Cu-NMR Study on Field-Induced Phase Transitions in Quantum Spin Magnet NH₄CuCl₃

Shin-ichiro Tani,¹ Hiroaki Inoue,¹ Takao Suzuki,¹ Shigeharu Hosoya,¹ Kaori Inokuchi,¹ Takao Fujiiwara,¹ Takayuki Goto,¹ Hidekazu Tanaka,² Takahiko Sasaki,³ Satoshi Awaji,³ Kazuo Watanabe³ and Norio Kobayashi³

¹Department of Physics, Sophia University, Tokyo 102-8554, Japan
²Research Center for Low Temperature Physics, Tokyo Institute of Technology, Tokyo 152-8551, Japan
³Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Cu-NMR study under high-field up to 17 T has been performed on the three-dimensional spin dimer system NH₄CuCl₃, which shows the two-stepped magnetization plateaus. The local magnetization of Cu-site measured by NMR showed a significant deviation from the macroscopic magnetization at low temperatures, suggesting the localization of the field-induced triplons. In the high field region around 16 T, two inequivalent Cu sites are observed. Only one of the two sites shows a split in the resonance line below $T_N' = 3.2$ K, indicating the existence of the field-induced magnetic order, to which a part of spins in the system participate.

§1. Introduction

NH₄CuCl₃ is a three-dimensional spin-dimer magnet with the ladder-like crystal structure¹ isomorphic with TlCuCl₃ and KCuCl₃. The latter two have a gapped ground state at zero-field.² The field-induced triplet dimers move around in the crystal as nearly free bosons to show the Bose-Einstein condensation at low temperatures.³⁻⁵ The title compound NH₄CuCl₃ does not have a spin excitation gap at zero field. With increasing the magnetic field, gap is switched to be open and closed to show the magnetization plateaus at 5.2–13.7 T and 18.5–26.1 T ($H \parallel b$-axis).¹ Recent specific heat⁶ and neutron⁷ experiments by Kurniawan and Ruegg have reported that there exists magnetic order in the low-field-gapless region of Phase-I (0–5.2 T, $H \parallel b$-axis), and that its transition temperature strongly depends on the applied field. From kinks in the $M$-$H$ curves at low temperatures, Kurniawan⁶ suggests the existence of the field-induced order at the higher-field-gapless regions (Phase-II, 13.7–18.5 T; Phase-III, 26.1–30.4 T). He also predicts that the quarter of spins order in Phase-I, the half in Phase-II, and finally the remaining quarter in Phase-III. This view is supported by recent theoretical investigations by Matsumoto,⁸ who predicts that the existence of the three inequivalent dimers can be the origin both for the field-induced magnetic orders and the magnetization plateaus.

The purpose of this work is to investigate directly by Cu-NMR the microscopic spin state in high field region,⁹ where the detailed spin state or the existence of the phase transition have not been confirmed. First, by comparing the Knight shift and the macroscopic magnetization in the paramagnetic state, we show that the field-induced triplons in NH₄ system are localized. Next, from the splitting of the
resonance peaks in the high-field region around 16 T, we show that there exist the three inequivalent Cu sites, and that only one of them exhibits a field-induced magnetic order in Phase-II.

§2. Experimental

Single crystals of NH$_4$CuCl$_3$ and KCuCl$_3$ have been synthesized by the evaporation method and the longitudinal Bridgeman method. The space group of the crystal at room temperature belongs to $P2_1/c$. The basal plane of Cu$_2$Cl$_6$ dimer is stacked along $a$-axis. In a unit cell, there are the two dimers with different orientation, connected with the glide symmetry.

NMR spectra were obtained by recording the spin-echo amplitude against either the applied field or the orientation angle of the crystal axis with respect to the magnetic field. Frequency spectra of NQR under zero-field were obtained by plotting the amplitude of spin-echo signal against the irradiating rf-frequency. The temperature dependence of the macroscopic magnetization was measured by SQUID magnetometer below 6 T, and by vibrating sample magnetometer (VSM) above 6 T.

§3. Results and discussion

Figure 1 shows zero-field $^{63/65}$Cu-NQR spectra of NH$_4$CuCl$_3$ and KCuCl$_3$. Only the latter shows clear two peaks of the two isotopes. No NQR signal of NH$_4$CuCl$_3$ is observed in the temperature range surveyed down to 2.1 K. This may be due to the fact that the nuclear spin-spin relaxation time is extremely shortened, that is, to be below a microsecond by the fluctuation of the active on-site 3$d$-spins. Under the magnetic field around 2–10 T, both the systems are NMR-visible as shown in Fig. 2. There are parallel-shifted two rotating patterns, indicating the existence of the two Cu sites with different principal axes of electric field gradient tensor. This is quite a natural consequence of the fact that there are two dimers oriented differently in a unit cell. The observed patterns of both systems are well-reproduced by a simple calculation assuming parameters of a very small Knight shift $K \simeq 0.1\%$ and the quadrupole interaction parameter $^{63}\nu_Q \simeq 39.2$ MHz with the principal axis of the electric field gradient tensor directed nearly perpendicular to the Cu$_2$Cl$_6$ basal plane. The smallness of the shift in NH$_4$ system indicates that the observed signal belongs to the singlet site. The signal from the triplet site is invisible through NMR, because of the strong spin fluctuation of onsite 3$d$-spins.

