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High-field ^{1}H-NMR study around a 1/4 plateau of quantum spin dimer system NH_4CuCl_3

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Abstract. We have investigated high-field TF-μSR and ^{1}H-NMR on the $S = 1/2$ three dimensional spin dimer system NH_4CuCl_3, which shows a magnetic order at $T_N = 1.29$ K under zero field and the two-stepped plateaus in high field regions $H_{C1} = 5.0$ T – $H_{C2} = 12.8$ T and $H_{C3} = 17.9$ T – $H_{C4} = 24.7$ T. Both probes showed spectra containing multiple peaks corresponding to different hyperfine fields, demonstrating the existence of magnetically inequivalent dimers in a unit cell. In the slope-state field region $H < H_{C1}$, the existence of magnetic order was confirmed by the splitting in some of the NMR peaks. The whole width of NMR and μSR spectra increased with increasing field, and no drastic change in their profile was observed at H_{C1}. This indicates that the change in the spin state is continuous on entering the plateau state, and that no liquid-solid transition of magnons takes place at the phase boundary.

1. Introduction

The magnetization process of quantum spin systems is attracting much interest, because some systems show the magnetization plateaus which cannot be understood in terms of the conventional classical spin vector models [1]. NH_4CuCl_3 is an $S = 1/2$ three dimensional spin dimer system, which shows two-stepped magnetization plateaus at 1/4 and 3/4 of the saturation magnetization. The plateaus appear for any field directions, indicating that its mechanism roots in the quantum effect. At zero field, NH_4CuCl_3 does not have a spin excitation gap, and shows a magnetic order at $T_N = 1.29$ K [2, 3], which slightly increases with increasing field, takes maximum of 1.6 K at 2.7 T, and decreases to zero at $H_{C1} = 5.0$ T, as shown in Fig. 1(a). The 1/4 plateau appears in the field region between H_{C1} and $H_{C2} = 12.8$ T, and the 3/4 plateau, between $H_{C3} = 17.9$ T and $H_{C4} = 24.7$ T for the field direction $H \parallel b$-axis [4]. So far, to explain the mechanism of plateaus, many theoretical models have been proposed [5, 6]. Among them, Matsumoto [7] and Rüegg [3] proposed independently the inequivalent dimer model, in which they suggest the existence of a gapless dimer and the other two dimers with different gaps. Although, $^{63/65}$Cu- and $^{35/37}$Cl-NMR [8] and μSR experiments [9] support the existence of such inequivalent dimers in the paramagnetic state below 70 K, detailed spin states in and out of the plateau-field region are still veiled. Another interesting topic in this compound is the possibility of change anomaly due to a non-collinear spin structure in the ordered state. In the magnon Bose-Einstein condensation (BEC) for the spin dimer system such as $TlCuCl_3$ [10, 11],

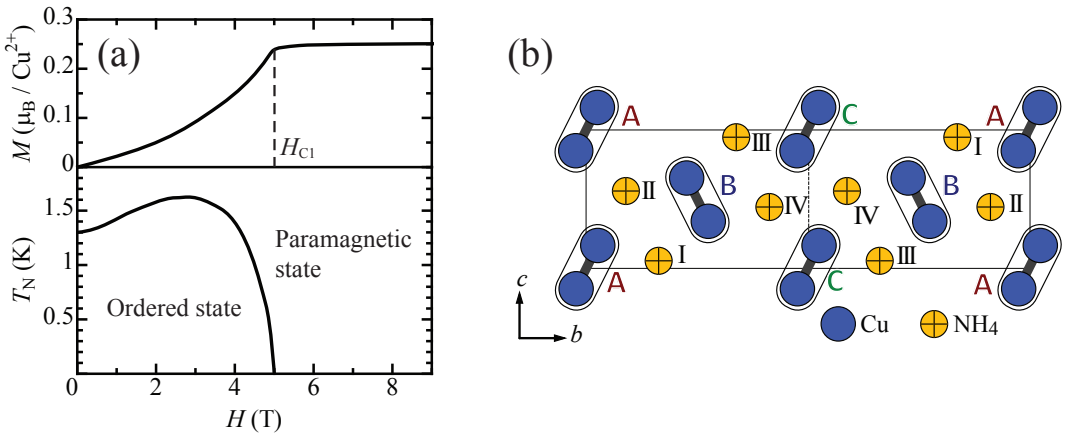

Figure 1. (a) Schematic phase diagram based on specific heat [2] and neutron scattering [3] (below) and magnetization curve in $H \parallel b$-axis [4] (top). (b) Schematic crystal structure of NH_4CuCl_3 below 70 K, where b-axis is doubled due to structural phase transition [3].

which is isomorphic to NH_4CuCl_3, the magnetic order within the moment perpendicular to the applied field is accompanied by the charge and lattice distortion [12, 13]. These can possibly be found in the present system. In order to investigate the spin state in the paramagnetic and ordered state microscopically, we have performed ^{1}H-NMR and transverse-field (TF) μSR in a wide field region up to 9 T.

