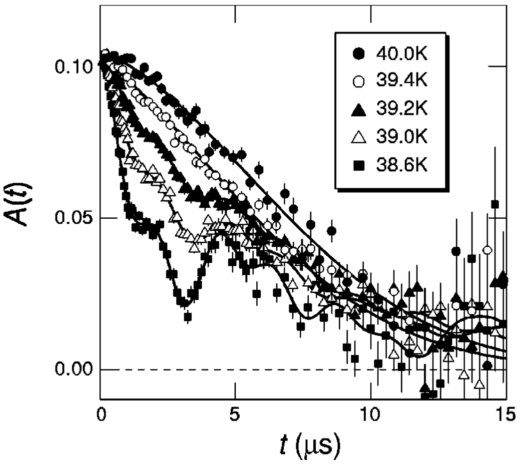

FIG. 1. ZF-μSR time spectra of β'-$(CH_3)_4P[Pd(dmit)_2]_2$ near T_N, which is estimated to be around 39.3 K. The solid lines for temperatures above and below T_N are the best fits to Eqs. (2) and (1), respectively.

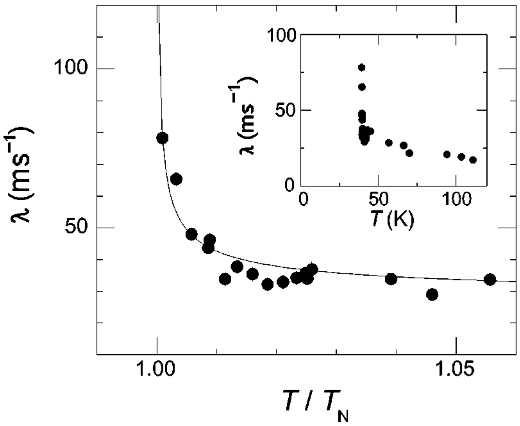

FIG. 2. Muon spin relaxation rate λ as a function of T/T_N. The solid line is the fitting result described in the text. The inset shows the temperature dependence of λ for a wide temperature range. The effects of muon hopping are not negligible above ~100 K.

tal field was compensated within 30 mG during the measurement.

Figure 1 shows the zero-field (ZF) μSR time spectra of β'-$(CH_3)_4P[Pd(dmit)_2]_2$. Clear muon spin precession signals were observed below 39.3 K, indicating the appearance of AFM ordering. T_N obtained for our μSR study is slightly higher than the results of the susceptibility and electron paramagnetic resonance (EPR) measurements.[16,17] The difference in T_N's observed in these measurements should be caused by their different time scales. The time spectra for the AFM phase were fitted with the following function:

$$A(t) = \sum_{i=1}^{n} A_i e^{-\lambda_i t} \cos(2\pi f_i t) + A_{ex} e^{-\lambda_{ex} t}. \quad (1)$$

For this system, the spectra contain three distinct oscillation components; thus $n=3$. Above 39.3 K, the time spectra were fitted with

$$A(t) = A e^{-(\sigma t)^2} e^{-\lambda t}. \quad (2)$$

In Eq. (2), the Gaussian part describes the muon spin relaxation due to the nuclear dipole field, which is random and static in the pulsed μSR time window, and σ corresponds to the distribution width of the internal field at the muon site. The exponential part describes the muon spin relaxation due to dynamically fluctuating internal fields. The background had already been subtracted. In the ZF-μSR time spectra, a small enhancement of the muon spin depolarization due to a critical slow-down effect was observed in a very narrow temperature range (39.3–40 K), below which the oscillation signals appeared. The time spectra did not show any remarkable changes above 40 K. The muon spin relaxation rate λ as a function of T/T_N is shown in Fig. 2. λ was fitted by $\lambda(T) = C(T-T_N)^{-\nu}+\lambda_0$, where C and λ_0 are constants. Under the assumption that $\lambda \propto \xi$ (ξ is the magnetic correlation length), $T_N=39.30(6)$ K was obtained for $\nu=0.5$ (mean-field value for Heisenberg antiferromagnets).[21] The obtained T_N is consistent with the temperature at which the oscillation signals appear. This value does not change remarkably for ν varying from 0.2 to 1. The fitting result is shown with a solid curve in Fig. 2. The AFM transition of this system observed by the μSR method is quite sharp. The temperature dependence of λ in this narrow temperature range is also shown in Fig. 3(a) with the fitting result. λ increases very rapidly from 40 to 39.3 K, while it maintains small values even just above T_N.

