

High-field and high-frequency ESR study of the Haldane state formed in the ferromagnetic and antiferromagnetic alternating Heisenberg chain system $(\text{CH}_3)_2\text{CHNH}_3\text{CuCl}_3$

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The compound $(\text{CH}_3)_2\text{CHNH}_3\text{CuCl}_3$ consists of ferromagnetic and antiferromagnetic alternating Heisenberg chains with $S=1/2$. According to recent electron spin resonance (ESR) experiments at 24 GHz, a pair of ferromagnetically coupled two spins, which is expressed as $\hat{S} \equiv \hat{S}_1 + \hat{S}_2$, behaves as a spin with $\hat{S}=1$ below 10 K, and therefore the magnetic ground state in this compound is the Haldane state. Then the dipole-dipole interaction and the anisotropic-exchange interaction between ferromagnetically coupled two spins act as a fictitious single-ion anisotropy, which removes the threefold degeneracy of the triplet state. To confirm the energy scheme of the nondegenerate triplet state, high-field and high-frequency ESR experiments up to 20 T and 540 GHz were performed on the single crystals. The absorption due to the $\hat{S}_z = -1 \leftrightarrow \hat{S}_z = 0$ transition in the triplet excited levels was observed below 330 GHz and 10 K. The sign and the value of the fictitious single ion anisotropy were determined to be $D^*/g\mu_B = -0.24$ to -0.48 T at 1.7 K. At 427.6 GHz and under an external field near 15 T, where the field-induced gapless state is formed, the absorption line that was thought to be antiferromagnetic resonance was observed at 1.7 K.

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I. INTRODUCTION

The $S=1/2$ compound $(\text{CH}_3)_2\text{CHNH}_3\text{CuCl}_3$ (abbreviated as IPACuCl₃) has been found to be a ferromagnetic and antiferromagnetic alternating Heisenberg chain system.¹ Since a pair of ferromagnetically coupled two spins, which we express as $\hat{S} \equiv \hat{S}_1 + \hat{S}_2$, behaves as a spin with $\hat{S}=1$, this compound is recognized as a good candidate of the Haldane system.² As a piece of evidence of formation of the Haldane state, the existence of an energy gap between the singlet ground state and the triplet first excited state was confirmed by magnetic susceptibility¹ and magnetization measurements.³ In an external field H , the triplet splits and the lowest component, $\hat{S}_z = -1$, crosses the singlet at a certain field, H_c . Above $H=10$ T, appearance of the magnetic-long-range order was confirmed by specific heat measurements under H .⁴ The magnetic-phase-transition temperature T_N versus the reduced magnetic field $gH/2$, reported in Ref. 4, is depicted as the line schematically drawn in Fig. 1. As can be seen in this figure, no phase transition occurs below the critical field $H_c(0 \text{ K}) = 10.1$ T.

In a recent paper⁵ concerning electron paramagnetic resonance (EPR) experiments performed on this compound at 24 GHz, the temperature (T) dependence of the EPR spectra was reported to exhibit phenomena that indicated a crossover of the spin state from $S=1/2$ to $\hat{S}=1$. That is, the EPR signal observed above 10 K is due to the $\Delta S_z = \pm 1$ transition between $S_z = +1/2$ and $S_z = -1/2$, whereas below 10 K, two signals that correspond to the $\Delta \hat{S}_z = \pm 1$ transition between $\hat{S}_z = +1$ and $\hat{S}_z = 0$, and between $\hat{S}_z = 0$ and $\hat{S}_z = -1$ were observed. Moreover, an additional weak signal due to the $\Delta \hat{S}_z = \pm 2$ transition between $\hat{S}_z = +1$ and $\hat{S}_z = -1$ was detected at half of the averaged field of the two signals. Therefore, we called it a half-field line.

The experimental result shown in Fig. 3(a) in Ref. 5, which exhibits split two lines, indicates that the degeneracy of the triplet at $H=0$ is removed for the following reason.⁵ Since the dipole-dipole interaction \mathcal{H}'_{DD} and the anisotropic-exchange interaction \mathcal{H}'_{AE} between ferromagnetically coupled two spins act as a single-ion anisotropy, $D^*[\hat{S}_z^2 - \hat{S}(\hat{S}+1)/3]$, such a fictitious single-ion anisotropy removes the threefold degeneracy of the triplet state, similar to the case of conventional $S=1$ compounds.⁶⁻¹⁴ From the angular dependence of the resonance field H_{res} at $T=4.2$ K shown in Fig. 7 in Ref. 5, the value of $|D^*|$ was determined. But the sign of D^* was impossible to determine from the data obtained at 24 GHz.

