Cl-NMR study on field-induced magnetic order in quasi-one-dimensional antiferromagnet (CH$_3$)$_2$CHNH$_3$CuCl$_3$

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Abstract. (CH$_3$)$_2$CHNH$_3$CuCl$_3$ is described as the spin ladder system, which is composed of a strong ferromagnetic rung and a weak antiferromagnetic leg. Since the ferromagnetic dimer behaves like $S=1$ spin, this system can be treated as the $S=1$ quasi-one-dimensional antiferromagnet spin chain (so-called Haldane chain). Cl-NMR study under high-field up to 17.5T has been carried out in order to investigate the field-induced magnetic order in this system. In the lower field region below 10T, the signals from Cl-sites were observed as sharp NMR lines. These paramagnetic lines showed the split above $H_{\text{red}} \approx 12T \ (T=1.85K)$, demonstrating the existence of the staggered field due to the field-induced magnetic order. Around $H_N$, the resonance lines disappeared due to the critical slowing down when the applied magnetic field was perpendicular to the ladder, whereas they did not when the field was nearly parallel to the ladder. These results indicate that the spin dynamics around the field-induced magnetic order is anisotropic in this system.

1. Introduction

Two-legged spin ladder systems with ferromagnetic rung and antiferromagnetic leg with $S = 1/2$ has recently attracted attention, because their magnetic properties are similar to those of antiferromagnetic Heisenberg chains with $S = 1$, when the ferromagnetic exchange is dominant. In such a system, the energy spectrum forms an energy gap between the ground states and the first excited state, as Haldane conjectured [1,2] for integer spins.

The title compound (CH$_3$)$_2$CHNH$_3$CuCl$_3$ (abbreviated as IPA-CuCl$_3$) is a typical example of this type spin ladder system. It has a triclinic structure (space group P1), which is composed of a single chain of Cu$_2$Cl$_6$ dimers stacked along a-axis [3-5]. Formation of the ferromagnetic dimer of $S=1$ is reported to take place below $T=10K$, where the existence of the effective single-ions anisotropy has been proposed [6,7]. From the high-field magnetization process at $T=0.5K$, the critical fields and g values were obtained to be $H_{\text{red}}^c=H_c/2=10.4T$ and $g_A=2.11$, $g_B=2.06$ and $g_C=2.25$ [8]. In the high field above $H=10T$, the existence of the magnetic long range order has been confirmed by specific heat measurements [9]. However, the spin state in the ordered phase of this compound has not been reported yet. The purpose of this work is to investigate the field-induced magnetic order in this system from a microscopic viewpoint of Cl-NMR.
2. Experimental

We prepared single crystals of IPA-CuCl$_3$ by slow evaporation of propylalcoholic solutions of CuCl$_2$ and (CH$_3$)$_2$CHNH$_2$·HCl at 30°C. As-grown crystals are black colored and have a flat rectangular shape. Following Manaka's notation in Ref. 4, the three orthogonal surfaces of the single crystal are named as A, B, and C plane. A recent neutron experiment has shown that the normals of A and C planes are parallel with crystallographic c and b*-axes, and the normal of B plane nearly with a-axis [10].

NMR spectrum was measured by the conventional spin-echo method. The sample size was 4×6×10mm$^3$. The measurements up to 17.5T were realized by the 20 T-CSM at High Field Laboratory for Superconducting Materials at IMR. In order to discriminate the magnetic shift and the electric quadrupolar shift, angular dependence of the peak position was measured and fitted to the theoretical curve obtained by the numerical diagonalization of nuclear spin Hamiltonian. The hyperfine coupling constant was estimated by the comparison between the temperature dependence of the peak shift and the uniform magnetization measured by VSM. The spin-spin relaxation $T_2$ was obtained from the decay rate of the spin echo amplitude against the separation between excitation and refocusing pulses.

3. Results and discussion

Figure 1 shows the rotation-angle dependence of the peak position of $^{35/37}$Cl at paramagnetic state ($T=4.2K$). Considering the fact that there exist crystallographically inequivalent three Cl sites in this compound, we expect that totally the eighteen peaks are observed in Cl-NMR spectra, though some lines are invisible because of less intensity. Theoretical curves are calculated by the perturbation method with the assumed parameters of Cl$_1$, Cl$_2$ and Cl$_3$ sites.
Figure 3. The rotation-angle dependence of the resonance lines of $^{35/37}$Cl under various fields at $T=1.85K$ for $\nu_0=45MHz$. In lower field region below 10T, NMR spectra are fitted with the theoretical curves of the paramagnetic state as shown in Fig. 2.