In this material with a distorted triangular lattice, the AFM interaction along one direction on the triangle, J, is weaker than those along the other two directions, $J+\Delta J$. Two kinds of crossover are expected in this situation.[18] Above ~100 K, the spin frustration operates on the approximately triangular lattice with the AFM interactions. The difference between the stronger and weaker interactions, ΔJ, becomes significant as temperature decreases below $\Delta J/k_B$. This is indicated to a rapidly decreasing χ_p behavior below its broad maximum at around 100 K. The frustration is thus released; the system crosses over from the frustrated paramagnet at high temperatures to a 2D antiferromagnetically correlating state. Here, we name it a "frustration-release crossover." Further cooling gives rise to the second crossover. This is a dimensional crossover from 2D to 3D, which is due to weak interactions between the layers. It is pointed out that ξ grows exponentially, as in the case of the square lattice, which emerges from the intralayer anisotropy ΔJ, such that it yields a 3D ordering in the presence of nonzero, but small, interlayer couplings.[18] The rapid enhancement of λ in a narrow temperature range just above T_N seems to be detecting a suppression of the spin fluctuation by this crossover. In fact, the ZF-μSR result for a more spin-frustrated $[Pd(dmit)_2]$ salt, β'-$Et_2Me_2P[Pd(dmit)_2]_2$, shows a slower increase in λ above T_N.[22] A 2D Heisenberg antiferromagnet with a square lattice, La_2CuO_4, which is the parent compound of a famous high-T_c superconductor, also shows no enhancement of the muon spin relaxation above T_N, because the temperature range of the crossover from 2D to 3D is too narrow to be observed.[23]

Three distinct muon spin precessions were observed below T_N, which corresponds to the three muon sites, i.e., pre-

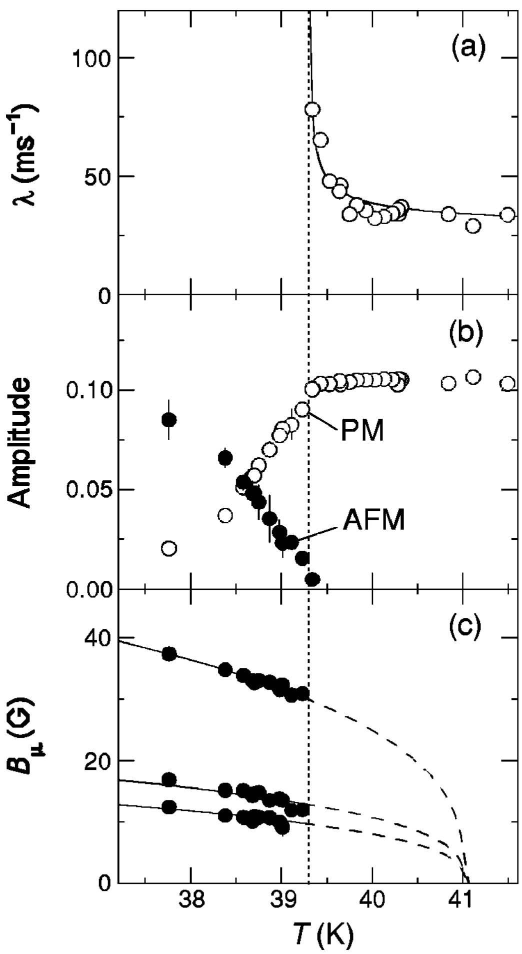

FIG. 3. Temperature dependences of (a) the relaxation rate λ, (b) the amplitudes for the paramagnetic ("PM" in the figure) and AFM fractions, and (c) the internal field at the muon site B_μ. The solid and dashed lines in (c) are the best fits to the equation described in the text. The data from 5 to 39.3 K are used. The doted lines indicate T_N obtained from λ.

