# ESR Study of the Opening and Closing of the Field-Induced Gap in $NH_4CuCl_3$

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ESR measurements in the double-chain compound $NH_4CuCl_3$, which has magnetization plateaus at one-quarter and three-quarters of the saturation magnetization, have been performed in magnetic fields up to 30 T in the frequency range ~95−762 GHz. It is found that the frequency versus field diagrams for $H \parallel a$ and $H \parallel b$ coincide when normalized by the $g$ factors. In each plateau region, a pair of excitations expressed as $\omega = \gamma(H - H_{\rm lc})$ and $\omega = \gamma(H_{\rm hc} - H)$ are observed, where $H_{\rm lc}$ and $H_{\rm hc}$ are the lower and higher edge fields of the plateau, respectively. These two modes correspond to the quantum gap in the lower- and higher-field halves in the plateau region. [S0031-9007(98)08295-7]

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Recently, the plateau of the magnetization curve in a quantum spin system has been attracting considerable attention. The magnetization plateau is predicted at one-third of the saturation magnetization $M_{\rm s}$ in a spin-$\frac{1}{2}$ Heisenberg chain with ferromagnetic-ferromagnetic-antiferromagnetic interactions [1,2] and at half of $M_{\rm s}$ in a spin-$\frac{1}{2}$ antiferromagnetic alternating Heisenberg chain with the next-nearest-neighbor interactions [3,4] and a spin-1 antiferromagnetic alternating Heisenberg chain [5,6]. The plateau results from the quantum gap which opens between the ground state and the lowest excited state in the appropriate magnetic field range. Since the magnetization plateau appears irrespective of the magnetic field direction, the plateaus in these systems are different from those observed in the metamagnetic systems. Recently, Oshikawa *et al.* [7] demonstrated that the magnetization curves of general quantum spin chains with axial symmetry can have plateaus, and that the magnetization is quantized at the plateaus as $n(S - m) =$ an integer, where $n$ is the period of the ground spin state, $S$ is the magnitude of spin, and $m$ is the magnetization per site in the unit of $g\mu_{\rm B}$. The excitation gap responsible for the plateau can exist only when this condition is satisfied. All of the above-mentioned plateaus satisfy this quantization condition. Experimentally, the magnetization plateau has been observed at $(\frac{1}{2})M_{\rm s}$ in an $S = 1$ antiferromagnetic alternating chain system [$Ni_2$(methyl-bis(3-aminopropyl)amine)$_2$($\mu$-ox)($\mu$-$N_3$)]$ClO_4 \cdot 0.5H_2O$ [8].

In our previous paper [9], we have reported that the magnetization curve of $NH_4CuCl_3$ has two plateaus at one-quarter and three-quarters of $M_{\rm s}$. $NH_4CuCl_3$ is isostructural with $KCuCl_3$ at room temperature [10,11]. The feature of the crystal structure is the double chain of edge-sharing $CuCl_6$ octahedra along the crystallographic $a$ axis. From the chemical point of view, the present system seems to be described as an $S = \frac{1}{2}$ Heisenberg double-spin chain system.

In $NH_4CuCl_3$, two plateaus are clearly observed at $(\frac{1}{4})M_{\rm s}$ and $(\frac{3}{4})M_{\rm s}$. It was confirmed that the magnetization curves for $H \parallel a$ and $H \parallel b$ coincide when normalized by the $g$ factor, and that the plateaus appear in every external field direction. Therefore, the origin of the plateaus is attributed not to the magnetic anisotropy, but to the quantum effect. In the Heisenberg spin system, the presence of the magnetization plateau is equivalent to the presence of the excitation gap. Thus, it is evident that the ground state is gapped in the plateau region in $NH_4CuCl_3$. Since the slope of the magnetization curve near zero field is finite even at 0.5 K, it was concluded that $NH_4CuCl_3$ has a gapless magnetic ground state at zero field in contrast to isostructural $KCuCl_3$ and $TlCuCl_3$ which have a singlet ground state with an excitation gap [12–15]. It is considered that the magnetic ground state at zero field is due to the interchain interactions. Recently, Kolezhuk presented a theory [16] which describes the magnetization plateaus observed in $NH_4CuCl_3$ in terms of the weakly coupled dimer model on a three-dimensional lattice.

