Magnetic excitation of $S = 1/2$ antiferromagnetic spin chain Cu benzoate in high magnetic fields

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Abstract. Magnetic excitation of $S = 1/2$ antiferromagnetic spin chain (AFC) Cu benzoate has been studied by means of high-frequency high-field electron spin resonance (ESR). A field-induced gap caused by staggered fields is directly probed by ESR and a distinct nonlinearity is found. Below the half of the saturation field, the magnetic field dependence of the gap can be interpreted quantitatively by using a sine-Gordon (SG) model with some renormalization of parameters. In higher field regions, the deviation from the model grows gradually and the gap even decreases towards the saturation field. Such behaviour illustrates the breakdown of the SG model. A cause of the breakdown is discussed by considering the large distortion of magnetic dispersion. Above the saturation field, another excitation gap is found to develop. It is interpreted as the excitation in the fully polarized spin state. The present study gives the first experimental result on the magnetic excitation of $S = 1/2$ AFC exposed to staggered fields over the whole range of the magnetic field.
1. Introduction

Antiferromagnetic spin chains (AFC) have been received considerable attention in modern magnetism. Important concepts, such as quantum criticality, soliton excitation, incommensurability, Haldane gap and spin–Peierls transition find theoretical or experimental realizations in AFC, which show the significance of quantum many body physics [1, 2]. Quantum fluctuation and nonlinearity are crucial ingredients of those fascinating phenomena.

Among many subjects, magnetic excitations of AFC are still an attractive target for research. Nonlinear excitations such as soliton, breather and their quantum mechanical analogues are widely investigated in different types of AFC [3]. In a classical system such as (CH$_3$)$_4$NMnCl$_3$:TMMC, the soliton is in the shape of a gradually twisted domain wall in a Néel state. On the other hand, the local $\pi$-rotation of a spin represents the soliton in an Ising system such as CsCoCl$_3$, where each Co ion carries a fictitious $S = 1/2$ spin. The domain wall in the Ising system is a doublet because of the accompanying magnetic quantum number and thus the soliton has an internal degree of freedom. This character originates from the quantization effect of the soliton in the $S = 1/2$ system, though the Ising system is often considered to be classical. Such a picture is inadequate in an isotropic and quantum mechanical AFC, namely, the $S = 1/2$ Heisenberg system. The magnetic excitation is gapless and the elementary particle is a massless spinon, which is an entirely quantum mechanical object. The excitation spectrum is dominated by a two-spinon continuum and its lower bound resembles a spin wave-like mode, but the energy is strongly renormalized. In the case of the classical solitons in TMMC, application of a magnetic field leads to the control of anisotropy, which results in the transition between different types of soliton regimes. In $S = 1/2$ Heisenberg AFC, the gapless feature is maintained in high magnetic fields. The wave vector of the gapless point shows the shift scaling with magnetization, which is called a dynamical incommensurability.

More recently, a new class of system, namely $S = 1/2$ Heisenberg AFC associated with staggered fields, has been studied intensively [4, 5]. The speciality of the system is that a drastic change of magnetic excitation is caused by the application of a uniform magnetic field [6]. Namely, the excitation spectrum becomes gap-full and the elementary excitation changes from spinon to soliton/breather [7]. It may be understood as a quantum phase transition of magnetic excitation. Another distinct character of the system is that the magnitude of the excitation gap...
can be tuned by the external magnetic field, which enables us to study the soliton and the breather of variable masses. Several model materials have been studied so far by different methods such as magnetic susceptibility, specific heat, electron spin resonance (ESR) and neutron scattering [8]–[13]. Those experiments, however, were performed in a low reduced field, a magnetic field normalized by exchange coupling. It has been highly desired to examine the nature of magnetic excitation in the whole range of magnetic field till the saturation, because such study can be a most crucial test for theories. Practically, it is essential to select an ideal one-dimensional (1D) material with appropriate values of exchange coupling, which matches with the accessible magnetic field range of existing experimental apparatuses. This is the exact reason why we select Cu benzoate from many possible candidates.

