Dzyaloshinsky-Moriya interaction in the $S=\frac{1}{2}$ quasi-one-dimensional antiferromagnet $Cu_2Cl_4 \cdot H_8C_4SO_2$ as determined via high-frequency ESR

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High-frequency ESR measurements have been performed on the $S=\frac{1}{2}$ quasi-one-dimensional antiferromagnet $Cu_2Cl_4 \cdot H_8C_4SO_2$ in the frequency range up to 360 GHz and the field range up to 12 T. Reflecting the small alternation of exchange interaction along the chain direction, very peculiar temperature dependences of g value and linewidth are observed. Moreover, we have observed the direct transition between the singlet ground state and triplet excited states in $Cu_2Cl_4 \cdot H_8C_4SO_2$ at $T=1.7$ K and determined the excitation gap (for c axis) $\Delta/k_B=7.9\pm0.4$ K. Considering the observed anisotropic nature of the direct transition and applying the selection rules of the direct transition proposed by Sakai [J. Phys. Soc. Jpn. **72**, Suppl. B 53 (2003)], we have come to the conclusion that the direct transition is caused by the Dzyaloshinsky-Moriya interaction and are able to determine the D vector in $Cu_2Cl_4 \cdot H_8C_4SO_2$ as $D_{a^*}:D_b:D_c=1.0:0.0:2.3\pm0.1$.

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The Bose-Einstein condensation (BEC) is one of the most exotic phenomena predicted by quantum mechanics. This concept is essential to understand superfluidity.[1] Moreover, the realization of BEC by ultracooling of dilute atoms has attracted much attention.[2] Recently, the field-induced Néel ordering in the spin-gap antiferromagnetic system $TlCuCl_3$ was interpreted as BEC of dilute magnons by Nikuni *et al.*[3] The spin gap is the energy gap between a singlet ground state and lowest excited triplet states. The application of an external magnetic field causes a linear reduction of the spin gap Δ by the Zeeman effect. At the critical field $B_c=\Delta/g\mu_B$, where g is the g value and μ_B is the Bohr magneton, the spin gap vanishes. Consequently, the magnetic moment perpendicular to the applied field appears. This field-induced quantum phase transition is the second-order transition and yields the long-range transverse magnetic ordering. The picture of the magnon BEC is in good agreement with the experimental data for $TlCuCl_3$,[3] which were unable to explain with the mean-field theory. One of such aspects is the behavior of the temperature dependence of magnetization M near the critical magnetic field $B_c(T)$ where the cusplike anomaly was observed.[3] Another aspect is the power-law behavior of the phase boundary: $B_c(T)-B_c(0)\propto T^{\phi}$. The phase boundary proposed by Nikuni *et al.*[3] showed qualitative agreement with the experimental data.

Since then, many researchers have found new compounds which show the BEC of dilute magnons, for example, $KCuCl_3$ (Ref. 4) and $BaCuSi_2O_6$.[5] The study of the spin-gap formation due to the BEC of magnons can be done, e.g., by measurement of the magnetization, magnetic susceptibility, specific heat, NMR, neutron scattering, and electron-spin resonance (ESR). As high-frequency ESR measurement is a powerful method to investigate a magnetic excitation with high sensitivity and high-energy resolution, the observation of the direct transition, which is a transition between the singlet ground state and lowest excited triplet states, are suitable for evaluating the spin gap directly and precisely. The high-frequency ESR method achieved great successes in determining the spin gap of many interesting magnetic systems, for example, the spin-Peierls system $CuGeO_3$,[6,7] orthogonal dimer spin system $SrCu_2(BO_3)_2$,[8] the diamond chain system $Cu_3(CO_3)_2(OH)_2$,[9] and the Haldane system $Ni(C_2H_8N_2)_2NO_2(ClO_4)$ (NENP).[10] Essentially the direct transition is forbidden by the conservation of the total spin quantum number in isotropic Hamiltonian. Sakai modified the selection rule into a suitable form by considering the Dzyaloshinsky-Moriya (DM) interaction[11,12] and the staggered inclination of the principal axis of the g tensor along chain axis (staggered g tensor) in order to interpret the experimental results of spin-Peierls compound $CuGeO_3$.[13]