ESR is a powerful method to investigate the magnetic excitation with the high sensitivity and high energy resolution. The ESR measurements have been performed in many quantum spin systems with the zero-field gaps, such as the Haldane chains NENP and NINO [17–20] and the spin-Peierls system $CuGeO_3$ [21,22], and the transitions between the singlet ground state and the lowest excited triplet have been observed. However, there is no experimental study on the magnetic excitations in the system in which gapless and gapped ground states appear alternately as the external field is increased. $NH_4CuCl_3$

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shows the first example of such behavior. In order to investigate the magnetic excitation of $NH_4CuCl_3$ and the nature of the field-induced excitation gap, we carried out the high-field ESR measurement using single crystals. In this paper, we report the results of this study.

Single crystals of $NH_4CuCl_3$ were prepared by the method described in Ref. [9]. The ESR measurement was performed at the Institute for Materials Research, Tohoku University, using a multilayer pulse magnet which produces magnetic fields up to 30 T. Far infrared lasers (~323–762 GHz), backward traveling wave tubes (~200–240 and ~330–380 GHz), and Gunn oscillators (~95–190 GHz) were used as light sources. The Faraday configuration was taken in the present measurement. The transmitted light power was detected by a InSb detector. Most of the ESR data were collected at 1.6 K, where the magnetization plateaus are clearly seen. The magnetic field was applied parallel to the $a$ and $b$ axes. These crystallographic axes can be easily determined from the crystal shape [9].

Figure 1 shows the ESR absorption spectra observed at 1.6 K for $H \parallel a$ and $H \parallel b$. The resonance fields are indicated by arrows. As intrinsic ESR signals, we took absorption signals observed at the same positions for both increasing and decreasing external fields. A strong ESR signal, the resonance condition of which is described by $\omega = \gamma H$ with a gyromagnetic ratio $\gamma$, and several weak signals are observed. We label the strong ESR mode as the $\omega_{\mathrm{p}}$ mode. The structure around the $\omega_{\mathrm{p}}$ mode may be due to the Walker mode. The $\omega_{\mathrm{p}}$ mode is always observed down to 1.6 K and shows no decreasing tendency with decreasing temperature. The intensity of the additional weak ESR signals decreases with increasing temperature. The signals are barely detected at 4.2 K.

In Fig. 2, we summarize the resonance positions obtained at 1.6 K. We labeled the observed ESR modes as shown in the figure. The critical fields are $H_{c1} = 4.7$ T, $H_{c2} = 13.3$ T, $H_{c3} = 17.7$ T, $H_{c4} = 25.4$ T, and $H_s = 29.1$ T for $H \parallel a$ and $H_{c1} = 5.1$ T; $H_{c2} = 14.2$ T, $H_{c3} = 19.1$ T, $H_{c4} = 27.4$ T, and $H_s = 30.5$ T for $H \parallel b$ which are determined from the magnetization data at 1.5 K. The magnetization plateaus exist in the field ranges $H_{c1} < H < H_{c2}$ and $H_{c3} < H < H_{c4}$.

Next we discuss our present results. From Fig. 2, we notice that the frequency versus field diagrams for $H \parallel a$ and $H \parallel b$ have the same pattern. Then using the $g$ factors, $g_a = 2.17$ and $g_b = 2.06$ which are determined from the slope of the $\omega_{\mathrm{p}}$ mode, we normalize the resonance fields as shown in Fig. 3. From Fig. 3, we see that the frequency versus field diagrams for both the field directions coincide when normalized by the $g$ factor, i.e., the resonance condition in $NH_4CuCl_3$ is essentially independent of the external field direction. This indicates that the magnetic anisotropy or the staggered magnetic field due to the staggered modulation of the $g$ factor is so small that their contribution to the energy levels is negligible.

