

NMR study on the competing spin chain $\text{Rb}_2\text{Cu}_2\text{Mo}_3\text{O}_{12}$

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Abstract. Quasi-one-dimensional $S = 1/2$ Heisenberg system $\text{Rb}_2\text{Cu}_2\text{Mo}_3\text{O}_{12}$ described by the $J_1 - J_2$ model with the nearest-neighbor ferromagnetic and next-nearest-neighbor antiferromagnetic exchange interactions have been investigated by $^{87/85}\text{Rb}$ -NMR under extended field range up to 18 T. From the thermal-activation-type temperature dependence of $1/T_1$, opening of the spin excitation gap was confirmed under the low field below 2 T. With increasing the field, the system becomes gapless, and the gap opens again in the high field saturation region, where the field dependence of the gap size showed the coherent excitation of the neighbouring two spins.

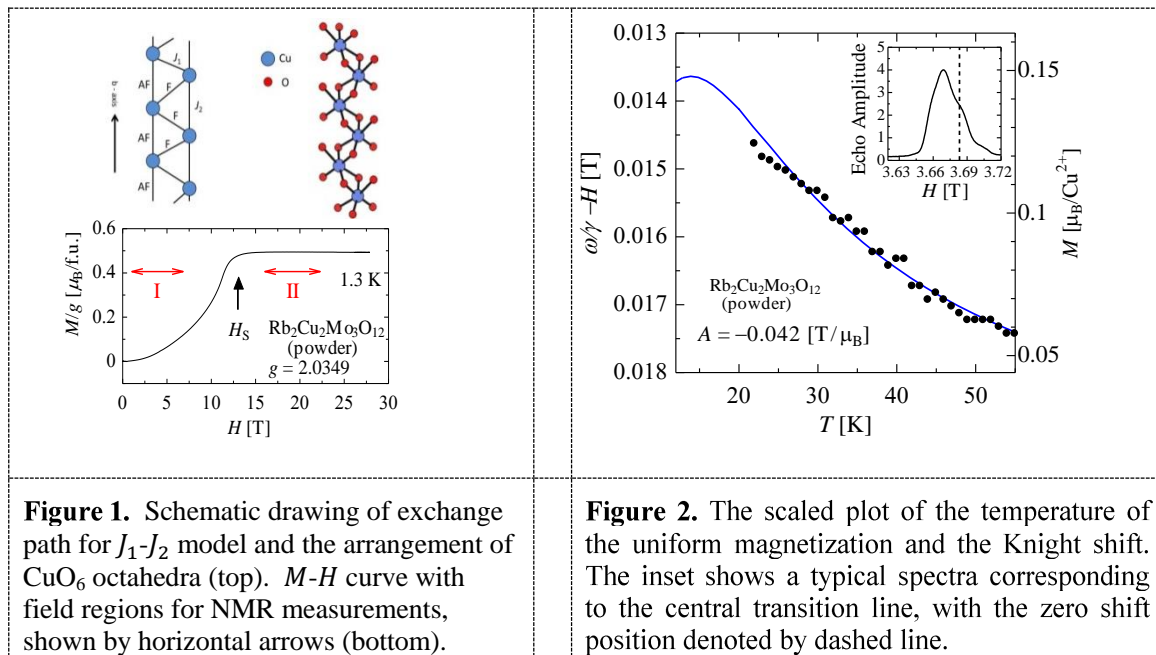
1. Introduction

One dimensional and quasi-one dimensional spin systems have brought and are still giving rich physics, in spite of their simple Hamiltonians. Among them, the $J_1 - J_2$ model, which has two dominant exchange interactions of the nearest-neighboring ferromagnetic J_1 and the second nearest-neighboring antiferromagnetic J_2 [1,2] attracts much interest recently, because of theoretical suggestion of spin-nematic state or spin-nematic Tomonaga-Luttinger liquid state, where vector-natured spins behave like quadrupoles [3-5]. So far, many model compounds are proposed, but an experimental evidence of its detailed spin state is unknown.

