NMR relaxation rate in the field-induced octupolar liquid phase of spin-$\frac{1}{2}$ $J_1$-$J_2$ frustrated chains

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Abstract. In the spin-$\frac{1}{2}$ frustrated chain with nearest-neighbor ferromagnetic exchange $J_1$ and next-nearest-neighbor antiferromagnetic exchange $J_2$ under magnetic field, magnetic multipolar-liquid (quadrupolar, octupolar, and hexadecapolar) phases are widely expanded from the saturation down to a low-field regime. Recently, we have clarified characteristic temperature and field dependence of the NMR relaxation rate $1/T_1$ in the quadrupolar phase. In this paper, we examine those of $1/T_1$ in the octupolar phase combining field theoretical method with numerical data. The relevance of the results to quasi one-dimensional $J_1$-$J_2$ magnets such as PbCuSO$_4$(OH)$_2$, Rb$_2$Cu$_2$Mo$_3$O$_{12}$ and Li$_2$ZrCuO$_4$ is shortly discussed.

1. Introduction
The spin-$\frac{1}{2}$ chain with nearest-neighbor exchange coupling $J_1$ and next-nearest-neighbor coupling $J_2$ is one of the representatives of frustrated spin systems [1]. If $J_2$ is antiferromagnetic (AF) i.e., $J_2 > 0$, the system has magnetic frustration regardless of the sign of $J_1$. Recently, several quasi one-dimensional (1D) edge-sharing cuprates [2, 3, 4, 5, 6, 7, 8, 9] such as LiCu$_2$O$_2$, LiCuVO$_4$, Rb$_2$Cu$_2$Mo$_3$O$_{12}$, PbCuSO$_4$(OH)$_2$ and Li$_2$ZrCuO$_4$, have been investigated as quantum multiferroic materials or frustrated magnets, and many of them are believed to be approximately described by a $J_1$-$J_2$ spin chain with ferromagnetic (FM) $J_1$ and AF $J_2$ [10, 11] at least in the high temperature regime above their ordering temperatures.

Recent theoretical studies have elucidated effects of external magnetic field $H$ on the $J_1$-$J_2$ chain [12, 13]. It was found that the field induces three multipolar Tomonaga-Luttinger (TL) liquid phases, i.e., quadrupolar, octupolar, and hexadecapolar TL-liquid phases, in the wide region of $(J_1/J_2, H)$. In these three phases, multipolar operators $\prod_{n=1}^{p} S_{j+n}$ with $p = 2, 3, 4$ are respectively shown to exhibit a quasi long-range order. In addition, in these phases, the longitudinal spin correlator also decays in an algebraic form, while the transverse spin correlator obeys an exponential-decay law.

It is generally difficult to experimentally distinguish magnetic multipolar phases in spin systems. There is no established method of measuring multipolar correlations, and static quantities such as specific heat and susceptibility exhibit no large difference between the multipolar and standard TL liquids. Recently, we have shown [14] for these multipolar TL liquids that (i) in contrast to usual TL-liquid phase, nuclear-magnetic-resonance (NMR) relaxation rate
$1/T_1$ of the multipolar liquid phases decreases with lowering temperature near the saturation, and (ii) gapless points and peak positions of dynamical structure factors are clearly different from those of usual AF spin chains. Furthermore, in Ref. [15] we have numerically evaluated $1/T_1$ of the quadrupolar phase as a function of temperature and magnetic field, combining field theoretical approach with numerical data. The obtained result demonstrated that field dependence of $1/T_1$ is also characteristic: $1/T_1$ decreases with increasing the field except for the vicinity of saturation. These features of dynamical quantities would be helpful to detect multipolar TL liquids in experiments for the above quasi-1D magnets. In this paper, using the same method as Ref. [15], we determine the field and temperature dependence of $1/T_1$ in the octupolar phase of spin-$\frac{1}{2}$ $J_1$-$J_2$ chain. The result is expected to be relevant for quasi-1D $J_1$-$J_2$ magnets with large FM $|J_1|$. For instance, PbCuSO$_4$(OH)$_2$ might be a possible candidate for the realization of octupolar TL liquid [16].