To determine the sign of D^* and obtain further information about the Haldane state in this compound, we performed

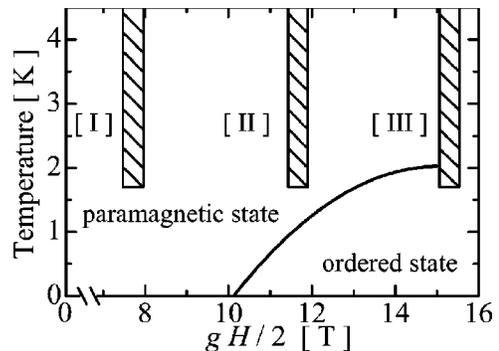


FIG. 1. Schematic drawing of the field-induced antiferromagnetic-transition temperature versus the reduced magnetic field $gH/2$ obtained by specific-heat measurements in Ref. 4. The critical field is $H_c(0 \text{ K}) = 10.1$ T. The three regions of the external field corresponding to the resonance frequencies, 216.4, 326.8, and 427.6 GHz are indicated as [I], [II] and [III], respectively. The lowest temperature in the present experiments was 1.7 K.

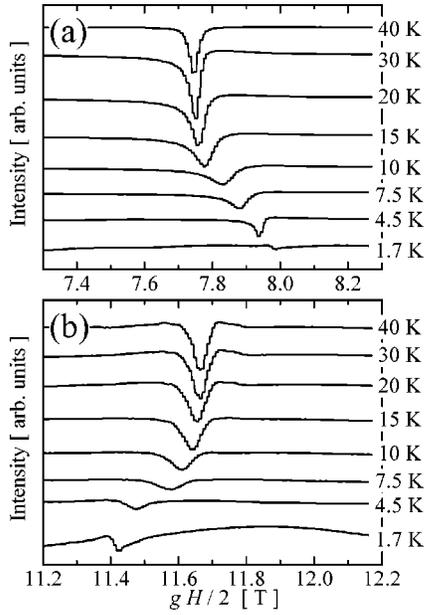


FIG. 2. The ESR spectra observed (a) at 216.4 GHz for $H \perp C$ plane and (b) at 326.8 GHz for $H \perp B$ plane. The abscissa is the reduced magnetic field given by $gH/2$.

electron spin resonances (ESR) measurements at frequencies up to 540 GHz. Corresponding to the increase in the frequency, the external field was also increased up to 20 T. Among the many experimental data that we obtained in the present experiments, here we show absorption spectra observed at three frequencies, 216.4, 326.8, and 427.6 GHz. The three regions of the external fields that correspond to these three frequencies are roughly indicated in Fig. 1, as [I], [II] and [III]. Since the minimum T in the present experiments was 1.7 K, region [I] and region [II] are over the paramagnetic state, whereas region [III] includes the antiferromagnetically ordered state as well as the paramagnetic state. Qualitative and quantitative changes in ESR spectra from paramagnetic to antiferromagnetic are therefore expected over region [III].

II. EXPERIMENTAL RESULTS AND DISCUSSION

ESR experiments were performed on single crystals at several frequencies in the range of 77–540 GHz using a millimeter vector network analyzer (AB millimeter, France) and a superconducting magnet (Oxford Instruments, UK). An external field H was applied along the normals of the three planes of the sample, A , B , and C plane, as named in Ref. 1. The direction of the magnetic chains is nearly parallel to the normal of the A plane. The absorption spectra were examined at various T in the range of 1.7–50 K.

