

Submillimeter-wave ESR Study on Quantum Spin Systems

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Various types of quantum spin systems have been studied by submillimeter wave ESR technique. In $\text{SrCu}_2(\text{BO}_3)_2$, it has been observed that many kinds of "multiple-triplet" excitations appear and this feature has been explained as the extreme localization of the excited states in the Shastry and Sutherland model. These localized excitation change to the spin-wave like mode, when the energy gap is collapsed in high magnetic field. For Cubenzoate, a distinct anomaly was found in the temperature dependence of the line width. Absence of the three dimensional ordering indicates that the anomaly is caused by the change of the spin dynamics, and it has been discussed in term of the "breather" picture recently proposed by Oshikawa and Affleck. The present results highlight the important role of ESR for the investigation of magnetic excitation in quantum spin systems, especially for high magnetic fields.

KEYWORDS: ESR, magnetic excitation, high magnetic field, quantum spin

§1. Introduction

Studies of magnetic excitations in quantum spin systems have attracted much interests in these decades. Among many different kinds of experimental methods to study magnetic excitations such as inelastic neutron scattering, Raman scattering and far-infrared spectroscopy, ESR is considered to be a unique tool for the following reasons: (1) high sensitivity, (2) high energy resolution and (3) possibility of high field measurements by using a pulsed magnetic field. The last feature of ESR is very important and, in fact, the magnetic excitations of many kinds of magnetic compounds have been studied by ESR in very high magnetic fields.¹⁾

ESR can be used to study many different types of magnetic excitations, for example, (1) spin wave in a ferromagnet or in an antiferromagnet, (2) spin gap excitation between the singlet ground state and the excited state, (3) transitions in a quantized energy levels such as spinon or the excited triplet states in gapped spin system and (4) particle like excitations such as soliton or breather.

A spin wave mode in an antiferromagnet is usually treated in the framework of "antiferromagnetic resonance (AFMR)". As is well known, much information about anisotropy, magnetic structure and exchange interaction are obtained by measuring AFMR. In quantum spin systems, a gap-less three-dimensional ordered state, in many case, appears when a energy gap is closed by a strong magnetic field. In this case, it is natural to speculate that a spin wave like mode exist and thus a sort of AFMR is observed. However, the conventional AFMR theory is based on the molecular field approximation and therefore no theory can be directly adapted to analyze such ESR mode. Moreover, for a spin density wave state appearing in many quantum spin systems, no theory, to

our knowledge, has been given for ESR mode.

The direct observation of the spin gap excitation had been considered very difficult and only a few cases has been reported so far. One of the reasons is that the ESR transition between the ground singlet state and the excited triplet state due to the mechanism of magnetic dipole transition is forbidden in principle. Moreover, the energy gap is usually order of a few meV and thus it requires the use the high frequency submillimeter-wave. However, for transition metal oxides, we often find out a sizable non-secular term to cause the mixing between the ground singlet state and the excited state. The selection rules for different types of non-secular terms are summarized in the appendix.

The most well known example of the transition in quantized levels is the spinon resonance in quantum spin chains. In this case, when temperature is well above the intrachain exchange coupling J , we observe a conventional paramagnetic resonance. When temperature becomes lower than J , a ESR absorption should be attributed to the Zeeman splitting of spinon. In the spinon regime, anomalies such as "g-shift" and the change of line width are observed. The general theory of ESR was invented by Kubo and Tomita long time ago,²⁾ however, the actual calculation of a correlation function for a quantum spin chain in the low temperature condition is non-trivial.^{3,4)} Recently, several breakthroughs have been made for the theory of ESR such as a field-theoretical approach and the numerical method and these methods open the new possibility to the apply ESR for quantum spin systems.^{5,6)}

An example of the breather excitation has been recently found for CuBeonzoate.⁷⁾ The exponential-type temperature dependence of the line width clearly shows that the width is governed by the collision between the particle