2. Properties of multipolar phases
Here we shortly review the low-energy properties of multipolar TL-liquid phases of spin-$\frac{1}{2}$ $J_1$-$J_2$ chain [12, 13]. The Hamiltonian of $J_1$-$J_2$ chain under magnetic field $H$ is defined as

$$\mathcal{H} = \sum_{n=1,2} \sum_j J_n S_j \cdot S_{j+n} - \sum_j H S_j^z,$$

where we focus on the case with $J_1 < 0$ and $J_2 > 0$. For the saturated state in high-field regime, two-, three- and four-magnon bound states with momentum $\pi$, respectively, become the lowest-energy excitation in the regions $0 < |J_1|/J_2 < 2.699$ ($0.371 < J_2/|J_1| < \infty$), $2.720 < |J_1|/J_2 < 3.514$ ($0.285 < J_2/|J_1| < 0.368$), and $3.514 < |J_1|/J_2 < 3.764$ ($0.266 < J_2/|J_1| < 0.285$). With decreasing field $H$ below the saturation field, these bound magnons are condensed, and the system can be regarded as a hard-core Bose gas of bound magnons. We call these gases of two-, three-, and four-magnon bound states, respectively, the second, third, and fourth order multipolar (quadrupolar, octupolar, and hexadecapolar) TL liquids [17]. These multipolar phases expand from the saturation down to the low-field regime and turn into the low-field vector-chiral phase with $\langle (S_j \times S_{j+1})^z \rangle \neq 0$. In the $p$-th order multipolar phase, correlation functions of both the longitudinal spin operator $S_j^z$ and the $p$-th multipolar operators $\prod_{n=1}^p S_{j+n}^\pm$ (i.e., creation/annihilation operator of bound magnons) can be calculated from the effective TL-liquid theory for the hard-core Bose gas of multi-magnon bound states [12]. They are shown to decay algebraically as follows:

$$\langle S_0^z S_j^z \rangle = M^2 + C_0 \cos \left[ (1 - 2M) \pi j/p \right] |j|^{-2\kappa} + \frac{p^2 \kappa}{2\pi^2} |j|^{-2} + \cdots,$$

$$\langle \prod_{n=1}^p S_n^+ \prod_{n=1}^p S_{j+n}^- \rangle = (-1)^p C_1 |j|^{-1/(2\kappa)} + \cdots,$$

where $M = \langle S_j^z \rangle$ is the uniform magnetization per site, $C_m$ are nonuniversal constants, and $\kappa$ is the TL-liquid parameter. On the other hand, correlators of $q(< p)$-th multipolar operators including transverse spin operator $S_j^x$ obey an exponential-decay form $\sim e^{-|q|r/\xi}$ [14] since any $q$-magnon excitation requires a finite excitation energy to break $p$-magnon bound states. The correlation length $\xi$ must be proportional to the inverse of the binding energy $\Delta$ of magnons. The absence of the quasi-long-range order in the transverse-spin correlation plays a key role in the following discussion of NMR relaxation rate.

3. NMR relaxation rate
For spin systems in solids, NMR relaxation time $T_1$ is usually determined through weak hyperfine interactions between electron and nuclear spins. Therefore, we can obtain information about
electron-spin correlations from measurement of $T_1$. The formula for $T_1$ [18, 19, 20] is given by

$$1/T_1 = \frac{1}{2} A_2^2 \left[ S^\pm(\omega) + S^\mp(\omega) \right] + A_2^2 S^{zz}(\omega),$$  \hspace{1cm} (4)

where $A_{\perp,\parallel}$ are the hyperfine coupling constants, and $S^{\mu\nu}(\omega)$ is the local dynamical structure factor

$$S^{\mu\nu}(\omega) = \int dt e^{i\omega t} \langle S^\mu_j(t) S^\nu_j(0) \rangle.$$  \hspace{1cm} (5)

The strength of $A_{\perp,\parallel}$ depends on kinds of nuclei, crystal structures, and direction of field $H$. The value of $\omega$ is fixed to a nearly resonating frequency of nuclear-spin precession motion, and it is generally much smaller than the energy scale of electron spin systems. Therefore, we take the limit $\omega/(k_BT) = \omega\beta \to 0$ in the following discussions. Utilizing these formulas, we will discuss the temperature and field dependence of $1/T_1$ in the octupolar liquid phase.

4. Temperature and field dependence of $1/T_1$

From Eqs. (2), (4) and (5) and field-theoretical method [18, 19, 20], $1/T_1$ in the multipolar liquid phases is obtained as

$$1/T_1 = A_2^2 C_0 \frac{2a}{u} \cos(\kappa\pi) B(\kappa, 1 - 2\kappa) \left( \frac{2\pi a}{\beta u} \right)^{2\kappa-1}$$

$$\quad + A_2^2 \frac{B^2\kappa}{\pi} \left( \frac{a}{u} \right)^2 \beta^{-1} + \ldots.$$  \hspace{1cm} (6)

Here, $\beta = 1/(k_BT)$, $u$ is the excitation velocity, $a$ is lattice spacing, and $B(x,y)$ is the Beta function. We note that Eq. (6) is valid for the temperature regime $k_BT \ll \min(u/a, \Delta)$, where the low-energy effective theory of the bound-magnon Bose gas is reliable. If spatial dependence of hyperfine couplings is taken account of beyond the formula (4), the prefactors $A_2^2$ in the first and second term of Eq. (6) are generally modified and become different.