2. Experimental

The sample of the single crystals is prepared by a slow evaporation method [4]. The crystal is of compressed hexagonal rod shaped with a typical size of 15 mm^3. The a-axis is along the rod, and the b, perpendicular to the largest facet. For discussion on NMR and μSR results, we refer here the detailed crystal structure, the schematic of which is shown in Fig. 1(b). At high temperatures, the unit cell contains net two dimers [14]. This unit cell is doubled along b-axis at 70 K due to a structural transformation, and at lower temperatures, there are three crystallographically inequivalent Cu_2O_6 dimers denoted as A, B and C [3]. The NH_4 molecules, which are an NMR-target, locate at the interstitial sites between dimers [14]. We denote them by the number as I – IV. For example, the NH_4 molecule II is located closer to the dimer A compared with III or IV, indicating that we may get information concerning the inequivalent dimers through ^{1}H-NMR.

^{1}H-NMR experiments were performed by the conventional spin-echo method at temperatures between 0.3 and 2.3 K, and in magnetic fields up to 8.3 T. Applied field was parallel with b-axis. NMR spectra were obtained by recording the spin-echo amplitude against magnetic field, which were slowly varied within a narrow region at around the zero shift position [15, 16].

Transverse-field (TF) μSR experiments were performed at the πE3 beamline of the Paul Scherrer Institute (Villigen, Switzerland), using the HAL-9500 μSR spectrometer [17]. Under the TF between 0.49 and 8.0 T parallel with b-axis, μSR time spectra were obtained at the temperatures of 0.1 and 1.5 K. The data length of each spectrum was 409600 bins, corresponding to the time span of 9.5 μs. They were converted to frequency spectra by FFT on the extended 933888 data points with the zero-filling technique.

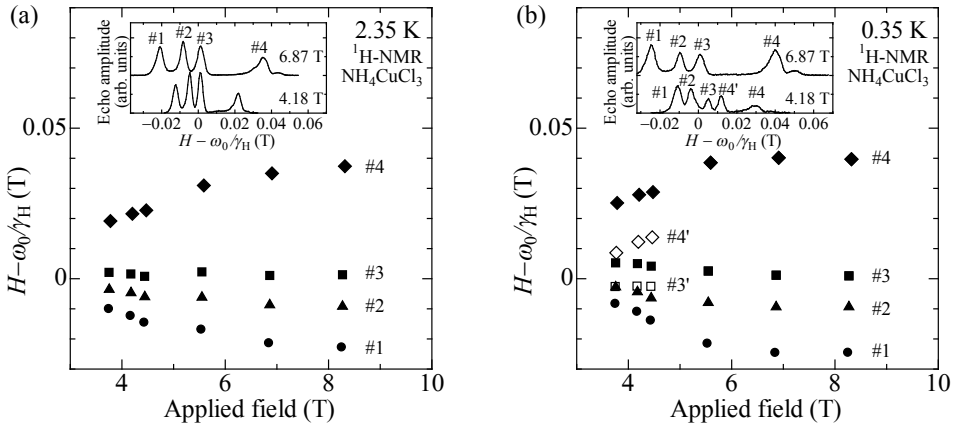

Figure 2. Field dependence of the peak shifts of ^{1}H-NMR at (a) 2.3 K and (b) 0.3 K, corresponding to the paramagnetic and the ordered state, respectively. Typical spectral profile are shown in each inset, where ω_0 is the frequency of NMR measurement. Observed peaks are denoted as #1–#4. At 0.35 K, the two of them, #3 and #4 showed splitting denoted as #3' and #4', respectively.

3. Results and Discussion

Typical profiles of ^{1}H-NMR spectra and the field dependences of the peak shifts of ^{1}H-NMR measured at 2.3 and 0.3 K are shown in Fig. 2(a) and (b), respectively. At 2.3 K, that is, in the paramagnetic state, the observed four peaks #1–#4 may come from the four NH_4 molecules in a unit cell. The signal from each proton nucleus within a molecule must be all integrated within a dipole width to form a single peak. Among four peaks, #4 has negative shift, and the other three, nearly zero or positive. With increasing field, the whole width of the spectrum, that is, the distance between #1 and #4 increased monotonically, and stopped increasing at H_{C1}. The spectral profile did not show any drastic change at H_{C1}. At 0.3 K, although the overall profile of the spectrum was unchanged from 2.3 K, extra splittings were observed for #3 and #4 peaks below H_{C1}, that is, in a slope part of the magnetization curve. With increasing field, splitting width of #3 and #3', and of #4 and #4' increased until $H = H_{C1}$, where the extra peaks #3' and #4' vanished abruptly. The temperature dependence of the spectral profile is shown in Fig. 3, where one can see that with decreasing temperature the peak #3 and #4 show a splitting at the vicinity of reported $T_N(4.45\ \mathrm{T}) = 1.08$ K.

