Spin dynamics of Mn pyrochlore lattice in YMn$_2$Zn$_{20-x}$In$_x$

M Miyazaki$^1$, R Kadono$^{1,2}$, H Hraishi$^1$, I Yamauchi$^1$, A Koda$^{1,2}$, K M Kojima$^{1,2}$, I Kawasaki$^3$, I Watanabe$^3$, Y Okamoto$^4$† and Z Hiroi$^4$

$^1$Muon Science Laboratory and Condensed Matter Research Center, Institute for Materials Structure Science, High Energy Accelerator Research Organization (KEK), Tsukuba, Ibaraki 305-0801, Japan
$^2$Department of Materials Structure Science, The Graduate University for Advanced Studies (SOKENDAI), Tsukuba, Ibaraki 305-0801, Japan
$^3$Advanced Meson Science Laboratory, RIKEN Nishina Center, Wako, Saitama 351-0198, Japan
$^4$Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan
E-mail: mmiya@post.kek.jp

Abstract. It is shown in a new class of pyrochlore compound YMn$_2$Zn$_{20-x}$In$_x$ (with $x = 2.36$) that the spin fluctuation rate ($\nu$) is proportional to temperature ($\nu \propto T$) below $T_0 \sim 10$ K where heavy-fermion (HF)-like behavior is observed. Such a linear $T$ dependence, commonly found in Y(Sc)Mn$_2$ and LiV$_2$O$_4$, is expected for intersecting quasi-1D Hubbard chains, suggesting that the quasi-1D character of the $t_{2g}$ band associated with the pyrochlore lattice plays an important role in the emergence of the HF-like state, where $T_0$ may correspond to intra-chain antiferromagnetic interaction energy between Mn spins.

1. Introduction
Geometrical frustration in the electronic degrees of freedom such as spin, charge, and orbit, which is often realized on the stages of highly symmetric crystals, has been one of the major topics in the field of condensed matter physics. In particular, the heavy fermion (HF) behavior in d-electron transition metal compounds such as Y$_{1-x}$Sc$_x$Mn$_2$ [1, 2, 3] and LiV$_2$O$_4$ [4, 5, 6] has been under the spotlight of broad interest, where such a local electronic correlation specific to highly symmetric pyrochlore structure may be of direct relevance to the formation of heavy quasiparticle (QP) state. However, despite decades of studies, the microscopic mechanism how such a local correlation is transmuted into the heavy QP mass of itinerant d-electrons in those compounds still remains controversial.

One of the bottlenecks for the investigation of the d-electron HF-like state is the limited variety of actual candidate compounds. Recent development of a ternary intermetallic compound, YMn$_2$Zn$_{20-x}$In$_x$ [7], might be a relief to this situation. It exhibits a Sommerfeld coefficient $\gamma \sim 200$ mJ/K$^2$mol [8] which is much larger than that calculated by the band theory for uncorrelated electrons, $\gamma_{\text{band}} = 34$ mJ/K$^2$mol in YMn$_2$Zn$_{20}$ [7].

† Present address: Department of Applied Physics, Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan.
The compound crystallizes in the cubic CeCr$_2$Al$_2$O$_{20}$ structure with the space group Fd$ar{3}$m (space group no. 227) shown in figure 1(a), where the Y and Mn atoms respectively occupy the 8$a$ and 16$d$ sites forming diamond and pyrochlore lattices common to the cubic Laves-phase YMn$_2$. Meanwhile, In atoms occupy the 16$c$ site forming pyrochlore lattice, and Zn

Figure 1. (a) Crystal structure of YMn$_{2+\delta}$Zn$_{20-x-\delta}$In$_x$, where Y, Mn, and Zn atoms are indicated by blue, red, and white spheres, respectively. A part of Zn at 96$g$ site is substituted by In to stabilize the CeCr$_2$Al$_2$O$_{20}$ structure. The actual compound exhibits a small amount ($\delta$) of excess Mn that occupies the 96$g$ site to substitute for Zn. The Mn-Zn tetrahedra form a network similar to the pyrochlore lattice, where the local interaction between Mn atoms is relatively weaker than that in Y$_{1-x}$Sc$_x$Mn$_2$ due to Zn atoms situated between Mn atoms. (b) Expected muon site at the center of Mn tetrahedra at 8$b$ site is shown.

atoms at the 48$f$ site are located between Mn atoms, and those atoms at the 96$g$ site are located around Y atoms, so that the pyrochlore lattice composed of the Mn atoms is almost doubly expanded in comparison with that in Y$_{1-x}$Sc$_x$Mn$_2$ without modifying the tetrahedral symmetry. Although the compound with the ideal YMn$_2$Zn$_{20}$ composition has not yet been obtained, partial substitution of Zn with In is known to be effective for stabilizing the structure.