The resonance line shift of KCuCl$_3$ in Fig. 3 shows the gap-like temperature dependence, which is identical to the macroscopic magnetization. This accordance indicates that the triplons are mobile in KCuCl$_3$ to produce a homogeneous field in the crystal. This picture is consistent with the inelastic neutron experiments on the triplon dispersion, and with the fact that triplons undergo the Bose-Einstein condensation at high field. The gap $\Delta_{\text{NMR}}$ decreases linearly with the applied field and reaches zero at $H_C^{||(1,0)\sim 25}$ T, which is consistent with the previously reported ESR results.
In NH₄ system, the temperature dependence of the local and the macroscopic magnetization differ below 6 K. As shown in Fig. 4, one can see a significant deviation of the two quantities below 6 K. The hyperfine coupling constant A determined in the temperature range above 6 K, where the two quantities are proportional, is about \( A \approx +7 \, \text{T/µ}_B \), which is positive and very small. Generally, divalent Cu atoms have a large and negative hyperfine coupling of a few tens Tesla, because of the core-polarization effect. So, the observed positive value means that the local magnetization probed by Cu-NMR and the macroscopic magnetization must show opposite temperature dependences. Note that this anomalous behavior is not merely due to the dipole anisotropy, and is originated in the electron spin state, for \( A \) takes the same value irrespective of the field directions parallel or perpendicular to the CuCl₆ basal plane, as shown in the left and the right panels of Fig. 4.

In order to explain this phenomenon, we have proposed the model that the field-induced triplons are spatially localized and contribute only to the macroscopic \( M \), but to the local magnetization of neighboring single sites. In high temperature limit, those triplons are mobile, and the system is homogeneous. As the temperature is lowered below a few tens Kelvin’s, they start to be localized and tend to stop at some spatial positions. For the local magnetic field at the singlet site is produced only by moving triplons, it always decreases with decreasing localization length of triplons, and hence with decreasing temperature. This follows the positive and small \( A \) in Fig. 4 above 6 K. Below 6 K, the localization length must be shortened to be below the mean dimer-dimer separation, so that the local magnetization completely saturates. This localization model is consistent with the recent neutron result reporting a very
Next, we show the result of the high field region, where the existence of the field-induced magnetic order of Phase-II has been suggested.\textsuperscript{6)} The profile of spectra at various temperatures is shown in Fig. 5. There observed the magnetically-inequivalent two sites, which show the opposite temperature dependence of the shift. We denote the peaks that show a decrease in the shift with decreasing temperature as site 1, and those which show an increase in the shift as site 2. The signals that come from the differently-oriented two dimers are degenerated, for the field is applied along the symmetric direction (\(k_b\)-axis). The temperature dependence of the shift is given in Fig. 6. Only the peaks belonging to the site 2 exhibit a split at \(T_N \approx 3.2\) K (\(\pm 0.2\) K). Other peaks belonging to the site 1 show no anomalies like a kink or jump at \(T_N\). The temperature dependence of the split width is shown in the lower panel of Fig. 6. There exists a finite jump around \(T_N\). The split widths of \(^{63}S_{2\pm}\) and \(^{63}C_{2\pm}\) at the lowest temperature 1.7 K are approximately 0.15 T and 0.3 T.

The observed split in the peaks of the site 2 is an evidence for the phase transition of Phase-II. This transition seems to be similar as that observed in the BEC in TlCuCl\(_3\), where the induced staggered moment causes the splitting through the anisotropy in the hyperfine coupling.\textsuperscript{10)} However, there is some fundamental differences between the two cases. First, we note that not all the spins contribute to the phase transition of Phase-II in NH\(_4\) system.\textsuperscript{6)} Apparently, peaks of the site 1 do not show any anomaly at \(T_N\). So far, Matsumoto has proposed the model,\textsuperscript{8)} that there exist the three inequivalent dimers with different critical fields. Our results
Fig. 5. Field-swept spectra at high field region in Phase-II. The assignment of the peaks are shown at the top of the panel, where S and C denote the satellite ($I_Z = +3/2 \leftrightarrow +1/2$) and central ($I_Z = +1/2 \leftrightarrow -1/2$) transition, and subscripts 1, 2 indexes the magnetically-inequivalent two sites.

are consistent with this model if one notes that only the two of them are observed by NMR. The site 1 corresponds to the quarter of dimers with the highest critical field. They are not occupied by triplons in the field region of Phase-II, and will order in higher field of Phase-III. The site 2 corresponds to the half of dimers\(^6\) with the intermediate critical field. They are partially occupied in the field region of Phase-II and \textit{do} order. The other quarter of dimers, which have already ordered in Phase-I, is NMR-inobservable, because of a strong fluctuation of the on-site 3d-spins. The opposite temperature dependence of the shift of the site 1 and 2 above $T_N$ is explained as the difference in the occupancy of localized triplons.\(^9,13\) The local magnetization of site 1, which are empty at $T = 0$ in the field region of Phase-II, always decreases with decreasing temperature as stated above. On the other hand, the local magnetization of site 2 always follows the macroscopic magnetization, because the site is considerably filled with triplons.

The finite jump in the split width at $T_N$ suggests the nature of the first order phase transition with a lattice distortion. However, the shift of the site 1 shows only smooth temperature dependence around $T_N$. This indicates that the lattice distortion, if exists, must be the one that retains the local structure around the site 1.

The split width at the lowest temperature in Phase-II is only one tenth of that reported in Tl-system.\(^10\) This implies that the ordered moment in NH$_4$-system is very small.\(^10\) We cannot determine at this stage whether or not the smallness comes from the fact that the field-induced triplons are localized in NH$_4$ system.
The experiment to determine the field-orientation dependence of the moment is in progress.

In summary, we have investigated Cu-NMR in NH$_4$CuCl$_3$ in the wide range of the field up to 17 T to find that the field-induced triplons tend to be localized at low temperatures, and that there exist the three inequivalent dimers, one of which shows the magnetic order at $T_N \approx 3.2$ K under the field around 16 T in Phase-II region.

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References

13) A. Oosawa et al., cond-mat/0304172.