# $^1$H-NMR study of the 2D spin-gap system $m$-MPYNN$\cdot$BF$_4$

Yutaka Fujii [a,1], Takao Goto [b], Wataru Fujita [c], Kunio Awaga [c]

[a] *Department of Applied Physics, Faculty of Engineering, Fukui University, Fukui 910-8507, Japan*
[b] *Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501, Japan*
[c] *Graduate School of Science, Nagoya University, Nagoya 464-8502, Japan*

**Abstract**

The organic radical salt $m$-MPYNN$\cdot$BF$_4$ is characterized as a spin-1 kagomé antiferromagnet and has been suggested to have a singlet ground state with a finite spin gap. $^1$H-NMR measurements for this salt have been carried out in the temperature range down to 0.05 K and under the magnetic fields up to 70 kOe. It is found that nuclear spin-lattice relaxation rate $T_1^{-1}$ increases with decreasing temperature below about 1 K under magnetic fields below about 8 kOe. Further, a gapped magnetic state is found at higher fields. Our results are interesting from the viewpoint of the crossover between gapless and gapped regimes, which has been studied intensively for quasi 1D spin-gap systems.

*Key words:* spin gap; kagomé antiferromagnet; 2D; nuclear spin-lattice relaxation time $T_1$

## 1. Introduction

The organic cation radical salt $m$-MPYNN$\cdot$BF$_4$ is known as a candidate of the *kagomé* antiferromagnet of integer spins ($S = 1$). [1] Further, great interest has been devoted to it, since the existence of the spin gap of $\Delta/k_B \simeq 0.25$ K between the nonmagnetic ground state and magnetic excited states has been found from the susceptibility measurement. [2] In this salt, each dimer consists of a pair of radicals ($S = \frac{1}{2}$) coupled through the ferromagnetic exchange interaction $2J_1/k_B = 23$ K, and the dimers form the *kagomé* lattice with antiferromagnetic interactions $2|J_2|/k_B = 3.1$ K. Recently, the hexagon singlet model was presented for this two-dimensional (2D) spin-gap state. [3] The 2D magnetic layers are well separated from each other by anions and crystal solvents (acetone).

It has been an attractive subject how a singlet-ground-state system behaves in high magnetic fields where the spin gap $\Delta$ collapses. Recently, from measurements of nuclear spin-lattice relaxation rates $T_1^{-1}$ for one-dimensional (1D) spin-gap systems, [4] it has been found that there exists a Tomonaga-Luttinger liquid (TLL) phase in the gapless regime $H > \Delta/g\,\mu_B$.

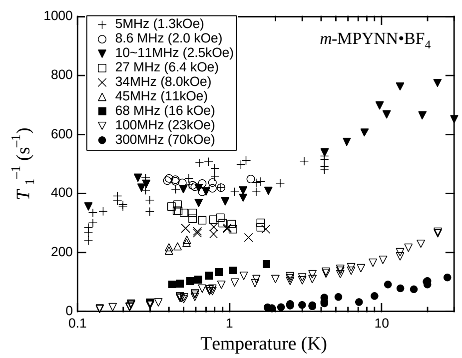


Fig. 1. Temperature dependence of $T_1^{-1}$ of $^1$H in $m$-MPYNN$\cdot$BF$_4$ at several values of the applied field.

We are interested in studying on dynamical properties from a microscopic viewpoint for a 2D spin-gap system $m$-MPYNN$\cdot$BF$_4$ in the magnetic field. We have measured $T_1^{-1}$ of $^1$H with a collection of tiny crystals ($< 1$ mm$^3$) by use of a pulsed NMR (spin-echo) method in the temperature range between 0.05 K and 300 K under the applied fields up to 70 kOe.