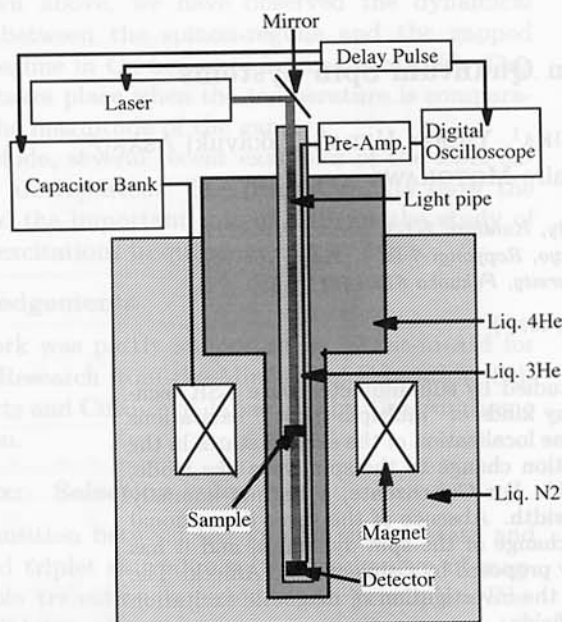


Fig. 1. Schematic view of the submillimeter-wave ESR equipment. The laser can be replaced to other radiation sources mentioned in the text.

like excitations.

Another type of important magnetic excitation is the spin-cluster excitation which appears for the Ising system. Such spin-flip like excitation is observed recently for the Heisenberg system $\text{SrCu}_2(\text{BO}_3)_2$, although the origin is not the strong anisotropy.

As shown above, a variety of magnetic excitations can be examined by means of ESR for quantum spin systems. In the following, we first describe the experimental procedure. Next, we show several recent examples of the ESR investigations.

§2. Experimental

Figure 1 shows the schematic set up of the ESR equipment. In most cases, a simple transmission method is employed for the insulating compounds. For metallic materials, either of a powder sample mixed with insulator powder, thin film, strip-line or co-axial type cavity is used.

As the radiation source, we combine three types of devices. For microwave region, conventional Gunn oscillators are employed. For frequency between 250 GHz and 7 THz, an optical pumped far-infrared laser is mostly used. The available frequencies of the laser, which have been used for the experiments, are summarized in Fig. 2. Backward travelling wave tubes are also employed, especially between 200-400 GHz. Such wide frequency range is covered by four different kinds of detectors as follows: InSb, GaAs, a field-tuned InSb and GeGa. It should be noted that this frequency coverage is equivalent to the energy which is available by a neutron triple-axis spectrometer installed in a reactor.

For the generation of magnetic field, a capacitor bank of 100 kJ is used and pulsed fields up to 40 T are gener-

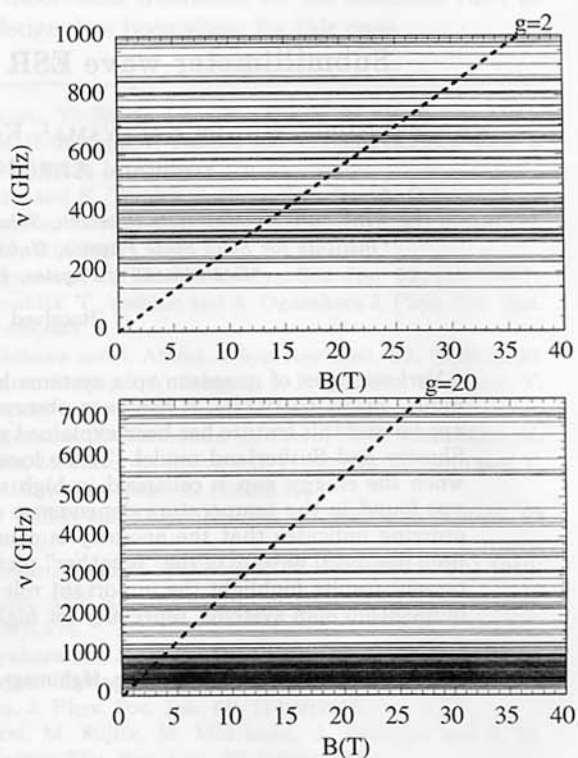


Fig. 2. The frequencies available in the Laser.

ated. The pulse duration time is between 5 and 8 msec and the inner diameter of the cryostat can be changed from 12 mm to 25 mm depending on the maximum field. A magnetic field up to 20 T can be generated by the split type pulsed magnet and it is used for the experiments for the Voigt configuration. The sample can be cooled down to 0.4 K by using a ^3He cryostat. The highest temperature up to 450 K is possible.