In this article, we focus on the quasi-one dimensional magnet $\text{Rb}_2\text{Cu}_2\text{Mo}_3\text{O}_{12}$, which can be described by the $J_1 - J_2$ model with $J_1 = -138$ K and $J_2 = +51$ K[6,7], and investigate its low-temperature spin state by NMR- T_1 under the wide field range up to 18 T. We pick up the two viewpoints for study. One is the magnetic ground state of the system. The investigations on macroscopic quantities reported that the system shows no long range magnetic order down to 0.3 K, and rather has a very small energy gap in the spin excitation spectrum, that is, the gap size is $\Delta = 1.6$ K, which is smeared out by the low field of $H_c = 2.3$ T.[8,9] This makes clear contrast with the isomorphic compound $\text{Cs}_2\text{Cu}_2\text{Mo}_3\text{O}_{12}$, which also can be described by the model with slightly different exchange parameters. The latter has been confirmed to exhibit a magnetic order below 1.8 K under zero and finite fields.[10] We will investigate microscopically how the spin state of $\text{Rb}_2\text{Cu}_2\text{Mo}_3\text{O}_{12}$ changes with magnetic field.

The second viewpoint is of the saturated region at high fields, where the spins are forced to be aligned ferromagnetically. Generally, in that state, the spin system has a finite energy gap, the size of which corresponds to the Zeeman energy of one-spin-flop state. However, a recent theoretical report suggests that the first excited state of those described by $J_1 - J_2$ model may be the two-magnon state.





By utilizing the temperature dependence of T_1 as a probe, we will demonstrate directly field-dependence of the gap[11-12].

2. Experimental

The sample of $\text{Rb}_2\text{Cu}_2\text{Mo}_3\text{O}_{12}$ was obtained in powder form by the conventional solid-state reaction method [6,14]. Magnetization measurement shows that the saturation field is approximately $H_s = 12.7$ T[6,9]. For better understanding of NMR results below, we refer the detailed crystal structure here. The space group of the crystal structure is $C2/c$, and the edge-sharing CuO_6 distorted octahedra form a so-called ribbon chain along b -axis (Fig. 1). As for the NMR-nucleus Rb, which are located between interstitial positions between chains, there are three inequivalent sites of $4d$, $4e$ and $8f$. The distances between these Rb and their nearest-neighboring Cu sites are within a range between 4.07 and 5.61 Å, indicating that all the Rb sites may have moderate hyperfine coupling with Cu moments.

We have performed NMR measurements mainly in the two regions I and II, the low field region below 5 T and the saturated region 13-18 T, respectively. The two isotopes of ^{87}Rb ($\gamma = 13.928$, $I = 3/2$) or ^{85}Rb ($\gamma = 4.1099$, $I = 5/2$) were chosen in measurements at the region I and II, respectively. Spectra were obtained by recording the spin-echo amplitude against magnetic field, which was ramped slowly around the zero-shift position [15,16]. Since the sample was powder, both the eqQ -powder pattern of the center line and the peak structure due to the signal from inequivalent sites are smeared out, so that only a single broad peak was observed; a typical spectrum profile is shown in the inset of Fig. 2. The longitudinal spin relaxation rate $1/T_1$ was obtained by the conventional saturation-recovery method with a pulse-train for saturation[17]. The nuclear spin polarization after the saturation was traced until its difference from the thermal equilibrium value reached one percent. The time evolution of the nuclear spin polarization was fitted by the function $0.1e^{-\tau/T_1} + 0.9e^{-6\tau/T_1}$ and $0.029e^{-\tau/T_1} + 0.18e^{-6\tau/T_1} + 0.79e^{-15\tau/T_1}$ for ^{87}Rb and ^{85}Rb , respectively.

3. Results and Discussion

The temperature dependence of the Knight shift the uniform magnetization are scaled and plotted together in Fig. 2, from which the effective hyperfine coupling constant $A = -420 \text{ Oe}/\mu_B$ was