$\nu_{Q1}=10.5MHz$, $\eta_1=0.68$, $K_1=6\%$, $P_1=(0.36, 0.93, -0.10)$, $\nu_{Q2}=13.1MHz$, $\eta_2=0.5$, $K_2=-6\%$, $P_2=(-0.15, 0.18, 0.97)$ and $\nu_{Q3}=11.1MHz$, $\eta_3=0.58$, $K_3=4\%$, $P_3=(0.55, 0.55, 0.61)$, where $\nu_Q$, $\eta$, $K$ and $P$ are quadrupole frequency, asymmetry parameter, Knight shift and the direction of principle axis of electric field gradient. Considering the rough approximation of neglecting the anisotropy in $K$, calculated curves seem to well reproduce the observed data. The rates of $\nu_Q$’s agree with the calculation by the point charge model, in which the summation over the $\pm 20$ unit cells were taken, for all the Cl sites. However $\eta_2$, $P_2$ and $P_3$ show an appreciable disagreement from the point charge model. The disagreement for Cl$_2$ and Cl$_3$ sites, which locate at the position near the adjacent dimer, are considered to be due to the slight change in the stacking interval or direction of Cu$_2$Cl$_6$ dimers at low temperatures.

Figure 2 shows plot of the resonance shift versus magnetization with an implicit parameter of temperature in the field $H \perp B$-plane. From the relation of $\delta K=AM$, Cl peaks are classified into the three groups with different hyperfine coupling constants, $A_1=3.5T/\mu_B$, $A_2=2T/\mu_B$ and $A_3=7T/\mu_B$, where the indices 1-3 correspond to these for $\nu_Q$.

Figure 3 shows the rotation-angle dependence of the resonance lines of $^{35/37}$Cl for various fields at $T=1.85K$. At this temperature the compound has been reported to undergo the magnetic order around $H_{N}^{\text{red}}=12T$ [8]. In lower field region below 10T, NMR spectra are fitted with the theoretical curves of the paramagnetic state. In high field region above the critical field $H_{N}^{\text{red}}=12T$, the number of the NMR resonance lines is explicitly increased. Figure 4 shows the field dependence of the number of NMR peaks. Above $H=12T$ the number of NMR peaks at $T=1.85K$ is twice larger than that at $T=4.2K$. These results indicate that resonance lines are split by the presence of the staggered field, and hence the spin structure in the field-induced ordered state is simple antiferromagnet.

One must note, in Fig. 3, that the resonance lines disappear due to the critical slowing down within the field region of 1.5 T width around $H_N$ when the applied magnetic field is along the normal of C plane, which was perpendicular to the ladder, whereas they don’t when the
Figure 4. The number of observed peaks versus magnetic field at $T=1.85$K and 4.2K. Above $H=12$T, the number of NMR peaks at $T=1.85$K becomes approximately twice larger than that at $T=4.2$K.

Figure 5. The temperature dependence of the spin-spin relaxation rate $T_{2G}^{-1}$. (a) The magnetic field of 11.9T is applied along the normal of A-plane. The transition temperature is $T_N \simeq 1.5$K. (b) The magnetic field of 9.45T is applied along the normal of C-plane. The transition temperature is $T_N \simeq 0.5$K.

magnetic field is along the normal of B plane, which is nearly parallel to the ladder. Figure 5 shows the temperature dependence of spin-spin relaxation time $T_{2G}$ in the configuration of $H \perp$ A-plane and C-plane. Around $T_N$ the spin-spin relaxation rate $T_{2G}^{-1}$ shows a diverging behavior, which is the cause of the disappearance of resonance lines around $T_N$. This divergence is considered to be brought about by the critical slowing down of the spin fluctuation around the second order phase transition.

4. Summary
We have investigated the field-induced magnetic order in $(\text{CH}_3)_2\text{CHNH}_3\text{CuCl}_3$ from microscopic viewpoint by means of the high-field Cl-NMR. At the paramagnetic state the hyperfine coupling constants and eqq-interaction parameters of $^{35}\text{Cl}$ have been obtained. In the ordered state above $H_N$, the paramagnetic lines have shown the split, demonstrating the existence of the staggered field in the field-induced ordered state. The disappearance of the signal due to the critical slowing down around $H=H_N$ has occurred only in the configuration that the applied field is perpendicular to the ladder, indicating that the critical phenomenon is anisotropic. Around $T_N$ the spin-spin relaxation rate $T_{2G}^{-1}$ has shown a diverging behavior, which is the cause of the disappearance of resonance lines around $T_N$.

References
[1] Haldane F D M 1983 Phys. Lett. A 93 464
[2] Haldane F D M 1983 Phys. Rev. Lett. 50 1153
[3] Roberts S A, Bloomquist D R, Willett R D and Dodgen H W 1981 J. Am. Chem. Soc. 103 2603
[4] Manaka H, Yamada I and Yamaguchi K 1997 J. Phys. Soc. Jpn. 66 564
[5] Masuda T, Zhelev A, Manaka H, Regnault L -P, Chung J -H and Qiu Y 2006 Phys. Rev. Lett 96 047210
[6] Manaka H, Yamada I, Hagiwara M and Tokunaga M 2001 Phys. Rev. B 63 144428
[7] Manaka H and Yamada I 2000 Phys. Rev. B 62 14279
[8] Manaka H, Yamada I, Mushnikov N V and Goto T 2000 J. Phys.Soc. Jpn. 69 675
[9] Manaka H, Yamada I, Honda Z, Aruga Katori H and Katsumata K 1998 J. Phys. Soc. Jpn. 67 3913
[10] Manaka H: private communication.