1H-NMR studies of quantum spin chain system (CH₃)₂NH₂CuCl₃ at very low temperature

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Abstract. We report ¹H NMR results for (CH₃)₂NH₂CuCl₃ measured at very low temperature down to 0.1 K using a dilution refrigerator. Field induced magnetic ordered state is revealed by the NMR measurements and a magnetic phase diagram for the system is proposed.

1. Introduction

Recently much attention has been paid to field-induced quantum phenomena such as field-induced magnetic orderings (FIMO) in low dimensional quantum spin systems. (CH₃)₂NH₂CuCl₃ is known to have unique magnetic chain forming an alternating chain of antiferromagnetic (S=0) and ferromagnetic (S=1) dimers coupled by an intervening weak interaction [1,2]. Quite recently specific heat measurements revealed an existence of FIMO phase at low temperature above 4 T [3]. Figure 1 shows the magnetic phase diagram proposed from the specific heat measurements. The system shows an antiferromagnetic ordering below T_N ~ 0.8 K at zero magnetic field. T_N decreases slightly with increasing magnetic field up to B = 2 T. The ground state of the system changes to a field-induced gapped state between 2 and 3.5 T. Above B = 3.5 T, field-induced antiferromagnetic magnetic ordered phase appears as shown in the fig. 1. The FIMO phase in the system seems to be quite unusual because the FIMO phase in the system seems to be quite unusual because the FIMO appears suddenly at T = 1.4 K around B = 4 T with increasing magnetic field. This is in sharply contrast to the usual FIMO phases reported in other typical magnetic systems such as TICuCl₃ [4] and BaCuSiO₆ [5] in which the FIMO phase starts to appear from the zero temperature and have a parabolic-like shape in the B - T phase diagram.

In order to shed light on the unusual FIMO phase in the system from a microscopic point of view, we have carried out ¹H-NMR measurements at low temperatures. We report T and B dependence of proton spin-lattice relaxation time (T₁), which provides new phase diagram for (CH₃)₂NH₂CuCl₃ where the FIMO phase have a parabolic-like shape in B - T phase diagram.
Figure 1. Magnetic field versus temperature phase diagram of (CH$_3$)$_2$NH$_2$CuCl$_3$ proposed from specific heat measurements [3]. Open circles and closed squares show the phase boundary proposed from specific heat [3] and present NMR measurements, respectively. Note that significant differences for the magnetic ordering temperatures between two experimental methods can be seen around 4 T. Thick solid line shows a proposed new phase boundary for the FIMO phase based on the present NMR results.

2. Experimental
A polycrystalline sample of (CH$_3$)$_2$NH$_2$CuCl$_3$ was prepared by the slow evaporation method as described in ref. 6. NMR measurements were carried out using a phase-coherent spin echo pulse spectrometer in the temperature region $T$ = 0.1 to 2 K using a $^3$He-$^4$He dilution refrigerator under the magnetic field of $B$ = 4 - 7 T. The nuclear spin-lattice relaxation time $T_1$ was measured by a saturation recovery method. The nuclear magnetization recovery was a non-single exponential function so that $T_1$ was determined by fitting the recovery curves with a stretched exponential function, exp(-(t/$T_1$)$^{0.5}$).

3. Results and discussion
Figure 2 shows temperature dependence of 1/$T_1$ measured at various magnetic fields. Clear and sharp peak of 1/$T_1$ around $T$ = 1.25 K at $B$ = 6 and 7 T can be observed. NMR spectra measured at same magnetic fields start to broaden by lowering the temperature just below the peak temperature of 1/$T_1$, indicative of magnetic ordering below the temperature. Thus the peak temperature of the 1/$T_1$ can be attributed to the field-induced magnetic ordering temperature. Actually, the peak temperature of 1/$T_1$ above 6 T coincides well with the magnetic ordering temperature reported by specific heat measurements, as showing in Fig. 1. The 1/$T_1$ is roughly proportional to $T^{3.2\pm0.3}$ below the magnetic ordering temperature, whose $T$-dependence is very close to the theoretical prediction of $T^3$ on the spin wave model for the three dimensional antiferromagnetic system [7]. Similar $T$-dependence of 1/$T_1$ was reported in a field-induced antiferromagnetic ordered state in KCuCl$_3$ [8] in which the antiferromagnetic ordering is interpreted as the Bose-Einstein condensation of the magnons. Therefore we conclude that the field-induced magnetic ordered state is a long-range antiferromagnetic ordered state in the present system.

Below 5 T, the peak position of the 1/$T_1$ shifts to lower temperatures with decreasing magnetic
Figure 2. Temperature dependence of proton-1/$T_1$ measured at various magnetic fields. Arrows show the peak position of $1/T_1$ for each magnetic field. Solid line is an eye-guide to show a slope for a relation of $1/T_1 \sim T^3$.

field as can be seen in the Fig. 2. This strongly indicates that the transition temperature for the field-induced antiferromagnetic ordered state phase decreases with decreasing magnetic field. It should be noted that the peak of $1/T_1$ becomes smaller in the height and broadens at lower magnetic fields. The peak temperatures of $1/T_1$ for the different magnetic fields are plotted by closed squares in Fig. 1. The thick solid line in the Fig. 1 exhibits the phase boundary expected from the present NMR results, in which the phase boundary for the FIMO seems to appear from zero temperature around $\sim 3.5$ T and the magnetic ordering temperature increases with increasing magnetic field up to 7 T.

Obviously, the magnetic ordering temperatures revealed by the NMR measurements differ from those by the specific heat measurements around $4 \sim 5$ T, although the transition temperatures almost coincide between two experimental methods above 6T. In the specific heat measurements, magnetic ordering temperature is estimated from the peak position of $T$ dependence of the magnetic specific heat ($C_m$). At higher magnetic fields above 6 T the peak of the $C_m$ due to the magnetic orderings is relatively sharp and clear, which leads to a certain transition temperature. On the other hand, below $\sim 5$ T, the peak of $C_m$ becomes broader with decreasing magnetic field, which would make some ambiguities to estimate the transition temperature.

As described above, similar to the case of the specific heat measurements, the peak in the $T$-dependence of $1/T_1$ is also smeared with decreasing the magnetic field. But, the phase transition can be still identified clearly by the sudden decrease in $1/T_1$ just below the transition temperature. The significant difference for the transition temperature around the critical magnetic field $B \sim 4$ T does not come from the difference of the samples used in the measurements because the transition temperature for the high magnetic field above $B \sim$
6 T coincides very well. Though the reason for the significant difference for the transition temperature around the critical magnetic field is not clear at present, it must be originated from the peculiarities of the magnetic properties around the critical field in the system.

4. Conclusion
We have carried out $^1$H-NMR at very low temperatures to investigate the magnetic properties of the field induced magnetic ordered (FIMO) state in $(\text{CH}_3)_2\text{NH}_2\text{CuCl}_3$. The dependence of $1/T_1$ on both $T$ and $B$ clearly reveals the existence of FIMO phase which is a long range antiferromagnetic ordered state. The FIMO phase is revealed to appear around $\sim 3.5$ T with a parabolic-like shape in $B - T$ phase diagram.

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