§3. Multiple-triplet excitation and ESR mode at magnetization plateau in $\text{SrCu}_2(\text{BO}_3)_2$

Recently, a strontium copper boron oxide $\text{SrCu}_2(\text{BO}_3)_2$ with a layered structure has been studied intensively as a unique two-dimensional (2D) spin-gapped system.⁸⁾ One of the reasons is that the material can be regarded as a model system with an exactly known ground state. The crystal structure belongs to the tetragonal space group $\bar{1}42m$. The Cu^{2+} ions form a 2D-network of $S=1/2$ spins as shown in Fig. 3.⁹⁾ In each layer, a dimer unit is made up of the neighboring pair of CuO_4 bond and these dimers are arranged orthogonally each other. This 2D lattice is topologically equivalent to a 2D square lattice with additional alternating diagonal interactions, which is called Shastry and Sutherland model.¹⁰⁾ The most important feature of $\text{SrCu}_2(\text{BO}_3)_2$ is that the ratio of the next-nearest-neighbor interaction J_2 to the nearest-neighbor interaction J is very close to the critical value of $J_2/J=0.70$ between the spin gap state and the Néel-ordered state.¹¹⁾ Miyahara and Ueda estimated the intra-dimer coupling of $J=100$ K and the next-nearest-neighbor one of $J_2=68$ K using the experimentally obtained Weiss temperature of -92.5 K and the energy gap

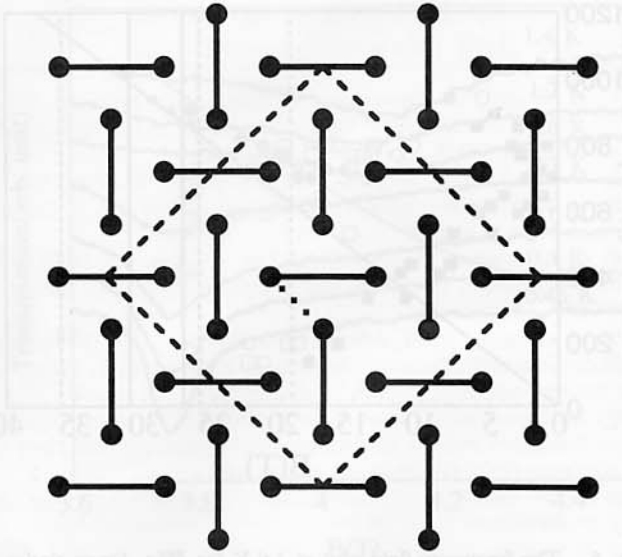


Fig. 3. The schematic spin arrangement of $\text{SrCu}_2(\text{BO}_3)_2$ in the c -plane. Closed circles, thick solid line, dotted line and dashed line show the Cu^{2+} ions, J , J_2 and the square lattice related to $1/8$ plateau, respectively.

of 30 K.¹²⁾

The most prominent effect of this system is the quantized plateaux in magnetization, for example, at one-quarter, one-eighth of the saturated moment, which have been realized due to the extremely localized nature of the excited states.⁸⁾ In each plateau, the propagation of the excited triplets are considerably suppressed and as a result, these triplets organize a regular lattice. In the previous work, we have investigated the spin gap excitation in the singlet ground state.¹³⁾ We found the lowest spin gap excitation which is the excitation in a dimer unit between the singlet ground state to the excited triplet state. In addition to this, we have also found a "multiple-triplet" excitation, which is related to the generation of a bound state of triplets coupled by inter-dimer interactions.

As is well known, for the gapped systems such as CuGeO_3 , the triplet bound state is observed as a two-spinon continuum.¹⁴⁾ In the present system, it has been pointed out that, for the extreme localization of the excited states, a continuum may be replaced by a different types of nearly localized "multiple-triplet" excitations. In this context, it is natural to speculate that a localized excitation appears at magnetization plateaux when the "triplet lattice" is hard enough to suppress the spin-wave like "twistable" excitation. In other case, a spin wave like excitation such as AFMR or a ESR mode related to the spin density wave (not much is known for such mode as mentioned before), is expected. In the following, we report the observation of a spin-wave like excitation above the critical field H_c where the gap is closed by the strong magnetic field.