$Cu_2Cl_4 \cdot H_8C_4SO_2$, which also has a gapped ground state, is a new candidate for magnon BEC systems.[14–18] From the crystal structural point of view, $Cu_2Cl_4 \cdot H_8C_4SO_2$ can be considered as an $S=\frac{1}{2}$ quasi-one-dimensional (quasi-1D) antiferromagnet. The magnetic susceptibility exhibits a broad maximum at 65 K, which is a characteristic feature of the 1D antiferromagnet. With further decreasing temperature, the magnetic susceptibility decreases rapidly toward zero, which indicates the gapped singlet ground state. The magnetic susceptibility was analyzed by an $S=\frac{1}{2}$ antiferromagnetic alternating Heisenberg chain; the Hamiltonian is described as $\mathcal{H}=\Sigma_i(J\boldsymbol{S}_{2i}\cdot\boldsymbol{S}_{2i+1}+J'\boldsymbol{S}_{2i+1}\cdot\boldsymbol{S}_{2i+2})$, where J and J' are the exchange interactions. The best fit is obtained with the exchange interaction $J/k_B=105.6$ K and the alternation parameter $\alpha(=J'/J)=0.98$. The magnitude of the gap Δ was estimated from the critical field $B_c=3.9$ T at $T=50$ mK as $\Delta/k_B=g\mu_B B_c/k_B=5.32$ K, assuming $g=2.03$.[14] This gap is much smaller than the dominant exchange interaction J. Fujisawa *et al.*[14,15] also investigated the magnetic-field-induced three-dimensional magnetic ordering in $Cu_2Cl_4 \cdot H_8C_4SO_2$ by using magnetization and specific-heat measurements under the magnetic field. Well-defined phase

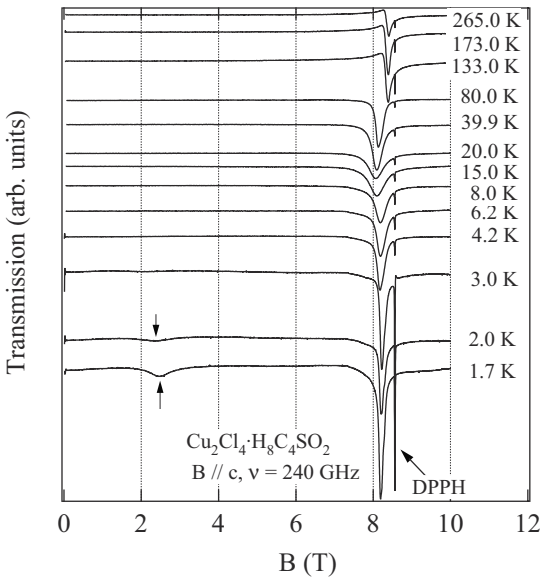

FIG. 1. Temperature dependence of ESR spectra observed at 240 GHz for $B\|c$ axis. The sharp absorption line is the DPPH signal, which is the standard of $g=2$. Arrows indicate the direct transition.

transition has been observed. The phase boundary can be expressed by the power law with an exponent $\phi=2.05$. This exponent is appreciably larger than $\phi_{\mathrm{BEC}}=3/2$ predicted by the theory of the BEC of dilute magnons.[3] Thus $Cu_2Cl_4\cdot H_8C_4SO_2$ has unique features. Especially, as the alternation parameter α is close to unity, this compound is suitable for investigating the crossover phenomena between the interacting spin dimer system with spin gap and the antiferromagnetic uniform chain with gapless spin liquid. Therefore, we performed high-frequency ESR measurement on $Cu_2Cl_4\cdot H_8C_4SO_2$ in order to investigate the spin dynamics and the magnetic excitation.

Synthesis method of $Cu_2Cl_4\cdot H_8C_4SO_2$ is described in Ref. 14. High-frequency ESR measurements were carried out in pulsed magnetic fields B up to 12 T using Gunn oscillators (60–315 GHz) and the backward traveling-wave oscillator (280–360 GHz). The temperature range is from 1.7 to 265 K. The Faraday configuration was taken in the present measurements. The transmitted light power was detected by an InSb detector. The magnetic field was applied parallel to the a^*, b, and c axes. The detailed experimental setup is described in Ref. 19.

Figure 1 shows the temperature dependence of ESR spectra observed at frequency $\nu=240$ GHz for $B\|c$ axis. The paramagnetic absorption lines are observed near 8 T. The linewidth becomes broadest around 20 K which is unusual in the quasi-1D system. Similar tendencies are also observed at other frequencies. In addition, the direct transition was observed around 2.5 T below 2.0 K. The origin of the peculiar temperature dependence is discussed in the following.

