NMR relaxation in the diluted one-dimensional Heisenberg antiferromagnets

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Abstract. Proton NMR of the diluted one-dimensional Heisenberg antiferromagnets has been observed by the conventional spin echo method in zero magnetic field below the Néel temperature. The temperature dependences of the spin-lattice relaxation rates $1/T_1$ have been obtained. $1/T_1$ in a pure system increases rapidly with the increasing temperature, which is attributed to the change of the relaxation mechanism from the two magnon to three magnon processes. A slight dilution caused the spin-lattice relaxation rates increase markedly at low temperatures. But at high temperatures, the temperature dependences of the diluted systems approach that of pure system. The results are discussed on the basis of the spin wave theory. The spin echo intensity decays as a function of the square of the interval time between two pulses. The temperature dependences of the spin-spin relaxation time $T_2$ measured from a Gaussian decay are reported, too.

1. Introduction

One-dimensional (1D) Heisenberg antiferromagnetic spin systems have attracted a lot of interest. The existence of a small interchain interaction causes the long range order. In the ordered state, one might anticipate a dramatic influence on the electron spin system especially induced by the dilution of the magnetic spins. The Nuclear magnetic resonance experiments provide us useful information on spin dynamics. The NMR relaxation rate is related to the fluctuations of the local moments. Therefore, we have a plan to measure the NMR relaxation of the diluted one-dimensional Heisenberg antiferromagnets in the ordered state.

We prepared two types of samples of the diluted 1D Heisenberg antiferromagnets, $(\text{CH}_3\text{NH}_3)\text{Mn}_{1-x}\text{Cd}_x\text{Cl}_3\cdot2\text{H}_2\text{O}$ (MMC-Cd) [1] and CsMn$_{1-x}$Cu$_x$Cl$_3\cdot2\text{H}_2\text{O}$ (CMC-Cu) [2]. It is reported that in the former samples the small remanent magnetizations are observed and in the latter samples not observed. It is interesting to know the difference of the spin dynamics between these compounds. In this paper, we report the results of the temperature dependence of the spin-lattice relaxation rate $1/T_1$ and the Gaussian spin echo decay rate $1/T_{2G}$ on these compounds.

In pure MMC [3, 4], the magnetic chains run along the $b$ direction of the crystal. The three dimensional ordering occurs at 4.12 K and the magnetic moments align along the $a$ axis. The intrachain interaction $J$ is $\sim$3.0 K and the interchain interaction is of the order of $10^{-2}$ of $J$. The ratio of the anisotropy to the exchange field is $4\times10^{-3}$. In pure CMC [5, 6], the magnetic chains run parallel to the $a$ crystallographic direction. The Néel temperature is 4.89 K and
the magnetic moments align along the $b$ axis. The intrachain interaction $J$ is $\sim 3.0$ K and the interchain interaction is also of the order of $10^{-2}$ of $J$.

2. Experiments and Results
The polycrystalline samples were prepared by the same method as reported previously [1,2]. The amount of substitution was determined by ICP spectrometry. A part of the obtained polycrystals was used for the measurement of AC magnetization and the rest for NMR measurement. AC magnetizations were measured by use of ACMS option of PPMS (Quantum Design) with the frequency 100 Hz and the field strength 10 Oe. Proton NMR signals were observed by a conventional spin echo technique below the liquid helium temperature in zero magnetic field. The temperature of the sample was determined by measuring the pressure of the helium vapor. The spin-lattice relaxation time was determined by measuring the echo recovery with $\pi/2$ and $\pi$ pulses sequence by changing the repetition time. The spin-spin relaxation time was obtained by measuring the spin echo decay with the sweep of the interval time between $\pi/2$ and $\pi$ pulses.

In Figure 1, the temperature dependences of AC magnetizations of MMC-Cd and CMC-Cu are shown. All samples exhibit a broad maximum, which is caused by the characteristic one-dimensional interactions. The diluted samples show the increase of AC magnetizations with decreasing temperature at low temperature. Eggert and Affleck [7] found that in the case of half-integer spin chain, the staggered magnetization appears near chain ends under a uniform field. The observed increase of AC magnetization may be attributed to this.

There are two magnetically nonequivalent proton sites of crystal waters in MMC-Cd. The protons are coupled to the electron spin system through dipole-dipole interaction. Then, two NMR lines are observed in the ordered state. In Figure 2, the observed spectra are shown for pure and $x=0.004$, 0.048 samples at the temperature 1.37 K. The signals due to the protons in $\text{CH}_3\text{NH}_3^+$ ions are also observed in the frequency range lower than these spectra and omitted from the figure. The substitution of Cd causes the broadening of the resonance lines. The observed frequencies at the peaks of the spectra are 10.73 MHz (site A) and 10.45 MHz (site B) at 1.37 K.