In the present work, high-purity bulk single crystals of $\text{SrCu}_2(\text{BO}_3)_2$ were grown by the travelling solvent floating zone (TSFZ) method.¹⁵⁾ By means of Laue X-ray back-reflection, the grown materials was checked and the

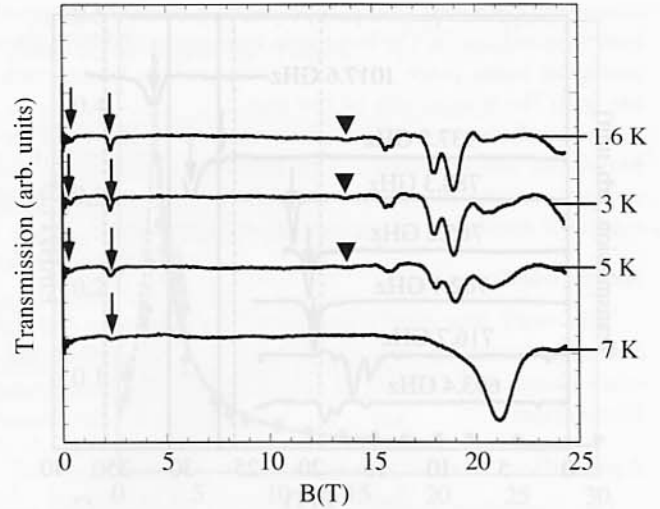


Fig. 4. Temperature dependence of ESR spectra for $B||c$ at 693.4 GHz. Arrows and closed triangles show the lowest spin gap excitation and the second-lowest spin gap excitation, respectively.

crystal axes were determined.

Since the results below the H_c were reported in the previous work, we focus on the ESR signal at higher fields. Figure 4 shows the temperature dependence of ESR spectra for $B||c$ at 693.4 GHz. Two ESR lines marked by arrows are the two nearly degenerated lowest spin gap excitations. The weak absorptions marked by closed triangles belong to the $S_z = -1$ branch of the second-lowest spin gap excitation. The signal located around 21 T is a paramagnetic resonance. Other absorptions observed between 15-20 T are considered as the excitations from the ground state. It is because the intensity of these ESR peaks decreases as the temperature is increased. It should be also noted that the intensity of these peaks is much stronger than that of the spin gap transitions marked by arrows and is comparable with that of paramagnetic signal. A possible interpretation for this behavior is the following. Since the field is just below the H_c , the energy of the lowest excited triplet state becomes very close to the singlet ground state. In this case, we can expect the strong mixing between these two states and thus the intensity of the excitation between the ground state and the "multiple-triplet" states becomes strong. It should be noted that the magnetization is non-zero even at 0.5 K in the field well below H_c ,⁸⁾ which supports our speculation. Here, H_c is defined the field where the Zeeman energy of the triplet is comparable to the lowest energy gap of 722 ± 2 GHz. However, it is difficult yet to describe such state theoretically because the mixing is usually caused by a small non-secular term in spin-Hamiltonian.

Figure 5 shows the change of ESR spectra at 1.6 K for $B||c$. In the plot, the dotted line shows the field where the magnetization becomes finite and it is little lower than the $H_c = 22$ T. The dashed lines indicate the critical fields where a jump of magnetization is found. The area between the two thick vertical lines are the place where

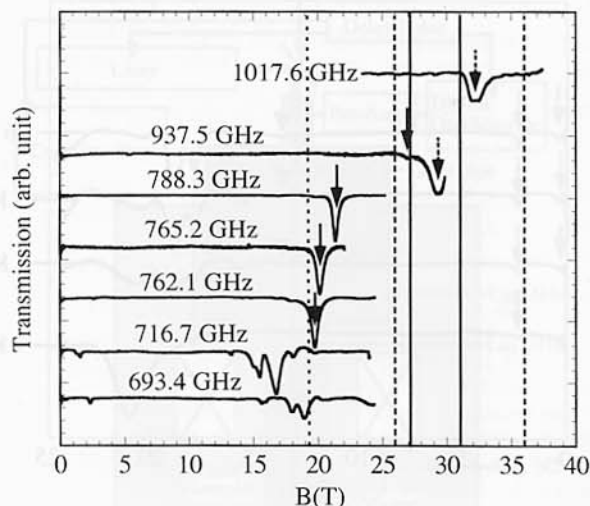


Fig. 5. ESR spectra at 1.6 K for $B||c$. The notation for the vertical lines are given in the text.

the plateau like shoulder is observed and it is related to the $1/8$ plateau.