The magnetic susceptibility, the g value, and the linewidth are closely related to the spin-spin correlation. Figure 2 shows the temperature dependence of (a) the magnetic susceptibility, (b) the g-value, and (c) the linewidth for $B\|c$ axis. The magnetic susceptibility exhibits a broad maximum

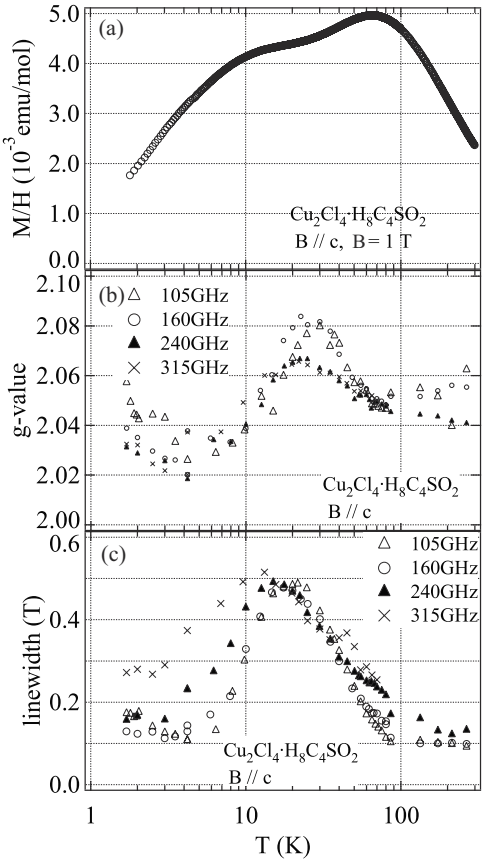

FIG. 2. Temperature dependence of (a) the magnetic susceptibility, (b) the g value, and (c) the linewidth for $B\|c$ axis.

at 65 K. With decreasing temperature from 65 down to 20 K, the magnetic susceptibility gradually decreases because of the development of short-range spin-spin correlation. The g value and linewidth for $B\|c$ axis are almost constant at high temperature but start to increase below 70 K. These results imply that the correlation is negligible above 70 K and ESR, the microscopic probe, suggests that the correlation starts to develop at a temperature where the magnetic susceptibility shows the maximum. With decreasing temperature from 70 to 30 K, the g value increases. Nagata and Tazuke[20] discussed the shift in the resonance field in the $S=\frac{5}{2}$ quasi-1D Heisenberg antiferromagnet $CsMnCl_3\cdot 2H_2O$. They concluded that the $g_{\|}$ of $CsMnCl_3\cdot 2H_2O$, which is parallel to the chain direction, increased with decreasing temperature down toward 0 K because of the development of spin-spin correlation. As the c axis of $Cu_2Cl_4\cdot H_8C_4SO_2$ is parallel to the spin chain direction and the g value for $B\|c$ axis shows the similar behavior as in the case of $CsMnCl_3\cdot 2H_2O$, the increase in the g value in $Cu_2Cl_4\cdot H_8C_4SO_2$ implies the development of the short-range spin-spin correlation. Moreover, with decreasing temperature from 70 down to 20 K, the linewidth increases. Ajiro *et al.*[21] explained the temperature dependence of the linewidth in $S=\frac{1}{2}$ quasi-1D antiferromagnet $CuCl_2\cdot 2NC_5H_5$. They suggested that the linewidth decreases with decreasing temperature and has a minimum. With further decreasing temperature down toward 0 K, the linewidth increases divergently because of the development of the spin-spin correlation. Therefore, the increase in the linewidth

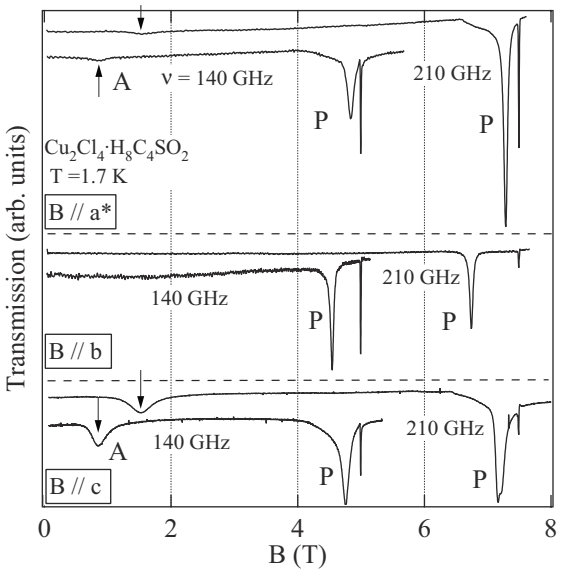

FIG. 3. Typical ESR spectra at $T=1.7$ K for $B\|a^*$, $B\|b$, and $B\|c$ axes. The sharp absorption line is the DPPH signal.

