# Nuclear Magnetic Relaxation in Anisotropic Heisenberg Antiferromagnet $MnCl_2 \cdot 4H_2O$

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We have studied the room temperature $^1H$ nuclear magnetic relaxation in anisotropic antiferromagnet $MnCl_2 \cdot 4H_2O$ using a wide range of $^1H$ NMR (nuclear magnetic resonance) field. Being a system of dense paramagnetic $Mn^{++}$ ions at room temperature, $MnCl_2 \cdot 4H_2O$ shows some features that can be expected from dilute paramagnetic systems, as well as some results that drastically deviate from the dilute paramagnetic approximations. Besides, $^1H$ nuclei exhibit an anomalous deviation in the spin-lattice relaxation time ($T_1$) around the field of 0.7 T.

## Ⅰ. Introduction

$MnCl_2 \cdot 4H_2O$ has a quasi-two-dimensional magnetic structure and the crystal belongs to the monoclinic system with the angle $\beta = 99.74°$. It undergoes an antiferromagnetic transition at $T_N = 1.62$ K[1]. In addition, $MnCl_2 \cdot 4H_2O$ is a good example of a system which exhibits simple antiferromagnetic order with small anisotropy energy, somewhat less than the exchange energy. Such a system can have three distinct phases, antiferromagnetic (AF), spin-flop (SF), and paramagnetic (P). The AF to SF transition is known to occur in the external magnetic field range of 0.7 to 0.8 T at low temperatures below the $T_N$ in $MnCl_2 \cdot 4H_2O$[2]. $MnCl_2 \cdot 4H_2O$ at room temperature is a paramagnetic system with dense $Mn^{++}$ ions with an anisotropy. Thus it is of interest to investigate the room temperature NMR properties to study the microscopic interactions in that system.

$MnCl_2 \cdot 4H_2O$ has been studied by zero-field ccntinuous-wave (cw) NMR in the antiferromagnetic phase and line spiltting due to the anisotropic field was observed.[3]

## Ⅱ. Theory

The relaxation transition probability of a nucleus at a distance r from a paramagnetic ion is, when averaged over the angle dependences,

$$P = (1/5\pi)(\gamma_p \gamma_n \hbar)^2 S(S+1) r^{-6} \tau (1+\omega^2 \tau^2)^{-1} = C r^{-6}, \quad (1)$$

where $\gamma_p$ and $\gamma_n$ are the gyromagnetic ratios of the paramagnetic ion and the nucleus, respectively. The correlation time of the $z$ component of the spin $S$ of the paramagnetic ion is denoted by $\tau$[4, 5]. The diffusion equation to be solved for the behavior of the nuclear spin system in the absence of radio-frequency excitation is then

$$\partial p/\partial t = D\nabla^2 p - C(p - p_0) \sum_n |\vec{r} - \vec{r_n}|^{-6}, \quad (2)$$

where $\vec{r_n}$ is the location of a paramagnetic ion, $p_0$ is the thermal equilibrium value of the nuclear spin magnetization density $p$, and $D$ is the diffusion constant. In the region of a given paramagnetic impurity, which we take as the origin, we may write the equation approximately as

$$\partial p/\partial t = D\nabla^2 p - C(p - p_0) r^{-6}. \quad (3)$$

Eq. (3) can be taken as a paramagnetic dilution limit for Eq. (2), where the effect only due to the nearest paramagnetic ion is considered[5].

Solutions to Eq. (3) for the paramagnetic impurity systems can be obtained for some special

cases. In the case of no spin diffusion, the magnetization recovery $M_z(t)$ after the nuclear magnetization is saturated is given by

$$M_z(t) = \frac{4}{3}\pi^{3/2} NC^{1/2} t^{1/2}, \quad (4)$$

for small $t$[5, 6].

In the case of diffusion-limited relaxation, where diffusion plays a significant role but not a dominant role in the spin-lattice relaxation at all times, it has been shown that for a sufficiently large time $M_z(t)$ approaches $M_z(\infty)[1-\exp(-t/T_1)]$. For a short time following saturation of the nuclear resonance line, however, the solution Eq. (4) should hold, since diffusion cannot be of importance at the start of the relaxation process. In the case of rapid diffusion, where diffusion plays a dominat role in the spin-lattice relaxation at all times, it is expected that $M_z(t)$ would follow an exponential function of time for all values of t and that the initial region in which $M_z$ is proportional to $t^{1/2}$ would be missing[5, 7].

The correlation time $\tau$ in the presence of exchange interaction is given by

$$1/\tau = 1/\tau_c + 1/\tau_{ex} \quad (5)$$

where $\tau_c$ is the correlation time in the absence of the exchange interaction and $\tau_{ex}$ is the reciprocal of the exchange frequency, $1/\omega_{ex}$. Thus the correlation time is expected to be shorter in the presence of the exchange interaction.