At 693.4 GHz and at 716.7 GHz, several peaks are observed and the resonance fields decrease as the frequency is increased. The frequency dependence indicates that these ESR lines are the gapped excitations and thus the manifestation of the localized "multiple-triplet" excitation. As the frequency is increased further, these excitations disappear and a single peak with strong intensity is observed, which is marked by the solid arrows. The resonance field of the peak continuously increases with increasing frequency. Around the plateau, this peak disappears and another peak with wide line width is found, which is marked by the dashed arrows. It is noticed that the new peak with a wide line width is composed of two ESR lines. The frequency-field plot is given in Fig. 6, where the notation of the vertical lines are identical with those in Fig. 5. The thin line shows the position of paramagnetic resonance (EPR) mode at 25 K (note that this mode is not observed at 1.6 K). The closed circles indicate the strong single peak observed when the magnetization becomes finite, which are marked by solid arrows in Fig. 5. To be different from other modes, the field dependence of this peak is non-linear to the field. Moreover, it shows an asymptotic behavior to the EPR mode and such behavior is expected for AFMR with easy-plane type anisotropy. It is unclear if the Néel-ordered state realized in this field regime. However, as mentioned before, this compound is located very close by the quantum critical point and thus it may be possible that the system drops into the Néel-state due to a small perturbation such as lattice distortion. Another possible interpretation is that the mode is caused by the long-range correlation of the transverse components of the spins. For the transverse components, we can expect that the magnetic excitation shows a spin-wave like character and the excitation energy can change continuously as a function of the magnetic field intensity.¹⁶⁾ Since only a few is

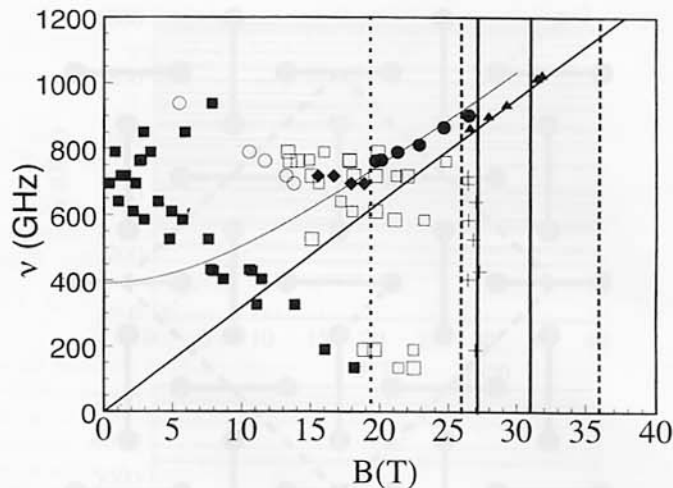


Fig. 6. The frequency-field plot at 1.6 K for $B||c$. Open circles, open rectangles and closed diamond show the second spin gap excitation, weak "multiple-triplet" peak and strong "multiple-triplet" peak, respectively. The notation of other marks are given in the text.

known for the ESR mode above H_c , to our knowledge, in any kind of spin gap system, further theoretical and experimental investigations are necessary to clarify this point.

The character of the ESR mode qualitatively changes for much higher fields. The slope of the ESR mode at $1/8$ plateau is parallel to that of the EPR mode and the frequency of the mode is about 20 GHz above the EPR line.

This offset shows that the ESR mode at the plateau is associated with a finite energy gap. In the plateau regime, we can expect different types of magnetic excitations. The first candidate is the creation of a new triplet bond in the space between the triplets organizing the regular lattice. We speculate that the energy to excite a new triplet may be close to that of the lowest triplet excitation, which is shown in Fig. 6, as long as the density of the triplets is low. Since the energy of the new mode is much different from that of the lowest triplet around the field and thus we exclude this possibility. A more plausible interpretation is that the ESR line is related to the excitation in the existing triplets forming the "triplet-lattice". Since a triplet is a $S=1$ spin object, three states such as $S_z=-1, 0, 1$ are possible. At the plateau, all the spins are parallel to the external magnetic field and thus the spins are in $S_z=1$ state. In this case, we can expect the transition between the $S_z=1$ state and $S_z=0$ state. The transition between $S_z=0$ and $S_z=-1$ is also possible. However, the intensity of such transition is very small because nearly all the spins are in $S_z=1$ state. The deviation from the EPR line may be related to the energy required to cause such excitation in the plateau state.