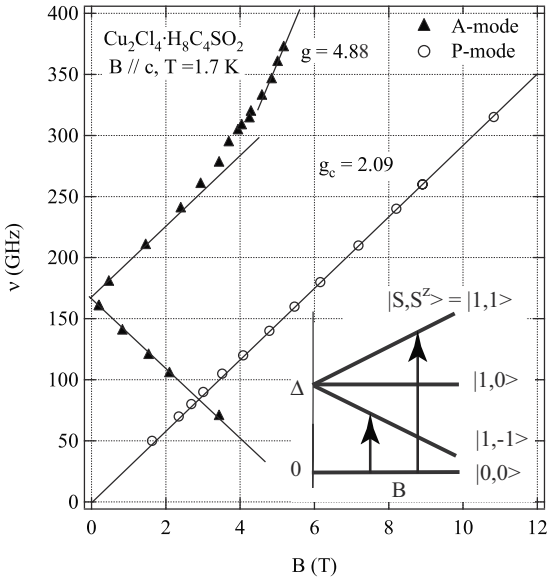

FIG. 4. Frequency-field diagram at $T=1.7$ K for $B\|c$ axis. The solid lines are the fitting. The inset shows a schematic energy diagram of spin-gap system under the magnetic field. $|S,S^z\rangle$ is the wave function with the spin quantum number S and the z component of spin quantum number S^z. The arrows mean the direct transition between the singlet ground state and triplet excited states in gapped spin systems.

for $Cu_2Cl_4\cdot H_8C_4SO_2$ implies the development of the short-range correlation. Thus, the temperature dependence of the magnetic susceptibility, the g value, and the linewidth above 20 K in Fig. 2 can be understood as the typical behavior of the quasi-1D antiferromagnet. On the other hand, the g value and the linewidth of $Cu_2Cl_4\cdot H_8C_4SO_2$ show the peculiar temperature dependence below 20 K. With decreasing temperature below 10 K, the magnetic susceptibility decreases rapidly toward zero which indicates the development of the gapped singlet ground state. With decreasing temperature below 20 K, the g value and the linewidth decrease rapidly, whose behaviors cannot be explained by typical quasi-1D antiferromagnet model. We propose the qualitative explanation for these peculiar experimental results. In general, the spin correlation is proportional to the square of the magnitude of the spin. In the spin-gap systems, the effective spin moment decays exponentially with decreasing temperature below $T=\Delta/k_B$ because most of the spins fall into the singlet ground state. Therefore, the decrease in the g value and linewidth can be attributed to the decay of the spin correlation below 20 K in this system. The temperature dependence of the g-value and the linewidth can be summarized as follows: it increases with decreasing temperature down to 20 K and decreases with further decreasing temperature below 20 K. The peculiar behavior can be attributed to the small alternation of exchange interaction along chain direction.

Finally, we will discuss the direct transition. As shown in Fig. 1, the direct transition is observed below 2.0 K. In order to investigate the direct transition, we have performed the frequency-dependence measurement of ESR at $T=1.7$ K. Typical absorption lines are shown in Fig. 3. A strong absorption line for $B\|a^*$, $B\|b$, and $B\|c$ axes and a weak absorption line for $B\|a^*$ and $B\|c$ axes have been detected. We label the strong absorption as the P mode and the weak one as the A mode, which is indicated by arrows in Fig. 3. The P and A modes can be assigned to the paramagnetic resonance and the direct transition, respectively, considering the frequency-field relation and the absorption intensity.