The spin echo intensity recovery was fit well by the single-exponential as a function of the repetition time. Figure 3 shows the temperature dependences of spin-lattice relaxation rates

![Figure 1](image1.png)

**Figure 1.** (a) Temperature dependences of AC magnetizations for $(\text{CH}_3\text{NH}_3)\text{Mn}_{1-x}\text{Cd}_x\text{C}_3\text{H}_2\text{O}$. (b) Temperature dependences of AC magnetizations for CsMn$_{1-x}$Cu$_x$C$_3$H$_2$O. The values of AC magnetizations are normalized at the temperature of 100 K.
for the line A of MMC-Cd. The tendency of the temperature dependences of the spin-lattice relaxation rates for each line A and B were not different. The values of the spin-lattice relaxation rates at the low temperature become markedly faster by a slight substitution. In the 0.4% diluted sample, the relaxation rate change still with the increasing temperature. On the contrary, in the 2.5% diluted sample, the relaxation rate is almost temperature independent. At the high temperature, the values of the relaxation rates for the diluted samples seem to approach the values of pure MMC. In Figure 4, the spin-lattice relaxation rates are plotted as a function of temperature for CMC-Cu. In the figure the result for pure CMC obtained by Nishihara et al. [8] is shown. In this system, a slight substitution causes the relaxation rate much faster at the low temperature, too. There is a difference from MMC-Cd system, that is, only 0.3% dilution gives rise to no temperature dependence of the relaxation rate at low temperature. At the high temperature the relaxation rates for the diluted samples approach the values of pure CMC and reveal the same temperature dependence.

The spin-spin relaxation was found to have a Gaussian behavior for all samples. We obtained the Gaussian spin-spin relaxation time $T_2G$ from the plots of logarithm of spin echo intensity vs. the square of the pulse separation time $\tau$. Figure 5 shows the temperature dependences of the Gaussian spin-spin relaxation rates for MMC-Cd and CMC-Cu. The change of the relaxation rate with the temperature is little. There is a tendency that the closer the temperature gets to Néel temperature, the faster each relaxation rate becomes a little.

3. Discussion
The NMR relaxation rate in magnetic materials is explained through the nuclear spins and spin wave coupling. Nishihara et al. observed the temperature dependence of the spin-lattice
relaxation rate for pure CMC and concluded that at the low temperature two magnon process dominates and at the high temperature the exchange-enhanced three magnon process [8]. As shown in Figures 3 and 5, the dilution is ineffective on the spin-lattice relaxation at the high temperature. Even in the diluted samples, the spin-lattice relaxation is dominated by three magnon process. But at the low temperature the dilution causes the apparent effect. The AC magnetizations at the low temperature are increased by the dilution, then the fluctuations of the local field are induced. In general, the spin-lattice relaxation rate is affected by the imaginary part of the dynamic susceptibility. The results suggest appearance of the complex spin wave mode.

The clear effect of the dilution on the Gaussian spin-spin relaxation rates is not observed in our experiments.

4. Summary
We measured the temperature dependences of the spin-lattice relaxation rates $1/T_1$ and the Gaussian spin echo decay rates $1/T_{2G}$ on two types of samples of the diluted 1D Heisenberg antiferromagnets $(\text{CH}_3\text{NH}_3)\text{Mn}_{1-x}\text{Cd}_x\text{Cl}_3\cdot2\text{H}_2\text{O}$ and CsMn$_{1-x}$Cu$_x\text{Cl}_3\cdot2\text{H}_2\text{O}$. The dilution causes the remarkable effect on the spin-lattice relaxation rates at the low temperature. The difference appears in the temperature dependence of the spin-lattice relaxation rates at low temperature between two slightly diluted systems. This fact may be related to whether the remanent magnetization is observed or not.

5. References
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Figure 5. (a) Temperature dependence of Gaussian spin-spin relaxation rate $1/T_{2G}$ for the line A of $(\text{CH}_3\text{NH}_3)\text{Mn}_{1-x}\text{Cd}_x\text{Cl}_3\cdot2\text{H}_2\text{O}$.
(b) Temperature dependence of Gaussian spin-spin relaxation rate $1/T_{2G}$ for the line A of CsMn$_{1-x}$Cu$_x\text{Cl}_3\cdot2\text{H}_2\text{O}$. 