Fourier spectra of TF-μSR taken at 0.1 K and under various fields up to 8.0 T are shown in Fig. 4. Each spectrum consisted of a central peak at the zero shift position and many satellites at the both sides of the former. The spectral shape was asymmetric; the lower side tail was longer and contained more peaks than the higher side. Although the central peak with a large amplitude may include a small contribution from the stray muons, it clearly indicates that an appreciable part of the sample is in the paramagnetic state. With increasing field, the whole width of the spectrum increased until $H = H_{C1}$, where it reached 0.2 T, and stopped further increasing. There was no drastic change in the overall spectral profile, that is, the spectrum seems to broaden with keeping the similarity of the shape, which can be clearly seen by the marker lines in Fig. 4. When the temperature was changed from 0.1 K to 1.5 K over T_N under the fiield 1.0 T, an appreciable deformation took place in the spectrum including changes in peak positions as shown in the bottom of Fig. 4. In the plateau region, however, this deformation was not observed. Note that observed spectra contained more than 9 peaks, the number of which is apparently larger than that of inequivalent dimer sites, indicating that there are multiple muon

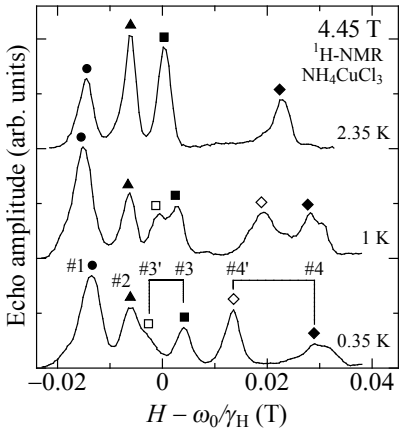

Figure 3. Temperature dependence of the spectra of ^{1}H-NMR at 4.45 T ($H < H_{C1}$).

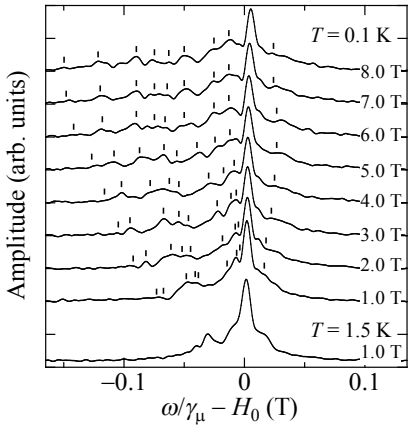

Figure 4. Field dependence of Fourier spectra of TF-μSR measured under constant field H_0 between 1.0 and 8.0 T. Vertical lines denote the peak positions.

stopping sites within a unit cell.

Now we discuss the spin state in and out of the first-plateau field region, and also over and below T_N. First, the observed four peaks in ^{1}H-NMR spectra do indicate that the four dimers in the unit cell are magnetically inequivalent. If all the dimers are equivalently magnetized along the same direction with the same amplitude, all four NH_4 sites have the same hyperfine field, hence one single peak in ^{1}H-NMR spectrum. Note that this dimer inequivalency exists not only in the ordered state but also in the paramagnetic state. These results are consistent with our previous μSR report [9]. Next, we discuss the relation between the magnetization process and the peak shifts. The peak shifts in spectra of both ^{1}H-NMR and TF-μSR increased monotonically with increasing field and stopped at $H_{C1} = 5$ T. This behavior simply traces the development of uniform magnetization M_z with increasing applied field [4]. Therefore, the difference in the shift of four peaks is considered to come from that in the z-component of the local magnetization borne by inequivalent dimers. For a rough estimation, if one assumes that only the A dimer is fully polarized within the plateau field region as proposed by Matsumoto [7], we can obtain the hyperfine field at NH_4 site II as -350 Oe, which is in accordance with the observation. The fact that the spectral profile was unchanged at H_{C1} demonstrates the continuity in the spin state with increasing the field. In other words, there is no solidification of field-induced magnons on entering the plateau region [18]. The detailed assignment of the observed NMR peaks to each NH_4 site is in progress.

In the field of slope region, the peaks #3 and #4 split at low temperature below T_N, supporting the existence of magnetic order with the ordered moment M_{xy} [7, 12]. The significant change in μSR spectra above and below T_N at 1 T is also considered to be due to this effect. In the plateau region, T_N becomes zero, and hence both the NMR and μSR spectrum should be unchanged with temperatures, as was observed.

Finally, we mention the possibility of lattice deformation. As stated above, in $TlCuCl_3$ isomorphic to the present system, the magnetic order was accompanied by the sizable change in the lattice constants and hence the finite jump in the hyperfine field at T_N [13]. In NH_4CuCl_3, we have observed the splitting width of the peaks #3 and #4 abruptly vanishes as entering the plateau region. However, in order to judge whether or not transition at H_{C1} is of first order, more detailed measurements in the vicinity of the phase boundary are necessary, and are now

in progress.

4. Summary

We have investigated the spin states of the $S = 1/2$ three dimensional spin dimer system NH_4CuCl_3 by high-field TF-μSR and ^{1}H-NMR. We have observed multiple peaks with different shifts both in NMR and μSR spectra, which clearly demonstrate the existence of inequivalent dimers in a unit cell. No drastic change in the spectral profile was observed at H_{C1}, indicating that the spin state changes continuously over H_{C1}, that is, no liquid-solid transition takes place in the field-induced magnons.

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