The form of $1/T_1$ in Eq. (6) consists of contributions from the longitudinal spin correlation; The first and second terms in Eq. (6) originate from the second and third terms in Eq. (2), respectively. Remarkably, both terms are power-law type functions of temperature. On the other hand, since the transverse spin correlation exhibits a gapped behavior, its contribution to $1/T_1$ is a thermal-activation form $\sim e^{-\beta\Delta}$. Therefore, if we consider the temperature region lower than the binding energy $\Delta/k_B$, the contribution from transverse spin correlation is negligible. The disappearance of transverse-spin contribution is a characteristic feature of multipolar TL liquids and makes the multipolar liquids distinct from the usual TL liquid in various quasi-1D AF magnets as discussed below.

Parameters $\kappa$, $u$, and $C_0$ can be evaluated as a function of field $H$ (or magnetization $M$) and $J_1/J_2$ at zero temperature by using density-matrix renormalization group method [12, 21]. Substituting them into Eq. (6), we obtain the temperature and field dependence of $1/T_1$. In particular, the temperature dependence of each term is determined by the TL-liquid parameter $\kappa$. For the multipolar phases, $\kappa$ is known to increase almost monotonically with increasing $H$ (or $M$) and approach unity at the saturation [12, 13]. We can thereby find that $1/T_1$ decreases with lowering temperature in the high-field region with $\kappa > 1/2$, while it diverges in the low-field region with $\kappa < 1/2$ [14]. This behavior highly contrasts to the usual TL liquid such as that of the spin-$1/2$ AF chain, in which one of the longitudinal- or transverse-spin contributions diverges at $T \to 0$ and $1/T_1$ is a monotonically increasing function of temperature in sufficiently low-temperature regime. Furthermore, for the quadrupolar phase ($p = 2$), the field dependence
of $1/T_1$ has also been determined rather accurately [15]. It has then been shown that with increasing $H$, $1/T_1$ decreases for low field regime and increases in the vicinity of the saturation field (see Fig. 1 of Ref. [15]). This peculiar non-monotonic field dependence of $1/T_1$ is expected to be a common property of all the multipolar TL-liquid phases in the $J_1$-$J_2$ chain and would be also a hallmark of them.

Let us now examine the temperature and field dependence of $1/T_1$ in the octupolar TL-liquid phase ($p = 3$). We evaluate $1/T_1$ combining the formula (6) with numerical estimates of $\kappa$, $u$, and $C_0$ which are obtained in the same manner as Refs. [12, 21, 22]. The coupling constant $A_{\parallel}$ is simply set to unity. Hereafter, we concentrate on the point of $J_2/|J_1| = 0.32$ ($J_1/J_2 = -3.125$), at which the octupolar phase widely exists for $0.07 \lesssim M < 1/2$ ($0.022|J_1| \lesssim H < H_c = 0.05|J_1|$) [12]. We note that in the octupolar phase, the excitation velocity $u$, i.e., the width of low-energy excitation band, is rather small compared to those of quadrupolar phase [15]. For instance, we evaluate $u/a \simeq 0.06|J_1| \simeq 0.19J_2$ for $M = 0.2$ and $u/a \simeq 0.01|J_1| \simeq 0.03J_2$ for $M = 0.4$ at the point of $J_2/|J_1| = 0.32$. This is a natural result because the parameter region of the octupolar liquid phase is closer to the ferromagnetic instability point $J_2/|J_1| = 0.25$ at zero field. The magnon binding energy is also evaluated as $\Delta \simeq 0.025|J_1| \simeq 0.078J_2$ for $M = 0.2$ and $\Delta \simeq 0.041|J_1| \simeq 0.13J_2$ for $M = 0.4$ at $J_2/|J_1| = 0.32$ [23]. Therefore, when we apply the formula (6) at this point, temperature must be low enough, say, $k_BT < 0.01|J_1|$. We also note that the numerical estimates of $C_0$ in the present calculation are subject to a rather large finite-size effect and the evaluated $1/T_1$ is less accurate than that of the quadrupolar liquid in Ref. [15]. However, we have checked that the result below is stable and semi-quantitatively unchanged against such an error of $C_0$.