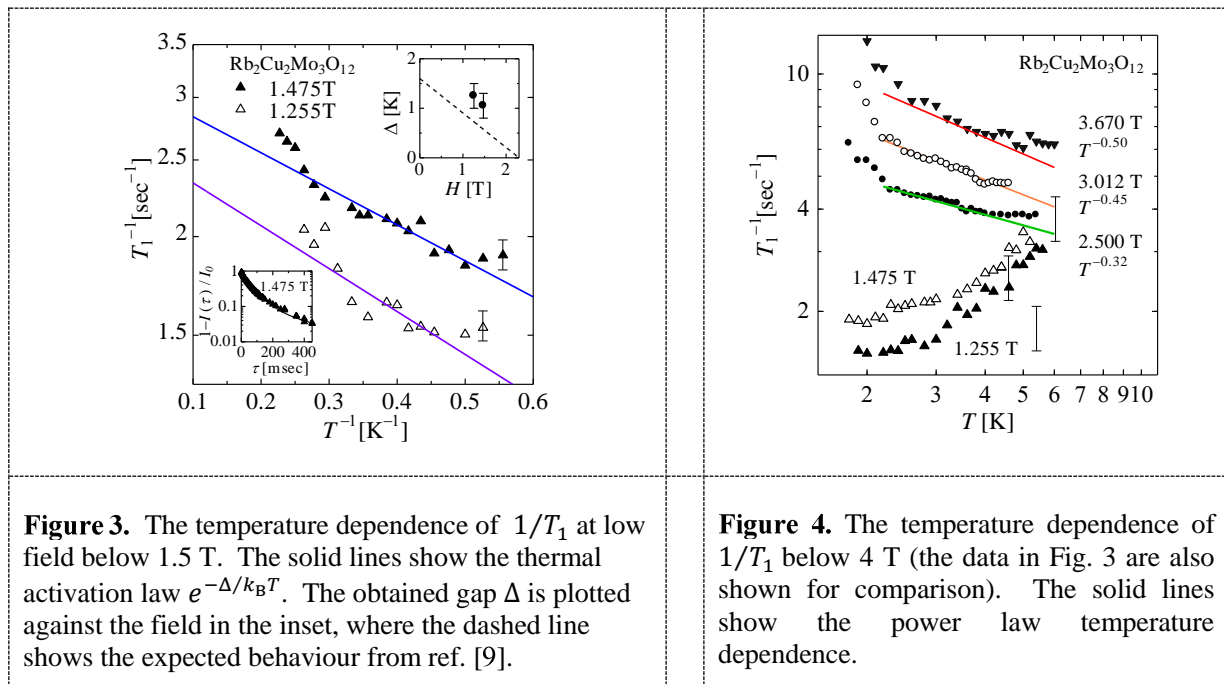


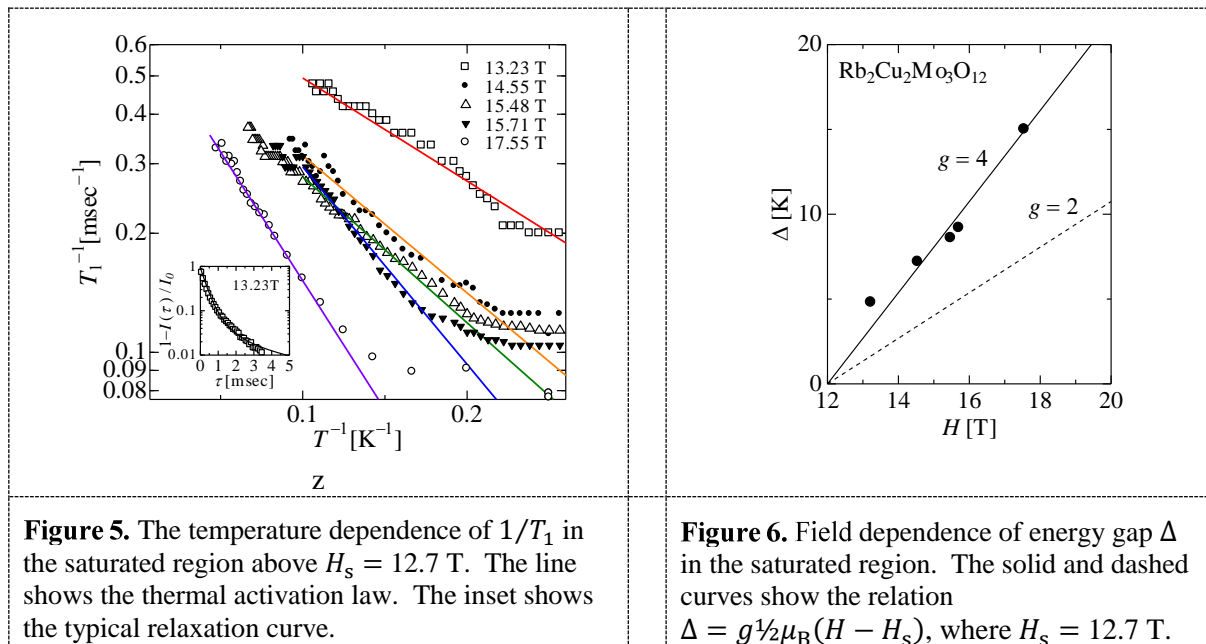
Figure 3. The temperature dependence of $1/T_1$ at low field below 1.5 T. The solid lines show the thermal activation law $e^{-\Delta/k_B T}$. The obtained gap Δ is plotted against the field in the inset, where the dashed line shows the expected behaviour from ref. [9].