sumably the three chemically distinguishable sulfur atoms of dmit. The observed frequency f can be converted to the internal magnetic field at the muon site, B_μ, with $f=\gamma_\mu B_\mu$, where γ_μ is the gyromagnetic ratio of the muon (=13.554 kHz/G). The temperature dependence of B_μ corresponding to the three observed frequencies is shown in Fig. 3(c). The spectra at 39.2 and 39.3 K cannot be well resolved because of the ambiguity of the signals. Only two components were obtained. Precession suddenly appears below 39.3 K with finite frequencies and very small amplitudes. The data were fitted with the phenomenological form, $B_\mu(T)=B_\mu(0)[1-(T/T'_N)^\alpha]^\beta$, where α and β are critical exponents. T'_N indicates the T_N value estimated from $B_\mu(T)$, which may differ from that from $\lambda(T)$. The solid and dashed lines in Fig. 3(c) are fits for the data from 5 to 39.3 K. $B_\mu(0)$, α, and β were obtained for the three components, as listed in Table I, while T'_N was assumed to be common.

β for each component shows a good agreement with the theoretical value ($\beta\sim0.38$ for a 3D Heisenberg system). It is difficult to determine T'_N precisely, since the B_μ values do not reach zero smoothly in our data. However, it is evident that the estimated T'_N value (=41.0±0.2 K) exceeds the value expected from the time spectra and the temperature dependence of λ. This discrepancy can be related to the presence of the dimensional crossover within a narrow temperature range between 39.3 and 41 K. The analysis of $B_\mu(T)$, which reflects the 3D characteristics, indicates that the magnetization appears below T'_N. However, the coherent precession signals, which imply the existence of a unique and static internal field, are not observed above T_N. It is expected that the growth of the unique internal field is overcome by dynamical fluctuation due to the undergrown 2D short-range correlation.

TABLE I. Fitting results of the α, β and $B_\mu(0)$ values for the three oscillation components.

Component	α	β	$B_\mu(0)$
I	1.37±0.18	0.36±0.02	26.9±0.5
II	1.56±0.12	0.35±0.02	33.1±0.3
III	1.56±0.07	0.35±0.01	78.8±0.3

The fraction of the muon which precesses seeing the unique internal field increases monotonically with decreasing temperature. Assuming that all of the muons in the AFM phase precess, this fact indicates that the AFM volume fraction begins to be observed at 39.3 K and increases in a narrow temperature region. In the polycrystalline sample case, 2/3 of the component for muons in a uniform magnetic field contribute to the oscillation, while the rest contributes to the longitudinal relaxation. Therefore, we can estimate the AFM fraction from the amplitudes of the oscillation signals. The amplitude for the paramagnetic fraction is given by subtracting that for the AFM fraction from the total asymmetry. The temperature dependence of the amplitudes for these fractions is shown in Fig. 3(b). The AFM amplitude increases as temperature decreases. The inhomogeneity of temperature cannot be responsible for this behavior because of the reason mentioned below. Since magnetization usually appears at T_N and sharply increases, the temperature inhomogeneity should cause a distribution of the internal field. The distributed field is evidenced by fast damping of the amplitude for the muon spin precession with a Gaussian shape. However, the observed damping is quite slow and exponential. We surmise the following scenario. When the interlayer magnetic interaction develops sufficiently, some small AFM fractions appear at first. This can suppress the fluctuation in the paramagnetic fractions around themselves so as to increase the volume of the AFM ones.

A ^{13}C-NMR study (94.743 MHz) reveals that the longitudinal relaxation rate T_1^{-1} starts to increase below ~70 K.[24] The increase in T_1^{-1} is expected to reflect the 2D short-range ordering due to the frustration-release crossover. The spin fluctuation in this frequency range is too fast to detect by the muon. We observed a gently increasing λ with decreasing temperature, as shown in the inset of Fig. 2. Though the slow increase may be due to some motional contribution, the possibility that the short-range correlation was detected, as observed in the ^{13}C-NMR study, cannot be completely ruled out. The observed slope is quite different from that just above T_N. In our μSR measurement, the effect of the dimensional crossover was emphasized by taking advantage of its own time window.