[1] Corresponding author. E-mail: yfujii@quantum.apphy.fukui-u.ac.jp

## 2. Experimental results and discussion

The [1]H-NMR spectrum consists of a broad line, which is shaped by the superposition of resonances from over 20 nonequivalent proton sites and is also related to orientational distribution of microcrystals. The spectrum is broadened as the temperature decreases and as the applied field is increased, according to the enhancement of the induced moment. [5]

Figure 1 shows the temperature dependences of the relaxation rate $T_1^{-1}$ of $^1$H at each constant frequency ranged from 5 MHz to 300 MHz. As shown, the temperature dependency of $T_1^{-1}$ below 1 K changes around 8 kOe: At lower fields, $T_1^{-1}$ increases with decreasing temperature. Such a behavior of $T_1^{-1}$ resembles those in the TLL states for the above-mentioned 1D systems. Then, the obtained results below 8 kOe are possibly related to the gapless state. At higher magnetic fields, in contrast, $T_1^{-1}$ shows a marked decrease with decreasing temperature, which is well represented by the activation-type phenomenological equation with a gap energy $\delta$, $T_1^{-1} \propto \exp(-\delta/k_\mathrm{B}T)$. Note that the ground state is magnetic in this field region. It has been already reported that, above about 2 K, such an activation-type behavior of $T_1^{-1}$ is related to the Zeeman energy between the triplet states of a ferromagnetic dimer. [6] In the low temperature, the effect of the inter-dimer interaction $J_2$ becomes important. From a qualitative fit of this equation to the experimental data for each value of $H$, field dependence of the effective gap $\delta$ is obtained as shown in Fig. 2.

Here, let us discuss our experimental results in analogy of 1D systems. [4] First, one may expect the lower critical field to be $H_{\mathrm{c1}} = \Delta/g\,\mu_\mathrm{B} = 1.9$ kOe, where the energy gap at zero field collapses. It should be remarked that $T_1^{-1}$ at the lowest field (5 MHz) has a tendency to decrease monotonously with decreasing temperature below about 0.5 K, as shown in Fig. 1. However, the effective gap might be $\delta = \Delta - g\,\mu_\mathrm{B}\,H = 0.08$ K, which is too small to discuss within the present results.

Secondly, in the high field region, the obtained results indicate the magnetic gapped state. Then, there must be the fully-polarized gapped state above the second critical field $H_{\mathrm{c2}}$. Considering that the temperature dependence of $T_1^{-1}$ changes at 8 kOe, we should put $H_{\mathrm{c2}}$ to be 8 kOe. Note that this value is smaller than $2|J_2|/g\,\mu_\mathrm{B} = 23$ kOe. Further, $\delta$ seems more gradual dependent on $H$ than $\delta \sim g\,\mu_\mathrm{B}\,H$, as shown in Fig. 2.

Lastly, for the intermediate region. As shown in Fig. 1, we have found $T_1^{-1} \sim T^{-\alpha}$ between 2.0 kOe and 6.4 kOe below 1 K. For 1D systems in the TLL state in $H_{\mathrm{c1}} < H < H_{\mathrm{c2}}$, the exponent $\alpha$ is around 0.5 and has a characteristic field dependence which strongly depends on the the bonding configuration (chain or ladder, and so on.) [4] From our present

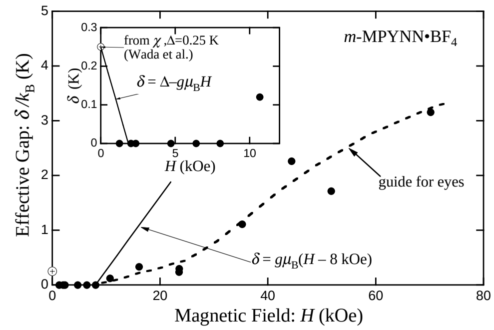


Fig. 2. The value of the effective gap $\delta$ estimated from the activation-type equation (see the text) as a function of the applied field $H$. The inset is an enlargement of a low-field region. Below 8 kOe, $\delta$ is tentatively put to be zero, which means that $\delta$ is too small to observe or the system is really gapless. The spin gap at zero field [2] is also shown. The solid lines represent $\delta \sim g\,\mu_\mathrm{B}\,H$.

results, the value of $\alpha$ is estimated to be $0.1 \sim 0.2$. Further, the value of $H_{\mathrm{c1}}$ could be around 2 kOe, though it is unclear so far. Theoretical or numerical studies in the gapless region for our system are needed for detailed discussion. It should be noted that we have no evidence for a KT-like phase transition proposed by Sachdev *et al.* [7], considering that $T_1^{-1}$ will diverge at a KT transition temperature. [8]

In summary, from the measurements of $T_1^{-1}$ of $^1$H in *m*-MPYNN·$BF_4$, it is suggested that there exists the intermediate (gapless) region below 8 kOe. The detailed data of magnetization, heat capacity etc. in the high fields, are required in order to understand precisely the effect of the applied field.

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