In Fig. 4, we summarized the frequency-field relation for $B\|c$ axis obtained at 1.7 K. We should point out that the frequency-field relation for $B\|a^*$ axis is similar to that of $B\|c$ axis, while that for $B\|b$ axis is different due to the absence of A mode. By applying the magnetic field to the gapped systems, as in the case of $Cu_2Cl_4\cdot H_8C_4SO_2$, the triplet level splits by the Zeeman effect as shown in the inset of Fig. 4. Generally, when the lower triplet state crosses the singlet state at B_c, the gap is closed and the ground state becomes magnetic. The observation of the direct transition can reveal the level splitting very precisely. From the observation of the direct transition in $Cu_2Cl_4\cdot H_8C_4SO_2$, the spin gap is precisely determined as $\Delta=164\pm8.2$ GHz $=7.9\pm0.4$ K. Here, we would like to point out that the determination of the spin gap by the direct transition is the direct method while that by the critical field from the magnetization measurement is the indirect method. The slope of the upper A mode changes at high frequency and rapidly increases above $B_c=4.5$ T. The slope of the upper A mode above 4.5 T corresponds to the g value $g=4.88$. As there is an ambiguity for the magnitude $g=4.88$ due to the limited frequency range above 4.5 T, it can be considered as in the order of magnitude corresponding to twice the g value $g_c=2.09$. Such a magnetic-field dependence of excitation energy is also observed in the typical field-induced magnetic-order system $TlCuCl_3$ by the neutron-scattering measurement.[22] Therefore, we can say from Fig. 4 that the critical field is $B_c=4.5$ T for $B\|c$ axis which is consistent with the magnetization measurement using the pulsed field.[14] However, it is clear from Fig. 4 that the lower A mode does not cross the singlet ground state at B_c. The origin of the

remaining spin gap at B_c is not clear at the moment but such a behavior is also observed in several spin-gap systems, for instance, $CuGeO_3$,[7] and it may be suggesting the existence of spin-lattice interaction.

Now, we will discuss the origin of the direct transitions observed in $Cu_2Cl_4 \cdot H_8C_4SO_2$. Although the direct transition is usually forbidden by the selection rule, the staggered magnetic field, which is caused by the staggered g tensor for the DM interaction, can allow the direct transition. It can mix the wave functions of the ground and excited states when the external field is applied. In such anisotropic Hamiltonian, the transition between the different spin quantum number is allowed. Two possible mechanisms, the staggered g tensor and the DM interaction, will be considered. First, the staggered g tensor prohibits the magnetic phase transition, for example, NENP, which has the staggered g tensor from the structure, has no magnetic phase transition but the crossover effect.[23] Second, Sakai predicted that the integrated intensity of the direct transition is proportion to B^2 in the case of the staggered g tensor.[13] Therefore, as such a field dependence of integrated intensity is not observed and $Cu_2Cl_4 \cdot H_8C_4SO_2$ has the magnetic phase transition; the staggered g tensor is not the origin of the direct transition. Next we will consider the DM interaction. According to Sakai,[13] if D vector has a component which is parallel to B in the Faraday condition, the direct transition occurs. However, the D vector is restricted by the crystal symmetry. Two Cu^{2+} ions, which are adjacent to each other along the c axis, have a twofold rotational symmetry axis. As this axis is almost parallel to the b axis, we expect that the D vector lies in the a^*c plane.[11]

Moreover, we consider the intensity of the direct transition. Sakai *et al.*[13] suggested that the intensity of direct transition is independent of the external magnetic field in our experimental condition and the intensity has the following relation to the components of the D vector, $I_{a^*}:I_b:I_c = (D_{a^*})^2:(D_b)^2:(D_c)^2$. We compared the intensity of the direct transitions for $B \| a^*$, b, and c axes. Each intensity is normalized by the intensity of the standard sample DPPH. The intensities for the a^* and c axes have shown no remarkable field dependence and the intensity for c axis turned out to be larger than that for the a^* axis. By averaging intensities of the a^* and c axes, we obtained the following relation: $I^{a^*}:I^b:I^c = 1:0:5.2 \pm 0.4$. Therefore, we can determine the D vector, $|D^{a*}|:|D^b|:|D^c| = 1.0:0.0:2.3 \pm 0.1$. This vector satisfies the condition that D vector exists in the a^*c plane. These results suggest that the DM interaction is the origin of the direct transition in $Cu_2Cl_4 \cdot H_8C_4SO_2$.

The DM-interaction-induced helimagnet possibly forms the chiral soliton lattice.[24] In such a case, the critical exponents of the field-induced BEC can be modified, as observed in the neutron-scattering experiment.[18,25]

In conclusion, high-frequency ESR measurements on $S=\frac{1}{2}$ quasi-1D antiferromagnet $Cu_2Cl_4 \cdot H_8C_4SO_2$ have been performed. The peculiar temperature dependence of the g value and the linewidth can be attributed to the small alternation of exchange interaction along the chain direction. We have observed the direct transition at $T=1.7$ K and estimated the spin gap as $\Delta/k_B = 7.9 \pm 0.4$ K. The origin of the direct transition can be attributed to DM interaction and the direction of the D vector is determined as $|D^{a*}|:|D^b|:|D^c| = 1.0:0.0:2.3 \pm 0.1$ by ESR.

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