2. Experiment
We have investigated the spin dynamics of Mn $d$-electrons by means of muon spin relaxation ($\mu$SR) under a zero/longitudinal field (ZF/LF) in a sample whose chemical composition is more precisely expressed as YMn$_{2+\delta}$Zn$_{20-x-\delta}$In$_x$ with $x = 2.36$, where the influence of excess Mn seems to be minimal [$\delta = 0.11(1)$]. The sample was a mosaic of single crystals glued with varnish on a sample holder made of high purity silver (12 mm$\phi$ disc). The experiment was carried out at RIKEN-RAL port 2 using the ARGUS spectrometer with “flypast” setup that allows low background measurements for small samples. $\mu$SR measurements were performed using two cryostats with different gas refrigerants, one with $^3$He covering a temperature range from 50 K to 300 mK and another with $^4$He from ambient temperature to 4.2 K, respectively.

$\mu$SR measurements for 300 K–4.2 K were made under LF = 10 mT to quench the depolarization due to random local fields from nuclear magnetic moments. Meanwhile, those for 50 K–300 mK were made under LF = 395 mT to discern depolarization due to excess Mn
very low temperature, where the respective yield of signals from pyrochore Mn and that from excess Mn was estimated from field dependence of LF-μSR spectra.

3. Results and analysis

Typical examples of ZF/LF-μSR spectra obtained at 4.2 K and 300 mK are shown in figure 2. The depolarization rate (λ) at 4.2 K is mostly independent of the magnitude of external field (mostly unchanged between 10 mT and 395 mT), indicating that the spectra are in the limit of motional narrowing. These spectra were analyzed by curve fits using a form,

\[ A(t) = A_0 G_{KT}(t) \exp(-\lambda t) + A_b \]  

where \( A(t) \) is the positron asymmetry, \( A_0 \) is the initial positron decay asymmetry, \( G_{KT}(t) \) is the Kubo-Toyabe relaxation function, and \( A_b \) is the time-independent background mainly coming from muons stopped in the sample holder made by silver. The signal to background ratio \( (A_0/A_b) \) was \( \sim 3.8 \) for the \(^4\)He cryostat and \( \sim 3 \) for the \(^3\)He cryostat over a time range of 0-20 µs, allowing reliable deduction of \( \lambda \) at small values (\( \sim 10^{-2} \) µs\(^{-1}\))[figure 3].

\[ \lambda \approx \frac{1}{T_1} = \frac{2\delta_\mu^2 \nu}{\nu^2 + \gamma_\mu^2 H_0^2} \frac{\chi_B T}{N_A \mu_B^2} \]  

where \( T_1 \) is spin-lattice relaxation time, \( \chi(T) \) is the magnetic susceptibility, \( N_A \) is the Avogadro number, \( \delta_\mu \) is the muon hyperfine parameter, \( \gamma_\mu = 2\pi \times 135.54 \) MHz/T is the muon gyromagnetic ratio, and \( H_0 \) is the external field. Assuming that muons located at the center of Mn tetrahedra (8b site, shown in figure 1(b)), \( \delta_\mu \) is calculated by the muon-Mn (electronic spin) dipolar tensor \( A_i^{\alpha,\beta} \) as

\[ \delta_\mu^2 = \sum_{\alpha,\beta} \left( A_i^{\alpha,\beta} \right)^2 = \sum_{\alpha,\beta} \left( \frac{\mu_3}{i} \delta_{\alpha,\beta} - \frac{3r_\alpha r_\beta}{r_i^3} \right)^2 \]  

(\( \alpha = x, y, \beta = x, y, z \)).
where \( r_i \) is the distance between muon and the \( i \)-th Mn atom, yielding \( \delta_\mu = \gamma_\mu \times 19.59 \text{ mT}/\mu_B = 16.68 \text{ µs}^{-1}/\mu_B \). The nuclear dipolar width can be estimated using the above equation by substituting \( \mu_i \) with those of the nuclear magnetic moments to yield \( \Delta = \gamma_\mu \times 0.1257 \text{ mT} = 0.107 \text{ µs}^{-1} \). The calculation of \( \delta_\mu \) includes contribution from Mn atoms situated at the nearest and next nearest neighboring tetrahedra. These values are in good agreements with those deduced from the curve fits, i.e., \( \Delta = 0.128(3) \text{ µs}^{-1} = \gamma_\mu \times 0.150(4) \text{ mT} \) at 4.2 K as a parameter of \( G_z(t) \) in eq.(1) and \( 15.9(28) \text{ µs}^{-1} = \gamma_\mu \times 18.7(33) \text{ mT}/\mu_B \) determined by longitudinal field dependence of \( \lambda \) at 0.303 K using eq.(2).