Figure 4. The temperature dependence of $1/T_1$ below 4 T (the data in Fig. 3 are also shown for comparison). The solid lines show the power law temperature dependence.

obtained. This value is large enough to study the magnetism in copper moments by NMR. In the following, we describe the results of $1/T_1$ measurements at low (region I) and high (region II) fields. First, we show in Fig. 3, the temperature dependences of $1/T_1$ at lowest fields below 1.5 T, where the opening of gap was reported by the temperature dependence of uniform susceptibility [9]. One can see that $1/T_1$ obeys the thermal activation law, from which a finite gap Δ was evaluated and plotted against the applied field shown in the inset. The gap size was 1.3 K under the field 1.255 T, and became smaller as the field is increased. This gives a microscopic demonstration on the existence of spin excitation gap at low fields, consistent with Fujimura's report on the uniform susceptibility [9]. Note that the small discrepancy of our gap estimation from the ref. 9 may be due to the fact that our measured temperature range is marginal, that is, comparable to the gap size, and hence the gap size and hence the gap size may be overestimated. Furthermore, at these low fields, the S/N ratio of NMR is quite low and only two field points were obtained (the inset of Fig. 2), which, we admit, are not enough to discuss the field dependence.

Next, we raise the field above 2 T, and plot the temperature dependence of $1/T_1$. The data below 2 T are also shown for comparison. The temperature dependence drastically changes at around 2 T, above which the energy gap seems to be collapsed. This boundary is very close to the reported on the magnetization $H_c = 2.3$ T [9]. We can fit the temperature dependence with the power law $T^{-\alpha}$ within a limited range between 2 and 5 K. The power law index α is field dependent and appreciably increases with increasing field. Though this may be an indicative of TLL state [19-23], one needs more data for the comparison with theories. Furthermore, the information on the anisotropy in the hyperfine tensor is indispensable to extract the Luttinger parameter K , which determines the spatial spin correlation, from the temperature dependence of $1/T_1$. This is because the longitudinal and transverse components of spin correlation contribute to $1/T_1$ and cause different temperature dependence as T^{2K-1} and $T^{1/2K-1}$, respectively [19,21]. In order to determine the hyperfine coupling tensor, NMR experiments on axially-aligned powder sample is now in the progress.

Above the higher temperature boundary of 5 K, $1/T_1$ tends to be temperature independent, that is, approaching to the paramagnetic behavior in the high temperature limit. And on the contrary, below the lower boundary, $1/T_1$ starts to diverge toward a possible critical temperature. Though this behavior still does not show any evidence for phase transitions, and there has been no reports on the existence of the field-induced magnetic order in this compound, one can refer at least that the spin gap



is closed, and the system becomes completely gapless to have the magnetic ground state. The measurement at still lower temperature region is under progress.

Next, we proceed to the high field of saturated region (region II), where $1/T_1$ obeys again the thermal-activation type law as shown in Fig. 5, indicating the existence of spin excitation gap Δ . Its field dependence is shown in Fig. 6, where one can see that the gap increases with the field as $\Delta = g^{1/2}\mu_B(H - H_s)$, and that g takes an anomalous value of 4. This clearly demonstrates that the two spins flip coherently from the ground state of forced ferromagnet in the saturated region[13]. Evidently, this coherency is considered to come from the ferromagnetic exchange interaction between the neighboring two spins.

Summary

NMR- $1/T_1$ measurements on the $S = 1/2$ Heisenberg competing spin chain system $\text{Rb}_2\text{Cu}_2\text{Mo}_3\text{O}_{12}$ were performed in the wide-field range from zero to 18 T. Under the low field of 1.255 T, existence of a small spin excitation gap $\Delta \approx 1.3$ K was confirmed. With increasing field the gap shrank above 2 T, and the ground state became magnetic. In the high field of saturated region, the system becomes gapfull again, and the gap size obeyed the field dependence of $\Delta = g^{1/2}\mu_B(H - H_s)$ with $g = 4$, indicating the coherent excitation of two-magnons.

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