μSR study on quantum spin system NH_4CuCl_3

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Abstract. The quantum spin dimer system NH_4CuCl_3 has a gapless ground state with $T_N = 1.3$ K, and shows plateaus in the high-field magnetization at 1/4 and 3/4 of the saturation magnetization, the mechanism of which has not yet been resolved until now. The three dimer model recently proposed by Matsumoto, which seems well accounting for the emergence of plateaus, predicts the existence of three magnetically-inequivalent dimers. In order to test the model, we have measured transverse-field (TF) muon depolarization curves. In fourier transform of TF muon depolarization curves, we observed homogeneous single peak at $T > 100$ K. Below 70 K, the peak showed rapid broadening, and split into multiple peaks in still lower temperatures, supporting the idea of the three dimer subsystems.

1. Introduction

Quantum spin systems have been attracting much interests in last two decades both experimentally and theoretically, because these systems exhibit numerous peculiar magnetic features, as represented by the triplon Bose-Einstein Condensation (BEC) in spin gap systems[1, 2] and the magnetization plateaus[3], which cannot be interpreted by conventional classical spin vector models. The former is observed as a field-induced magnetic ordering in the spin gap systems such as $KCuCl_3$ and $TlCuCl_3$[4, 5, 6], which are isomorphous of the title compound NH_4CuCl_3[7, 5, 8]. The field-induced magnetic ordering was captured as the Bose-Einstein condensation of triplons by mapping the spin gap system to the system consisting of boson with magnetic moment, triplon[2]. Namely the ordering can be interpreted as the superfluid-insulator transition induced by varying the chemical potential μ corresponding to the magnetic field H in the original spin system. The superfluid-insulator transition occurs when the hopping of triplon t is more dominant than the repulsive interaction of triplons U, and hence the triplons are mobile[9].

On the other hand, when U is more dominant than t, the created triplons prefer to distance from one another so that a superlattice of triplons, which can be interpreted as the formation of the Wigner crystal of triplons, may appear at a certain fractional number of triplons. In the superlattice phase, a finite energy is needed to create an additional triplon, *i.e.* $dn/d\mu = 0$, where n is the total triplon density corresponding to the magnetization M in the original spin system so that the magnetization plateau emerges in the superlattice phase. Actually, such superlattice of triplons has been observed in the orthogonal dimer system $SrCu_2(BO_3)_2$[10] at the 1/8-plateau phase[11, 12]. However, the case is not directly applied to NH_4CuCl_3 system, which basically has the same crystal structure as those BEC-systems of $KCuCl_3$ and $TlCuCl_3$; its only major difference is the existence of non-centrosymmetric molecule NH_4[7]. At room temperatures, where NH_4 molecules are rapidly spinning, the space group belongs to $P2_1/c$, the same as that for $KCuCl_3$ and $TlCuCl_3$. With lowering temperature as reported recently by the elastic neutron experiment, the NH_4 system exhibits the two structural phase transitions at $T_1 \approx 156$ K and at $T_2 \approx 70$ K. At $T = T_1$, crystal structure changes into $P\bar{1}$. At $T < T_2$, the unit cell size along the b direction is doubled[13]. These phase transitions are believed to be concerned with a freezing of rotational motions of NH_4 molecules.

Based on these experimental results, Matsumoto[14] has recently proposed a completely different theoretical model, which assumed three distinct magnetic dimer sublattices and successfully reproduced the magnetization plateaus as well as the field dependence of the resonance frequencies of ESR[15, 16]. He also proposed a possible geometrical configuration of field-induced triplons, which however was not in accordance with the recent NMR results[17]. The motivation of this paper is to test the model by investigating whether or not there exist magnetically-inequivalent dimers in the paramagnetic state by μSR technique, which is a powerful tool for the detection of microscopic inhomogeneity, both static or dynamic[18, 19, 20].

Before showing experimental procedures, we briefly describe the structural and magnetic properties of NH_4CuCl_3. The crystal structure shown schematically in Fig. 1 is composed of planar dimers of Cu_2Cl_6, in which Cu^{2+} ions have spin-1/2. The dimers are stacked on top of one another to form infinite double chains parallel to the crystallographic a-axis. These double chains are located at the corners and centre of the unit cell in the b-c plane, and are separated by NH_4^+ molecules. Under zero field, NH_4CuCl_3 is a gapless antiferromagnet with $T_N = 1.3$ K[13]. It shows in the magnetization process at one-quarter and three-quarters of the saturation magnetization[8], *i.e.*, for $H||a$, these plateaus are observed in 5.0 T $< H < 12.8$ T, and 17.9 T $< H < 24.7$ T, respectively, and the magnetization saturates at 29.1 T. The magnetization plateaus are observed irrespective of the field direction, suggesting that the origin of the plateau can be attributed to quantum effect.