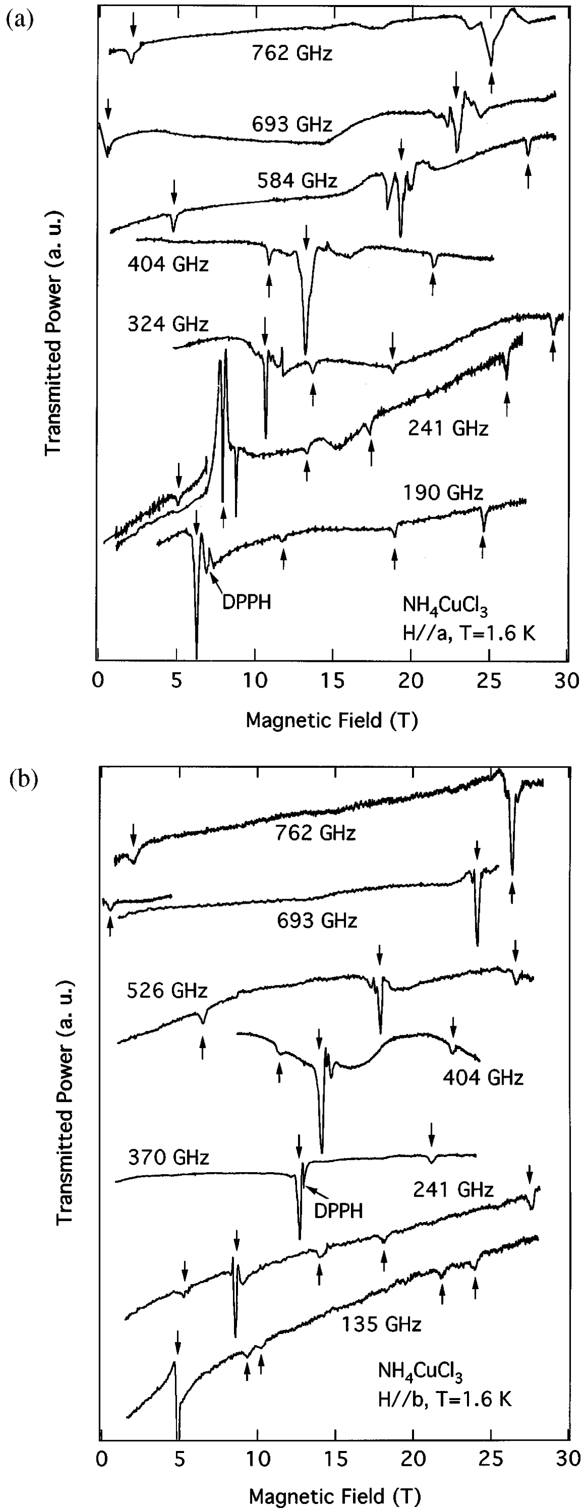

FIG. 1. ESR signals of $NH_4CuCl_3$ observed at 1.6 K for (a) $H \parallel a$ and (b) $H \parallel b$.

The intensity of the $\omega_{\mathrm{p}}$ mode is strong, irrespective of the resonance field and temperature. The $\omega_{\mathrm{p}}$ mode is assigned to the paramagnetic resonance mode or to the