The fluctuation rate of the hyperfine field is deduced by modifying eq.(2),

\[
\nu = \frac{2\delta^2}{\lambda} \cdot \frac{\chi k_B T}{N_A \mu_B^2} + \sqrt{\left(\frac{2\delta^2}{\lambda} \cdot \frac{\chi k_B T}{N_A \mu_B^2}\right)^2 - \gamma_2^2 H_0^2},
\]

(4)

where \( \lambda \) and \( \chi \) are the quantities determined experimentally. Here, in order to avoid influence of excess Mn, we rely on \( \lambda \) obtained from data under LF with magnitude greater than 100 mT and \( \chi \) evaluated for the Mn atoms forming pyrochlore lattice, i.e., \( \lambda = 0 \text{ cm}^3/\text{mol} \) and \( \theta_W = -11 \text{ K} \) for \( \delta \to 0 \) [8]. Taking \( \delta_\mu = 16.68 \text{ µs}^{-1} \), we obtain \( \nu \) vs \( T \) as shown in figure 4.

**Figure 3.** Temperature dependences of muon spin depolarization rate (\( \lambda \)) in YMn\(_{2+\delta}\)Zn\(_{20-x-\delta}\)In\(_x\) with \( x = 2.36 \) (\( \delta = 0.11 \)), where two sets of symbols correspond to the data obtained using different cryostats (see text).

**Figure 4.** The fluctuation rate (\( \nu \)) of the hyperfine field vs \( T \) in YMn\(_{2+\delta}\)Zn\(_{20-x-\delta}\)In\(_x\) with \( x = 2.36 \) (\( \delta = 0.11 \)). Solid lines are results of curve fits using a power-law (\( \nu = cT^\alpha \)), with \( c \) and \( \alpha \) being free parameters, for the respective range of temperature. \( T_0 \) is the suggested onset temperature for the spin correlation of quasi-1D Hubbard chains. Inset: Susceptibility of YMn\(_{2+\delta}\)Zn\(_{20-x-\delta}\)In\(_x\) with \( x = 2.36 \) (\( \delta = 0.11 \), red circles) which includes contribution from excess Mn other than the intrinsic \( \chi \) for \( \delta = 0 \) (blue dashed line)[8].
4. Discussion
It is noticeable that \( \nu \) is linearly dependent on temperature (\( \nu \propto T \)) below \( T_0 \sim 10 \text{ K} \). Such a behavior is in marked resemblance with those observed in \( \text{Y}_{1-x}\text{Sc}_x\text{Mn}_2 \) [9] and \( \text{LiV}_2\text{O}_4 \) [10, 11], which is understood as a characteristic property of spin-spin correlation predicted for intersecting Hubbard chains as a theoretical model for pyrochlore lattice [12]. This implies the crucial role of \( t_{2g} \) orbitals as one-dimensional (1D) chains that are under a strong geometrical constraint of pyrochlore lattice structure, and further suggests the dimensional crossover due to coupling between these chains as a possible origin of the heavy-fermion state [13]. Then, the onset temperature \( T_0 \) might be interpreted as the energy scale for an effective intra-chain exchange interaction which would be thermally disrupted above \( T_0 \).

It is interesting to note that \( T_0 \) seems to correspond to the temperature below which the HF-like behavior sets in, as suggested from the temperature dependence of the Sommerfeld coefficient (\( \gamma \)) [8]. The relatively limited range of temperature for the HF-like behavior in \( \text{YMn}_{2-x}\text{Zn}_x\text{Mn}_2 \) may be understood as a consequence of weaker Mn-Mn interaction in comparison with that in \( \text{Y}_{1-x}\text{Sc}_x\text{Mn}_2 \) due to nearly doubled Mn-Mn distance.

The behavior of \( \nu \) above \( T_0 \) might evoke the “Korringa relation”, i.e., \( \nu \propto 1/T_1T \rightarrow \text{const.} \) in normal metals, where one would expect \( \nu_F \approx 1/\hbar N(E_F) = 2\pi^2 k_B^2 N_A/3\hbar \gamma \). However, \( \nu_F \) is estimated to be \( \approx 10^{13-14} \text{ s}^{-1} \) from \( \gamma = 80-200 \text{ mJ/K}^2\text{mol} \), which is three orders of magnitude smaller than that in normal metals. Thus, the observed spin fluctuation above \( T_0 \) does not seem to be directly related with the Pauli paramagnetism.

5. Summary
Spin fluctuation rate of Mn spins in a d-electron heavy fermion like compound \( \text{YMn}_{2-x}\text{Zn}_x\text{Mn}_2 \) has been deduced from ZF/LF-\( \mu \)SR measurements. The temperature dependence of \( \nu \) below \( T_0 \sim 10 \text{ K} \) shows \( T \)-linear dependence that is expected for the spin fluctuation in quasi-1D Hubbard chains as a model of the pyrochlore lattice. It comprises the third example of such a behavior next to \( \text{Y}_{1-x}\text{Sc}_x\text{Mn}_2 \) and \( \text{LiV}_2\text{O}_4 \). The HF-like behavior seems to set in below \( T_0 \), in good correspondence with the emergence of quasi-1D-like spin fluctuation. The relatively small \( \gamma \) compared with \( \text{Y}_{1-x}\text{Sc}_x\text{Mn}_2 \) may be understood as due to a small effective intra-chain exchange energy suggested by low \( T_0 \).

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