In conclusion, we studied the spin dynamics in a frustrated 2D spin system on a distorted triangular lattice, β'-$(CH_3)_4P[Pd(dmit)_2]_2$, by the μSR method. A very sharp AFM transition was observed within a narrow temperature range (<0.8 K), suggesting the characteristics of growth of the magnetic correlation, as in 2D square-lattice systems without any frustration. T_N was estimated to be 39.3 K from the temperature dependence of λ, which reflects the spin dynamics associated with the critical slow-down effect. On the other hand, muon spin precession signals suddenly appeared at 39.3 K. The obtained T'_N value ($\sim$41 K) is definitely higher than T_N obtained from $\lambda(T)$. This is evidence for the existence of a dimensional crossover from 2D to 3D. Moreover, we found that some tiny AFM fractions appeared near T_N, and the volume gradually increased just below T_N. We surmise that the small AFM fractions appear to suppress the spin fluctuation in the paramagnetic fractions, and increase the volume of the AFM ones.

This work is supported partly by a Grant-in-Aid for Scientific Research (No. 15550135) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

*Electronic address: ohira@riken.jp

[1] P. W. Anderson, Mater. Res. Bull. **8**, 153 (1973).
[2] L. Capriotti, A. E. Trumper, and S. Sorella, Phys. Rev. Lett. **82**, 3899 (1999).
[3] H. Kino and H. Fukuyama, J. Phys. Soc. Jpn. **65**, 2158 (1996).
[4] R. H. McKenzie, Comments Condens. Matter Phys. **18**, 309 (1998).
[5] H. Kino and H. Kontani, J. Phys. Soc. Jpn. **67**, 3691 (1998).
[6] J. Merino, R. H. McKenzie, J. B. Marston, and C. H. Chung, J. Phys.: Condens. Matter **11**, 2965 (1999).
[7] H. Morita, S. Watanabe, and M. Imada, J. Phys. Soc. Jpn. **71**, 2109 (2002).
[8] T. Koretsune and M. Ogata, Phys. Rev. Lett. **89**, 116401 (2002).
[9] S. T. Bramwell *et al.*, J. Phys.: Condens. Matter **8**, L123 (1996).
[10] Y. Shimizu, K. Miyagawa, K. Kanoda, M. Maesato, and G. Saito, Phys. Rev. Lett. **91**, 107001 (2003).
[11] R. Coldea, D. A. Tennant, A. M. Tsvelik, and Z. Tylczynski, Phys. Rev. Lett. **86**, 1335 (2001).
[12] A. Kobayashi, H. Kim, Y. Sasaki, K. Murata, R. Kato, and H. Kobayashi, J. Chem. Soc., Faraday Trans. **86**, 361 (1990).
[13] R. Kato, Y.-L. Liu, S. Aonuma, and H. Sawa, Solid State Commun. **98**, 1021 (1996).
[14] R. Kato, Y.-L. Liu, Y. Hosokoshi, and S. Aonuma, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **296**, 217 (1997).
[15] S. Rouzière, J.-I. Yamaura, and R. Kato, Phys. Rev. B **60**, 3113 (1999).
[16] M. Tamura and R. Kato, J. Phys.: Condens. Matter **14**, L729 (2002).
[17] T. Nakamura, T. Takahashi, S. Aonuma, and R. Kato, J. Mater. Chem. **11**, 2159 (2001).
[18] M. Tamura and R. Kato, J. Phys. IV **114**, 383 (2004).
[19] R. S. Hayano, Y. J. Uemura, J. Imazato, N. Nishida, T. Yamazaki, and R. Kubo, Phys. Rev. B **20**, 850 (1979).
[20] Y. J. Uemura, T. Yamazaki, D. R. Harshman, M. Senba, and E. J. Ansaldo, Phys. Rev. B **31**, 546 (1985).
[21] A. Schenck, and F. N. Gyax in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (Elsevier, Amsterdam, 1995), Vol. 9, pp. 57–302.
[22] S. Ohira, M. Tamura, R. Kato, I. Watanabe, and M. Iwasaki, J. Phys. IV **114**, 355 (2004).
[23] J. I. Budnick *et al.*, Europhys. Lett. **5**, 651 (1988).
[24] T. Nakamura, Research Report on Metal-Assembled Complexes (Grant-in-Aid for Scientific Research on Priority Areas) Ministry of Education, Culture, Science, Sports and Technology (Japan), 2000, p. 249 (unpublished).