As shown above, we have observed several strong ESR modes above the H_c . It is found that the ESR mode changes in accordance with the change of the magneti-

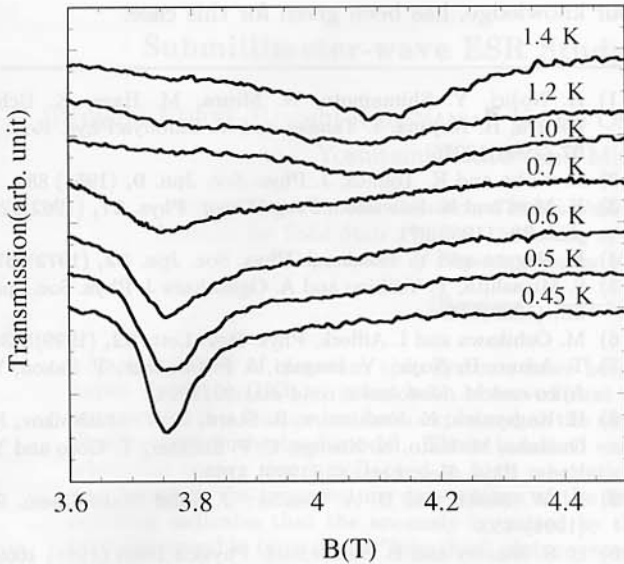


Fig. 7. Temperature dependence of ESR spectra for $B//c$ at 135 GHz.

zation. Below the $1/8$ plateau, the resonance field of the ESR mode shows a field dependence similar to that of a AFMR with easy-plane type anisotropy. At the $1/8$ plateau, a ESR mode parallel to the EPR line with a finite gap is found. It is probably the transition between the $S_z=1$ state and $S_z=0$ state of the triplets which form the regular lattice.

§4. Breather excitation in CuBenzoate

Cu benzoate $\text{Cu}(\text{C}_6\text{H}_5\text{COO})_2 \cdot 3\text{H}_2\text{O}$ had been known as a good model of $S = 1/2$ Heisenberg spin chain with an exchange coupling $J = 8.6 \text{ K}$.¹⁷⁾ Recently, a field induced energy gap was observed in specific heat, neutron scattering and susceptibility.^{18,19)} Oshikawa and Affleck^{20,21)} claimed that the gap is caused by the staggered fields acting between neighboring spins in a chain and a new elementary excitation, so called "breather excitation", appears when the temperature is well below the gap. Since no Néel ordering was found at least down to 0.1 K, the field-induced gap should be attributed to the dynamical character of the system. The ESR measurement of this compound below 1 K was reported more than 20 years ago and a new ESR peak was found.²²⁾ This ESR signal was interpreted as the AFMR, which is not compatible with the most present results as mentioned above. To solve this controversy, we performed the ESR measurements at different frequencies.⁷⁾

Figure 7 shows the temperature dependence of ESR spectra. As the temperature is decreased, the shift of the resonance field and the broadening of the line width are observed. Such behavior are observed in many $S = 1/2$ Heisenberg spin chain and the origin is the increase of the correlation-length of the spinon excitation which develops at low temperature. The anomalous character of this compound is that a new peak appears in low field side besides the spinon ESR mode. Moreover, these two signals are coexisting in some temperature regime and