We show in Fig. 1 the temperature dependence of $1/T_1$. The result confirms the previous prediction that, as temperature decreases, $1/T_1$ increases divergently for the low-field regime ($\kappa < 1/2$) and decreases for the high-field regime ($\kappa > 1/2$). Figure 2 shows the field dependence of $1/T_1$ for several fixed temperatures. It is remarkable that, for the sufficiently low temperature $k_BT = 0.001|J_1|$, $1/T_1$ decreases with increasing $H$ (or $M$) except for the vicinity of the saturation field. The contribution from each term in Eq. (6) is plotted in Fig. 3 separately. It is clear that the first term in Eq. (6) proportional to $\beta^{-(2\kappa-1)}$ contributes dominantly to a peculiar behavior of $1/T_1$, decrease with increasing $H$, for a wide field range. This feature becomes less significant as temperature increases and the field dependence of $1/T_1$ becomes nearly flat for a rather high temperature, $k_BT = 0.01|J_1|$. The $T$ and $H$ dependence of $1/T_1$ found above is qualitatively the same as that of the quadrupolar TL liquid [15], as expected. Even in the neighboring hexadecapolar liquid phase, similar properties must be realized (although the formula (6) would be valid only in extremely low temperature regime).

Quasi-1D $J_1$-$J_2$ magnets with high crystallographic symmetry often have principal axes for hyperfine coupling tensor. For such a case, we can eliminate all the contributions from the
longitudinal spin correlations, i.e., $A_3$ terms, in $1/T_1$, setting the field $H$ parallel to a principal axis. As a result, thermal activated contribution $\sim e^{-\beta \Delta}$ proportional to $A_3^2$, which is the hallmark of the multipolar liquids, becomes detectable in $1/T_1$. In this case, therefore, we can easily distinguish the multipolar TL liquid and usual TL liquid phases from temperature dependence of $1/T_1$.

5. Discussions

We have studied the NMR relaxation rate $1/T_1$ in field-induced octupolar TL liquid of the spin-$\frac{1}{2}$ $J_1$-$J_2$ chain. Substituting numerical estimates of parameters $\kappa$, $u$, and $C_0$ into the field-theoretical result, we have evaluated $1/T_1$ as a function of temperature and magnetic field. We have then found that, similarly in the quadrupolar liquid, $1/T_1$ in the octupolar TL liquid also exhibits characteristic features which are qualitatively different from those in the usual TL liquid: In the octupolar liquid, (i) $1/T_1$ decreases (increases) with increasing temperature $T$ for the low- (high-)field regime, and (ii) for sufficiently low temperatures, $1/T_1$ decreases with increasing magnetic field $H$ for a wide field range except the vicinity of the saturation field. These features can be understood from the absence of the quasi-long-range order in the transverse-spin correlation, which is a natural consequence of the formation of magnon bound states, and therefore be generally expected in all the multipolar TL liquids in $J_1$-$J_2$ chain. We note that the above features of $1/T_1$ in the octupolar phase is observed only in sufficiently low temperature regime ($k_B T < 0.01 |J_1|$), and gapless behavior of bulk quantities (specific heat, susceptibilities, etc.) present an indirect but strong evidence for multipolar TL liquids.

It has been reported [5, 6, 7, 8, 9] that three quasi-1D cuprates PbCuSO$_4$(OH)$_2$, H$_3$Co$_3$(OH)$_6$Cl$_2$, and H$_3$Co$_3$(OH)$_6$Cl$_2$ are such examples. In these cases, we can confirm the multi-longitudinal spin correlation by NMR experiments: (i) $1/T_1$ decreases with increasing temperature in the low-field regime, which could be useful to detect a signature of the multipolar TL-liquid phases. However, only the temperature dependence of $1/T_1$ could not be a sufficient evidence for them. For instance, $1/T_1$ also decreases with lowering temperature in high-field spin-gapped states such as magnetization plateaus. Therefore, we propose that observations of both characteristic behavior in $1/T_1$ and gapless behavior of bulk quantities (specific heat, susceptibilities, etc.) present an indirect but strong evidence for multipolar TL liquids.

Figure 2. Field dependence of NMR relaxation rate $1/T_1$ in the octupolar TL-liquid phase for $J_2/|J_1| = 0.32$ ($J_1/J_2 = -3.125$). Symbols represent the data obtained from Eq. (6) with numerical values of $\kappa$, $u$, and $C_0$. Lines are guide for the eyes.

Figure 3. Field dependence of each contribution in NMR relaxation rate $1/T_1$ [Eq. (6)] in the octupolar TL-liquid phase for $J_2/|J_1| = 0.32$ ($J_1/J_2 = -3.125$) and $k_B T/|J_1| = 0.001$. 

\[ J_2/|J_1| = 0.32, k_B T/|J_1| = 0.001 \]
Rb$_2$Cu$_2$Mo$_3$O$_{12}$, and Li$_2$ZrCuO$_4$ have relatively large value of $|J_1|$ ($2 \lesssim |J_1|/J_2 \lesssim 4$). We expect that our result will be helpful for searching for the appearance of octupolar phase in these compounds under high magnetic field.

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