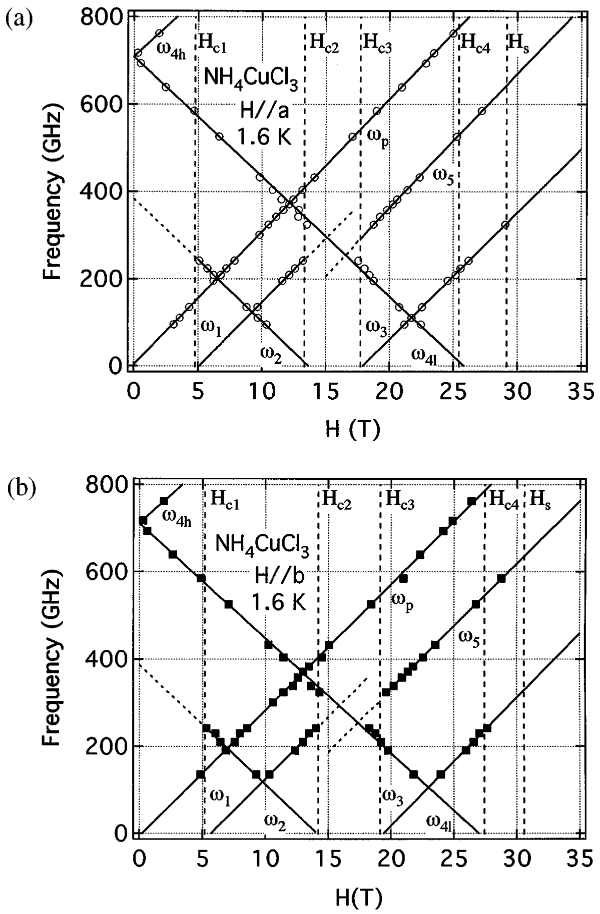

FIG. 2. Frequency versus field diagrams of $NH_4CuCl_3$ obtained at 1.6 K for (a) $H \parallel a$ and (b) $H \parallel b$.

collective mode such as the antiferromagnetic resonance (AFMR) mode. Even if the magnetic ordering exists at 1.6 K under the presence of magnetic fields, one of the AFMR modes can be written as $\omega = \gamma H$, because the magnetic anisotropy is very small in the present system. The presence of the strong $\omega_p$ mode for $H < H_{c1}$ is consistent with the gapless magnetic ground state at zero field.

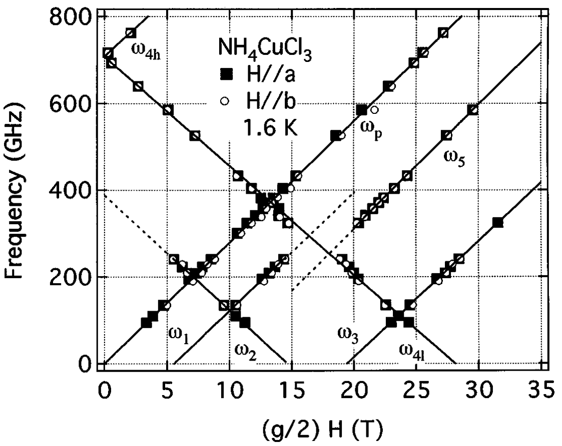

FIG. 3. Frequency versus field diagram of $NH_4CuCl_3$ normalized by the $g$ factors.

In each plateau region, a pair of weak ESR modes exists, i.e., the $\omega_1$ and $\omega_2$ modes for the first plateau, and the $\omega_3$ and $\omega_{41}$ modes for the second plateau. Their resonance conditions are described as $\omega_1 = \gamma(H - H_{c1})$, $\omega_2 = \gamma(H_{c2} - H)$, $\omega_3 = \gamma(H - H_{c3})$, and $\omega_{41} = \gamma(H_{c4} - H)$. It is noted that the $\omega_1$ and $\omega_2$ modes are observed only in the first plateau region, while the $\omega_3$ and $\omega_{41}$ modes are observed even outside the second plateau region. Besides the $\omega_1 \sim \omega_4$ modes, there is a weak $\omega_5$ mode. This mode is observed for $H > H_{c3}$.

In ESR, the excitation is restricted to the excitation at $Q = 0$ and the transition for $\Delta M_S = \pm 1, 0$ between two states with the same total spin $S$ is allowed, where $M_S$ is the magnetic quantum number. The transition between two states with different $S$ values and different wave vectors is forbidden in principle. However, the $\Delta S = \pm 1$ transitions between the singlet ground state at $Q = 0$ and the lowest excited triplet at $Q \neq 0$ have been observed in many spin gap systems, such as the Haldane chains NENP and NINO [17–20], the spin-Peierls system $CuGeO_3$ [21,22], and also in $KCuCl_3$ and $TlCuCl_3$ [23,24]. The transitions have been interpreted in terms of the additional interaction such as the staggered Zeeman interaction due to the staggered inclination of the principal axis of the $g$ tensor [25] and the Dzyaloshinsky-Moriya interaction [22–24], both of which are antisymmetric with respect to the interchange of the interacting spins. These interactions have matrix elements between the singlet ground state and the lowest excited triplet, so that the ground state has a small amount of triplet component, and that the small excited sate with the same energy level as that for the lowest excited triplet is produced at $Q = 0$. Consequently, the ESR transition for $\Delta S = \pm 1$ and $Q = 0 \rightarrow Q \neq 0$ can be observed, although its intensity is weak.