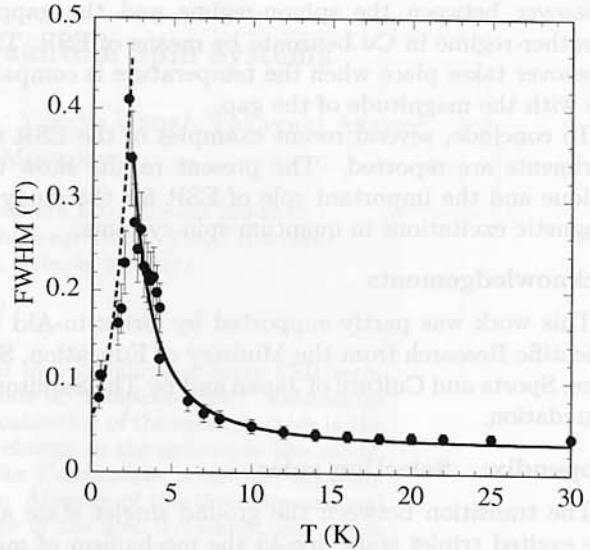


Fig. 8. Temperature dependence of the ESR line width for $B//c$ at 135 GHz. Solid line and dashed line are the fitting curves given in the text.

thus the anomaly should be considered as a crossover phenomenon.

The crossover nature is more pronounced when we plot the line width as a function of temperature, which is depicted in Fig. 8. As the temperature is decreased, the line width rapidly increases. The temperature dependence is well fitted by the $(1/T)^2$ type function, which is represented by the solid line. This functional form, for Cu benzoate, is theoretically proposed considering the a staggered field which give rise to the field induced gap.⁶⁾ Below 2 K, the temperature dependence of the line width becomes completely different and the width rapidly decreases as temperature is lowered. The temperature dependence is well fitted by the exponential function with a small residual line width. Such function is expected when the ESR line width is governed by the collisions between the thermally-excited particles such as soliton and breather. Hence, we conclude that the anomalous crossover behavior found for Cu benzoate is caused by the change of the dynamical nature of the magnetic excitation from the spinon type excitation to the gapped breather type excitation. At this point, it is worth mentioning that the crossover temperature is much higher than that observed in the previous work at lower frequencies.²²⁾ In fact, we found that the crossover temperature increases as the frequency is increased. The increase of the frequency is directly associated with the increase of the resonance field and thus is associated with the increase of the the field induced gap. It is natural that the crossover temperature becomes higher when the field induced gap is increased. Moreover, the crossover temperature shows the $H^{2/3}$ -type field dependence, in which the exponent is identical of that of the field dependence of the gap. These findings support our interpretation that the anomaly in the line width is the manifestation of the spinon-breather crossover.

As shown above, we have observed the dynamical crossover between the spinon-regime and the gapped breather-regime in Cu benzoate by means of ESR. This crossover takes place when the temperature is comparable with the magnitude of the gap.

To conclude, several recent examples of the ESR experiments are reported. The present results show the unique and the important role of ESR for the study of magnetic excitations in quantum spin systems.

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Appendix: Selection rules

The transition between the ground singlet state and the excited triplet state due to the mechanism of magnetic dipole transition is forbidden in principle. Possible candidates of such term are (i) Dzyaloshinsky-Moriya(DM) interaction, (ii) Staggered field and (iii) Anisotropic exchange(AE) interaction.

An example for the case (i) is CuGeO_3 and, in this case, both the optical triplet branch and the acoustic triple branch were observed by ESR.²³⁾ The selection rules are proposed by Sakai as follows:(a)when $\mathbf{D}\parallel\mathbf{B}$, ESR is observed for Faraday configuration and the intensity shows no strong field dependence, (b)when $\mathbf{D}\perp\mathbf{B}$, ESR is observed for Voight configuration and the intensity strongly depends on the field, where \mathbf{D} is the DM-vector.²⁴⁾ The most well known example for the case (ii) is NENP. The experiment was made by Lu *et al.*²⁵⁾ and the theory was invented by Shiba and Sakai.²⁶⁾ They proposed two distinct features (a) strong field dependence of the intensity and (b) the observation of the signal for Voight configuration where $\mathbf{H}_{rf}\parallel\mathbf{B}$, here \mathbf{H}_{rf} is the polarization of the incident radiation. The last case may be realized for $\text{SrCu}_2(\text{BO}_3)_2$.¹³⁾ In this case, the Zero field splitting can be observed between the two branches of $S_z=+1$ and $S_z=-1$ for certain direction and the strong signal is observed in Faraday configuration in this direc-

tion. No theoretical treatment for the selection rule, to our knowledge, has been given for this case.

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