2. Experimental details

Single crystals of NH_4CuCl_3 were made by evaporation method[6]. They were distorted hexagonal rod-shaped with a typical size of 100 mm^3. Transverse-field (TF) muon spin depolarization was measured on the DOLLY instrument at Paul Scherrer Institute (PSI) utilizing positive muons with an energy of 4.1 MeV implanted into the samples. The angle between muon spin polarization and muon-beam direction is set as 45 degrees by the spin rotator. About 10 crystals were mounted on the silver plate so as that b-axis was parallel to the muon-beam direction. An external magnetic field of 0.49 T was applied parallel to the sample b-axis. All TF experiments were carried out after a field-cooling procedure. A conventional ^{4}He flowing cryostat was used for temperature control for the temperature range between 2.3 to 140 K. Each relaxation curve contains approximately 10000 data bin with a width of 0.977 ns. Fast fourier transform was applied to 16384 data extended by zeros-filling, which enabled us to obtain the frequency resolution of 0.0625 MHz. The typical statistical average for each curve was 50 Mev.

3. Results and discussion

Observed TF muon depolarization curves are shown in Fig. 2, where one can clearly see the muon spin rotation with a frequency approximately 66.4 MHz in the TF of $H_0 = 0.49$ T. The amplitude of oscillation decays monotonically with time. The decay becomes faster with lowering temperatures. In fourier transform of TF muon depolarization curves shown in Fig. 3,

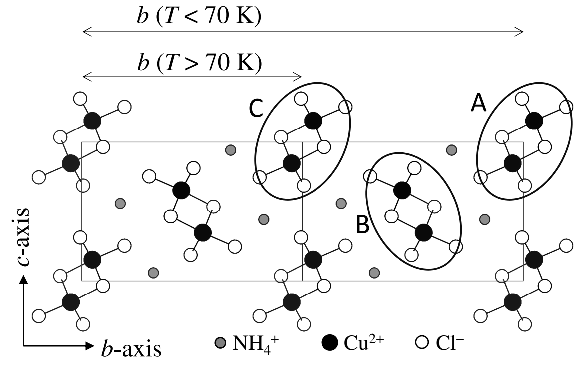

Figure 1. The unit cell of NH_4CuCl_3 in the bc plane below 70 K. A-, B- and C-dimers denote the magnetic dimer structure of Cu^{2+} ions proposed by Matsumoto et al[14]. The temperature dependent b-axis is shown by horizontal arrows[13].

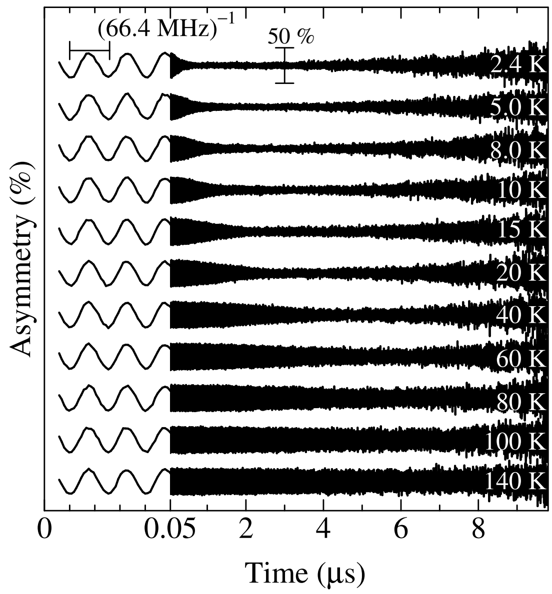

Figure 2. Transverse-field (TF) μSR time spectra obtained under $H = 0.49$ T at various temperatures.

we observed homogeneous single peak with a narrow width of nearly the resolution limit in high temperature region $T > 100$ K. With decreasing temperature, it shows a gradual broadening below 70 K and bears three peaks overlapping with each other as can be seen by the Gaussian deconvolution shown in Fig. 3. With further decreasing temperature, the distance between these three peaks increases, and at around 10 K, still other peaks emerge. At 2.4 K, the entire width reaches 4 MHz, which corresponds to 0.029 T of the hyperfine field. We plotted the peak positions against the temperature in Fig. 4.