Examples of the spectra observed at 216.4 GHz for the $H \perp C$ -plane and 326.8 GHz for the $H \perp B$ plane, i.e., over region [I] and over region [II] are shown in Figs. 2(a) and 2(b), respectively. As can be seen in these two figures, only a single absorption line was observed. The half-field line, which was observed at 24 GHz, was not detected. The position of the absorption line, H_{res} , observed at 40, 30, and 20

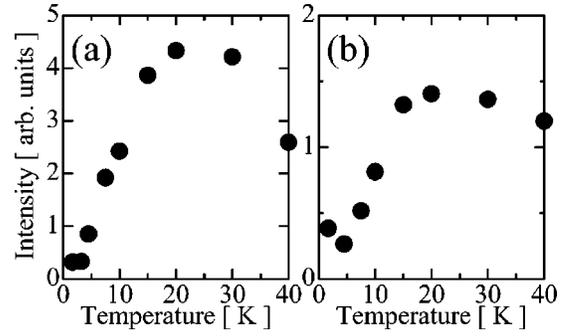


FIG. 3. The temperature dependence of the absorption intensity (a) at 216.4 GHz for $H \perp C$ plane and (b) at 326.8 GHz for $H \perp B$ plane. Both results indicate the existence of the energy gap.

K is almost the same in each case. But with further decreasing T , it shifts to the higher-field side for the $H \perp A$ plane as well as for the $H \perp C$ plane, whereas the single absorption line observed for the $H \perp B$ plane was found to shift to the lower-field side. Similar to the results observed at 24 GHz, the linewidth seems to reach a maximum around 10 K. The g values for the three directions of H determined below 330 GHz at 30 K were the same as those determined at 24 GHz.⁵

The T dependence of the absorption intensity of the observed lines at 216.4 and 326.8 GHz is shown in Figs. 3(a) and 3(b), respectively; the intensities in both cases tend to approach zero when T approaches 0 K, which is quite similar to that observed at 24 GHz.⁵

We now discuss the experimental results shown above. The resemblance of the intensities of the split two lines observed at 24 GHz indicates that the populations of spins on the $\hat{S}_z = -1$ level and the $\hat{S}_z = 0$ level are comparable with each other at H corresponding to 24 GHz. For resonance frequencies above 200 GHz corresponding to H above 7 T, however, the population of spins on the $\hat{S}_z = -1$ level should be extremely higher than that on the $\hat{S}_z = 0$ level. The intensity of the absorption line that corresponds to the $\hat{S}_z = 0 \leftrightarrow \hat{S}_z = +1$ transition is estimated to be less than 10^{-3} of the $\hat{S}_z = -1 \leftrightarrow \hat{S}_z = 0$ transition, and therefore the absorption due to the $\hat{S}_z = 0 \leftrightarrow \hat{S}_z = +1$ transition should be too weak to detect. The decrease in absorption intensity, shown in Fig. 3, is due to the decrease in the spin population on the triplet excited levels.

Referring to Eqs. (3.1) and (3.2) in Ref. 5, we try to determine the sign of D^* from the data shown in Figs. 2(a) and 2(b). When $H \parallel r$ where r is a vector of the distance between S_1 and S_2 , the resonance condition at a fixed frequency ω is

$$\hbar\omega = E_{1,0} - E_{1,-1} = g_{\parallel}\mu_B H_{\text{res}} - D^*, \quad (2.1)$$

where g_{\parallel} is the g value for $H \parallel r$. The observed shift of H_{res} to the lower-field side for the $H \perp B$ -plane ($H \parallel r$) indicates $D^* < 0$, shown in Fig. 2(b), because the decrease in $g_{\parallel}\mu_B H_{\text{res}}$ must be compensated by $-D^*$, which indicates that $-D^* > 0$. Similarly, if $|D^*| \ll g_{\perp}\mu_B H_{\text{res}}$, the resonance condition at a fixed frequency ω for $H \perp r$ is simplified as