## Ⅲ. Experimental

The powder sample of $MnCl_2 \cdot 4H_2O$ used in this work was commercially available. A home-built quadrature-detection pulsed NMR spectrometer was used for the experiments and a 12″ Varian electromagnet was employed for various $^1H$ NMR fields at room temperature. Solid echo sequences were used for the measurements of the lineshapes. For the spin-lattice relaxation time ($T_1$) measurements, inversion recovery method was used, which is one of the magnetization saturation techniques.

## Ⅳ. Results and Discussion

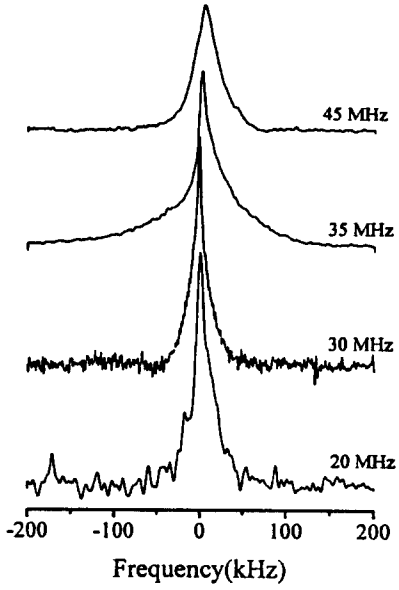


Fig. 1. Room temperature $^1H$ NMR lineshapes at various resonance frequencies.

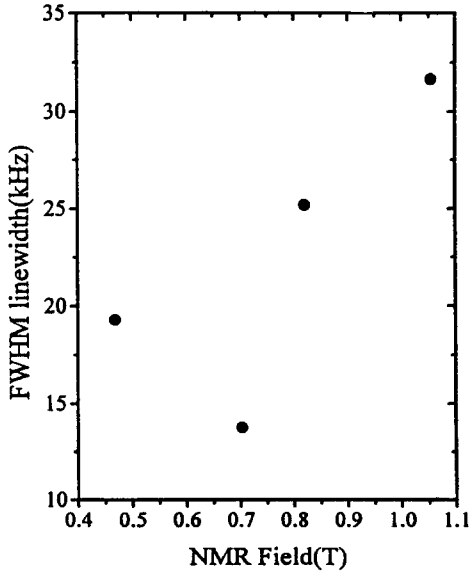


Fig. 2. FWHM NMR linewidth vs. the resonance frequency.

The roughly Lorentzian $^1H$ NMR lineshapes in Fig. 1 show relatively narrow linewidths considering the presence of the paramagnetic $Mn^{++}$ ions in their vicinity. This is interpreted as a result of the exchange narrowing of the paramagnetic fields from the dense ions[8, 9]. The FWHM (full-width at half-maximum) linewidths at various resonance frequencies are shown in Fig. 2, where an anomalous dip at 30 MHz (corresponding to a field of about 0.7 T) is noticed.

The nuclear magnetic relaxation consists of a fast-recovery initial non-exponential part and a long-time exponential recovery part, as shown in Fig. 3. The initial recovery of the nuclear magnetization, $M_z(t)$, plotted as a function of $t^{1/2}$ in Fig. 4 shows that our system looks like a typical case of the diffusion-limited relaxation[7]. From the slope in Fig. 4, the correlation time $\tau$ is estimated to be $2 \times 10^{-10}$ s using Eqs. (1) and (4). In addition, the diffusion constant $D$ was estimated to be $1.6 \times 10^{-12}$ cm$^2$/s, the constant $C$ in Eq. (1) to be $2.2 \times 10^{-26}$ cm$^6$/s, and the diffusion barrier radius $b$ to be $2.3 \times 10^{-4}$ cm. These values were calculated using the dilute impurity approximation. Thus it is not clear what thier physical

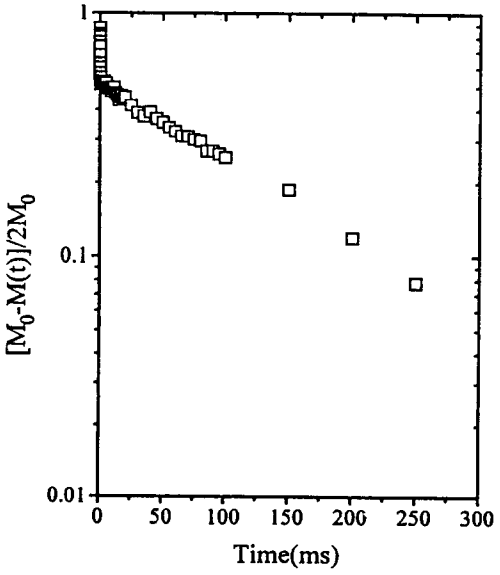


Fig. 3. Nuclear magnetic relaxation at the $^1H$ NMR frequency of 35 MHz.