The temperature where the peak starts to split is around 70 K just corresponds to the structural phase transition reported by the elastic neutron experiments[13]. Below this temperature, and above 20 K, muons sense three different hyperfine fields, the fact of which indicates two possiblities. One is that there are three muons' stopping sites in the elongated unit cell show in Fig. 1, and that each site has a different hyperfine field. In this case, observed peak split shows a direct evidence for the existence of three magnetically-inequivalent dimers in the unit cell. These dimers are expected to show a magnetic order with many sublattices. Actually, the recent zero-field (ZF) μSR in the ^{3}He temperature range reports a muon rotation spectrum with multiple components below $T_N = 1.3$ K[13, 21].

On the other hand, however, if there is only one muons stopping site in the unit cell, the observed split should indicate the macroscopic phase separation of the sample in the paramagnetic state. Since no anomaly is reported sofar in the paramagnetic susceptibility [8], the latter possibility seems to be unlikely. However, in order to confirm the existence of multiple muon stopping sites, the potential calculation by the density functional theory (DFT) is indispensable, and is now in the progress. The knowledge of the hyperfine fields obtained by the present work must be of help for the calculation.

Finally we refer the emergence of a wide spectrum bearing multiple peaks below 10 K. This can be due to the development of antiferromagnetic instability toward the phase transition at $T_N = 1.3$ K[13]. Generally, in the vicinity of the critical temperature, the slow fluctuation dominated with a long wavelength component grows in samples. However, considering the hyperfine coupling constant in other usual quantum spin magnets [18], the magnitude observed hyperfine fields in spectra seems to be a little bit too large to be considered as broaden by this instability. So we also consider the other possibility that the number of the muon stopping site may be larger than three.

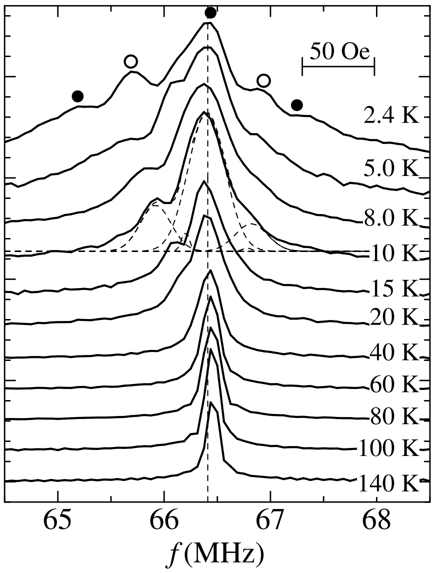

Figure 3. Fourier transform of TF muon spin depolarization curves. The vertical line shows the zero shift position. Dots at T = 2.4 K correspond to Fig. 4. Dashed curves show Gaussian deconvolution.

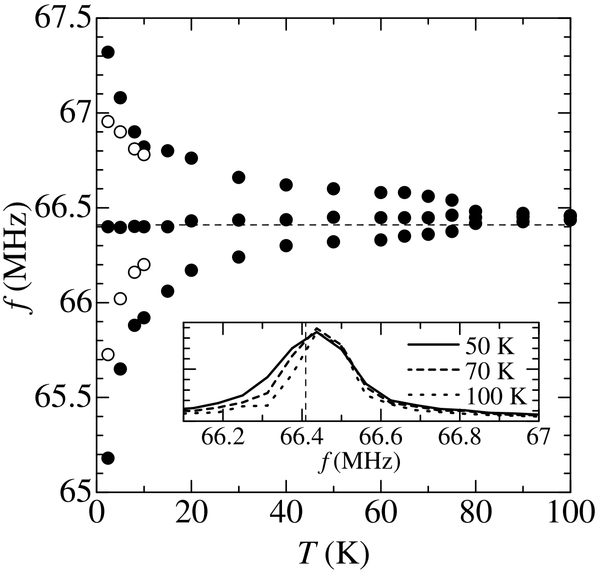

Figure 4. The temperature dependence of the peak positions in the FT spectra. Horizontal line shows the zero shift position. Inset shows the enlarged spectra around 70 K.

4. Conclusion

We have measured TF-μSR spectra for NH_4CuCl_3, and observed that a peak splits into three below 70 K, indicating the possibility of the existence of three inequivalent dimers in unit cell.

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