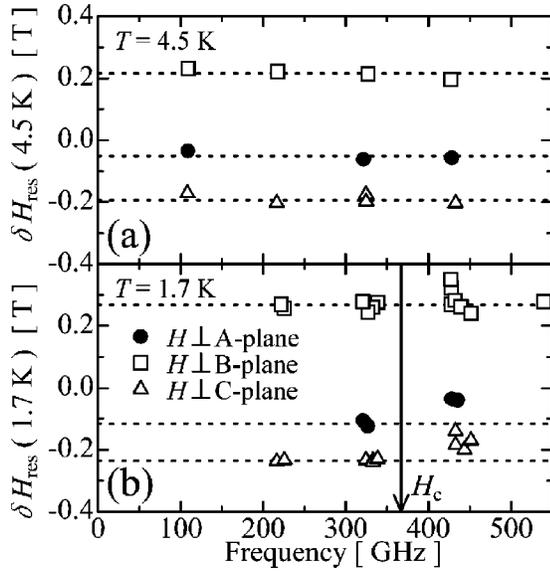


FIG. 4. The shift of the resonance field H_{res} from $H_{\text{res}}(30 \text{ K})$; $\delta H_{\text{res}}(T) \equiv H_{\text{res}}(30 \text{ K}) - H_{\text{res}}(T)$ for the absorption lines observed (a) at 4.5 K and (b) at 1.7 K are plotted up to 540 GHz. The ordinate is the reduced field given by $gH/2$. The arrow shown in (b) indicates the critical field $H_c(1.7 \text{ K}) = 13.1 \text{ T} = 367 \text{ GHz}$, at which the magnetic-phase transition from the paramagnetic state to the antiferromagnetic state occurs. The dashed lines show the fitting of $\delta H_{\text{res}} = \text{const}$ for the experimental data in the paramagnetic region.

$$\hbar \omega = E_{1,0} - E_{1,-1} = g_{\perp} \mu_B H_{\text{res}} + D^*/2, \quad (2.2)$$

where g_{\perp} is the g value for $\mathbf{H} \perp \mathbf{r}$ ($\mathbf{H} \perp \mathbf{A}$ and \mathbf{C} plane). Thus the shift of H_{res} to the higher-field side, as can be seen in Fig. 2(a), must be compensated by $D^*/2$, which indicates $D^* < 0$.

To confirm the shift of H_{res} from $H_{\text{res}}(30 \text{ K})$ at low T for several resonance frequencies, the values of $\delta H_{\text{res}}(T) \equiv H_{\text{res}}(30 \text{ K}) - H_{\text{res}}(T)$ observed at 4.5 K and at 1.7 K are shown in Figs. 4(a) and 4(b), respectively. As can be seen in Fig. 4(a), $\delta H_{\text{res}}(4.5 \text{ K})$ does not change with frequency. Moreover, $\delta H_{\text{res}}(1.7 \text{ K})$ below the critical field $H_c(1.7 \text{ K}) = 13.1 \text{ T} = 367 \text{ GHz}$, shown in Fig. 4(b), seems to be constant. This finding is reasonable because δH_{res} must be $-D^*$ for $\mathbf{H} \perp \mathbf{B}$ plane and $D^*/2$ for $\mathbf{H} \perp \mathbf{A}$ and \mathbf{C} planes, respectively, and thus it should be frequency independent. The disagreement of δH_{res} for $\mathbf{H} \perp \mathbf{A}$ plane with that for $\mathbf{H} \perp \mathbf{C}$ plane is probably due to the difference in the fictitious single-ion anisotropy between these two directions, which we neglected in the present analysis. From the data shown in Fig. 4(b) below H_c , we obtain $D^*/g\mu_B = -0.24$ to -0.48 T at 1.7 K. Since $D^* < 0$ is clarified, the energy schemes of the nondegenerate triplets for different directions of \mathbf{H} are like the ones shown in Figs. 10(b) and 10(c) in Ref. 5.

The absence of the half-field line in the present experiments is explained as follows. The three states $|\hat{S}_x, \hat{S}_z\rangle = |1,1\rangle, |1,0\rangle$ and $|1,-1\rangle$ are not eigenstates because non-diagonal elements, which are caused by \mathcal{H}'_{DD} and \mathcal{H}'_{AE} between ferromagnetically coupled two spins, can not be neglected. Therefore, the transition between $|1,1\rangle$ and $|1,-1\rangle$,