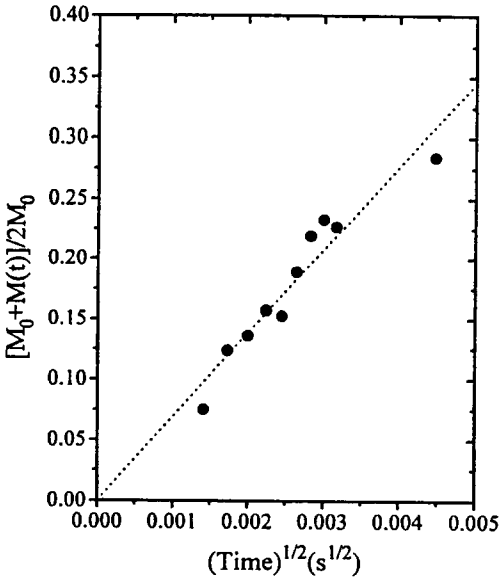


Fig. 4. Recovery of magnetization $M_z(t)$ immediately after saturation, from Fig. 3. The dotted line is the straight line fit.

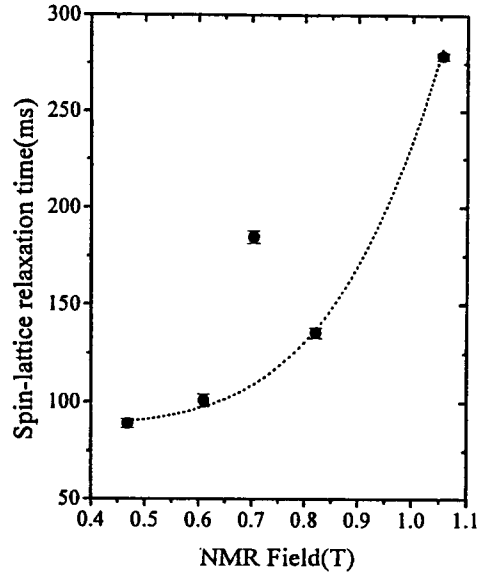


Fig. 5. The long-time spin-lattice relaxation time $T_1$ vs. the external magnetic field. The dooted line is a fit of $T_1 \propto H^{5.5}$ excluding the point at 0.7 T.

significances are since our system actually consists of dense paramagnetic ions.

The spin-lattice relaxation time ($T_1$) for the long-time exponential relaxation as a function of the external magnetic field is shown in Fig. 5. An anomalous deviation around 0.7 T is noticed again, which corresponds to the field of an anomalous dip in the linewidth. It is not yet clear whether this anomalous behavior has anything to do with the spin-flop transition observed around 0.7-0.8 T at very low temperatures[2]. From a computer fit excluding this point, it is seen that the $T_1$'s follow the field dependence of $T_1 \propto H^n$, where $n = 5.5$.

It is interesting to compare this exponent with those from the magnetic field dependence of the nuclear magnetic relaxation when interactions between the paramagnetic ions are not considered. In that case, for $\tau < 1/\omega$ and $\tau < T_2$, field independence of $T_1$ is expected for the diffusion-limited case and $T_1 \propto H^1$ dependence is expected for the rapid diffusion case[5, 6, 10]. Obviously, our result deviates drastically from any of these dependences. This is in contrast to the previous relaxation behavior which looked like a diffusion-limited case. These apparent anomalies are understood considering that in our system, the no interaction approximation of the paramagnetic ions is not valid. In addition, a quasi-two-dimensional nature and the anisotropy in this system are expected to play a crucial role in the relaxation behaviors.

In summary, we have studied the external field dependences of the room temperature $^1H$ NMR of the anisotropic Heisenberg antiferromagnet $MnCl_2 \cdot 4H_2O$. As a result, we have seen some new behaviors previously not reported in the dilute paramagnetic systems. Anomalous behaviors in the linewidth and the spin-lattice relaxation time at the magnetic field of 0.7 T were also observed.

## Acknowledgements

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# Heisenberg 반강자성체 $MnCl_2\ 4H_2O$의 핵자기완화 연구

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넓은 범위의 $^1H$ 핵자기공명 자기장에서 Heisenberg 반강자성체인 $MnCl_2\ 4H_2O$에 대하여 상온 수소 핵자기완화를 연구하였다. $MnCl_2\ 4H_2O$는 상온에서 밀집한 상자성 $Mn^{++}$ 이온계이지만 희박한 상자성계에서 예상되는 특성을 보인 반면에 희박한 상자성 근사와 매우 다른 결과도 보였다. 또한 수소 원자핵들은 0.7 T의 외부자기장 부근에서 스핀-격자 완화시간의 이상거동을 보였다.