In $NH_4CuCl_3$, the AFMR modes should be represented as $\omega = \gamma H$ and $\omega = 0$, because the anisotropy is very small. Therefore, the weak ESR modes ($\omega_1 \sim \omega_5$ modes) cannot be interpreted in terms of the AFMR modes. The $\omega_{41}$ and $\omega_{4h}$ modes with the zero-field frequency of 710 GHz are typical of the transitions for $\Delta M_S = \pm 1$ and $\Delta S = 1$. We assign all the weak ESR modes to the transitions for $\Delta M_S = \pm 1$ and $\Delta S = \pm 1$. We consider that the weak ESR modes can be observed due to the same mechanism as mentioned above. If the staggered Zeeman interaction is responsible for these transitions, their intensity should increase with increasing resonance field. However, such behavior is not observed in the present system. We suggest that the Dzyaloshinsky-Moriya interaction which can exist between the neighboring $Cu^{2+}$ ions along the double chain enables these weak ESR excitations.

In each plateau region, we can see a pair of ESR modes $(\omega_1, \omega_2)$ and $(\omega_3, \omega_{41})$. Their resonance conditions can be expressed as $\omega = \gamma(H - H_{lc})$ and $\omega = \gamma(H_{hc} - H)$ with the lower and higher edge fields $H_{lc}$ and $H_{hc}$.

We conclude that these modes correspond to the lowest excitations from the gapped ground state, because their resonance frequencies become zero just at the edge fields. The $\omega_1$ and $\omega_3$ modes indicate that the excitation gaps start to open at the lower edge fields $H_{c1}$ and $H_{c3}$, while the $\omega_2$ and $\omega_{41}$ modes indicate that the excitation gaps close at the higher edge fields $H_{c2}$ and $H_{c4}$. At the center of the plateau, the gap attains the maximum $\Delta_{\max} = g\mu_B(H_{hc} - H_{lc})/2$, which is estimated as $\Delta_{\max}/k_B = 5.7$ and 5.0 K for the first and the second plateaus, respectively. At present, the meaning of the weak $\omega_5$ mode is not known.

In conclusion, we have presented the results of the high-field ESR measurements of $NH_4CuCl_3$ which shows the first example of the successive gapless-gapped phase transitions in magnetic fields. A strong ESR mode ($\omega_p$) expressed by $\omega_p = \gamma H$, and several weak modes are observed. The presence of the $\omega_p$ mode at low fields is consistent with the gapless ground state at zero field. It is found that the resonance conditions as well as the magnetization curves for $H \parallel a$ and $H \parallel b$ coincide when normalized by the $g$ factor. This indicates that the magnetic properties of $NH_4CuCl_3$ are isotropic both statically and dynamically. In the magnetization plateau region, there exists a pair of ESR modes expressed as $\omega = \gamma(H - H_{lc})$ and $\omega = \gamma(H_{hc} - H)$ with the lower and higher edge fields $H_{lc}$ and $H_{hc}$. These findings indicate that the quantum gap starts to open at the lower edge field of the plateau and closes completely at the higher edge field. The gap is described as $\Delta = g\mu_B(H - H_{lc})$ for $H_{lc} < H < (H_{lc} + H_{hc})/2$ and $\Delta = g\mu_B(H_{hc} - H)$ for $(H_{lc} + H_{hc})/2 < H < H_{hc}$. Thus, the magnitude of the gap becomes maximum at the center of the plateau.

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