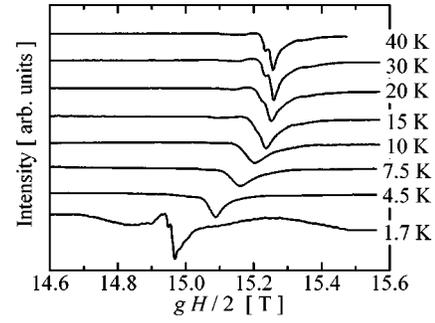


FIG. 5. The EPR spectra observed at 427.6 GHz for $\mathbf{H} \perp \mathbf{B}$ plane. The asymmetric lineshape observed above 10 K is caused by the mixture of dispersion when using a transmitted light pipe. The absorption observed at 1.7 K is probably due to antiferromagnetic resonance.

i.e., the $\Delta \hat{S}_z = \pm 2$ transition, becomes allowed. If $|D^*| \ll g\mu_B H_{\text{res}}$, however, the non-diagonal elements are regarded as 0 compared with the Zeeman energy. As a result, the intensity of the half-field line becomes substantially zero, which is the reason for the absence of the half-field line in the spectra obtained at 77–330 GHz.

We next show and discuss the spectra observed at frequencies higher than 330 GHz. As indicated in Fig. 1, region [III] includes the field-induced long-range ordered state. The resonance is therefore expected to change from paramagnetic to antiferromagnetic when T becomes lower than about 2 K. The variation of the spectrum with T observed at 427.6 GHz for $\mathbf{H} \perp \mathbf{B}$ plane is shown in Fig. 5. Although the results above 4.5 K shown in Fig. 5 seem to be similar to those in Fig. 2(b), the spectrum at 1.7 K for the frequency of 427.6 GHz is expected not to come from paramagnetic resonance by the following reasons.

If the antiferromagnetic-phase transition occurs, H_{res} above H_c should shift from those obtained below H_c . The frequency dependence of $\delta H_{\text{res}}(4.5 \text{ K})$ shown in Fig. 4(a) does not change up to 440 GHz, as mentioned earlier. On the other hand, as can be seen in Fig. 4(b), $\delta H_{\text{res}}(1.7 \text{ K})$ above H_c for the three directions of \mathbf{H} seem to deviate from those below H_c , although it is impossible to find a drastic change

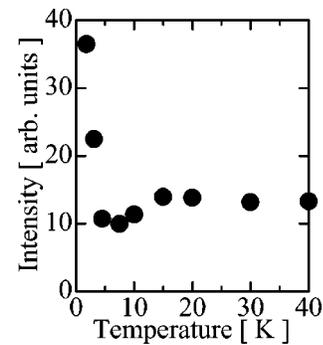


FIG. 6. The temperature dependence of the absorption intensity at 427.6 GHz for $\mathbf{H} \perp \mathbf{B}$ plane. The intensity does not tend to approach zero with decreasing temperature, which indicates the transition from the paramagnetic state to the field-induced antiferromagnetic state.

of δH_{res} above H_c from that below H_c because the scattering of δH_{res} (1.7 K) is about ± 0.05 T. This fact probably implies that the antiferromagnetic-resonance line becomes close to the paramagnetic one at high fields. Moreover, the confirmation of the paramagnetic-antiferromagnetic phase transition is understood when we see the T dependence of the absorption intensity $I(T)$, shown in Fig. 6. When $I(T)$ in Fig. 6 is compared with those shown in Fig. 3, we find a clear difference. Both $I(T)$ shown in Fig. 3 tend to approach to zero when the temperature goes down to 0 K, whereas the $I(T)$ at 427.6 GHz, shown in Fig. 6, increases at low temperatures. This increase is probably due to the precursory phenomenon of the magnetic-phase transition induced by the external field.

In conclusion, ESR experiments performed at frequencies and external fields up to 540 GHz and 20 T, respectively, detected the absorption signal corresponding to the $\hat{S}_z = -1 \leftrightarrow \hat{S}_z = 0$ transition. From analysis of the shifts of H_{res} , $D^*/g\mu_B = -0.24$ to -0.48 T is obtained at 1.7 K.

The half-field line, which was observed at 24 GHz, was not detected because its absorption intensity was expected to

be too weak to detect at high fields as in the case of the present experiments. Moreover, no signals indicative of the transition from the singlet to the triplet were observed. This is reasonable because the perturbation term such as the Dzyaloshinsky-Moriya antisymmetric exchange interaction, which allows the singlet \leftrightarrow triplet transition, does not exist in the case of this compound.

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