Cu(C₆H₅COO)₂·3H₂O, alias Cu benzoate, has been known as a model material of $S = 1/2$ AFC for decades past. The studies of the magnetic property were stated in the 1960s and one-dimensionality was found in the magnetic susceptibility following the well-known Bonner–Fisher curve [14]. ESR investigations were made in detail and the angular dependence of the line width was analysed by considering the anisotropy of exchange coupling. The first sign of the anomalous magnetic excitation was found by ESR experiments [15]. Besides a conventional paramagnetic signal, a new signal emerges at low temperatures below 1 K. Although it was assigned as an antiferromagnetic resonance, the result was the first sign of the gapped excitation in $S = 1/2$ Heisenberg AFC associated with staggered fields. More recently, a new stage of investigation was triggered by the neutron scattering experiment of Dender et al [4] aiming at the observation of dynamical incommensurability. A considerable shift of the low energy mode was confirmed, however, an unexpected excitation gap was found in the mode. Moreover, the excitation spectrum consisting of discrete peaks was found. Those observations are not compatible with the expectation for an $S = 1/2$ Heisenberg AFC. The existence of the gap was confirmed by the successive investigation of the specific heat in high magnetic fields [5]. It was found that the gap develops with a power-law of magnetic field intensity.

An interpretation of the field-induced gap was proposed by Oshikawa and Affleck [6] and, subsequently, by Essler and Tsverik [16, 17]. They claimed that these effects were caused by the staggered fields. In fact, such alternating fields are possible in Cu benzoate because of the alternation of the principle axes of the $g$-tensors and of the axes of the Dzyaloshinsky–Moriya (DM) interactions [18, 19]. Based on a field-theoretical approach, they interpreted the discrete excitations found in the neutron scattering as the manifestations of solitons and breathers in a quantum sine-Gordon (SG) model. An SG model has been studied intensively for decades and various properties have been calculated by using the exact integrability. Hence, it is very interesting to complete the experimental study in some ideal model systems such as Cu benzoate. In an SG model, it is theoretically proposed that the excitation spectrum consists of breather, soliton, anti-soliton and multi-particle continua [20]. The ‘breather’ is the soliton–anti-soliton bound-state and one of the well-known elementary excitations in the SG model. Experimental studies of the breather have been made in a variety of classical SG systems so far, however, the investigation of a fully quantum SG system, $S = 1/2$ AFC, is rare. Moreover, the experiment in the whole field range till the saturation has not been made.

The main issue of the present study is to complete the investigation of the magnetic excitations in the ideal model system of $S = 1/2$ Heisenberg AFC under uniform and staggered magnetic fields. In the following, the experimental procedure of ESR and the description of the structure of Cu benzoate are given first. They are followed by the experimental results and the discussion on the basis of different theoretical models.
2. Experimental procedure

2.1. ESR apparatus

Figure 1 shows the schematic view of the Terahertz ESR Apparatus (TESRA-IMR) installed in the magnetism division of Institute of Materials Research (IMR), Tohoku University. The system consists of several parts, a pulsed field generator, cryostats, detectors, light sources and data acquisition instruments.

The source of the field generator is a 90 kJ capacitor bank designed and assembled at IMR. A thyristor is used as a switch and a crowbar circuit is installed. A typical rise time is 2.5 ms and the full pulse width is about 25 ms. Three types of solenoid magnets with inner diameters of 16, 21 and 27 mm are used. A split type magnet of 20 mm gap is also used to measure the angular dependence in Voight configuration up 20 T.

Four types of cryostats are installed to cover the wide temperature range between 0.2 and 350 K. Above 80 K, a gas-flow type cryostat is used. Between 80 and 1.5 K, a conventional 4He bath type cryostat is used. A sample is installed in the stainless-can filled with exchange gas and the temperature is controlled by a film heater attached near the sample. The light guide in which a sample is fixed can be replaced by a top-loading mechanism. Below 1.5 K, a 3He cryostat is used and a sample is directly immersed in liquid 3He. A sample is located inside the stainless-can with double-wall thermal insulation in the bottom part and fast pre-cooling is possible for the sealed-off air in the vacuum space. At 3He temperature, a radiation source is operated in pulsed mode to avoid the sample heating. As an option, a plastic dilution refrigerator of 70 mK base temperature can be used. A thermocouple, a manometer and a Cernox resistance thermometer...
are used for temperature measurement. A sample is mounted on a plate made of polyethylene and different magnetic field orientations are possible. A Voight configuration, where the propagation vector $k$ of the radiation is perpendicular to the magnetic field, can be also used.

A wide frequency range up to 7 THz is covered by four kinds of detectors: InSb, GaAs, a field-tuned InSb and GeGa. For the bath type cryostats, a detector is installed in the bottom of the detector holding pipe, into which the light pipe with a sample is inserted. To reduce the magneto-resistance effect, the detector is located outside of the magnet with a thick metal shield. For the gas-flow cryostat, a field-tuned InSb installed in HDL-5 dewar (IR-lab Inc.) is used.

As the radiation source, we combine three types of devices. For the microwave region, conventional Gunn oscillators are employed. For frequencies between 250 GHz and 7 THz, an optically pumped far-infrared laser is used. The number of available frequencies of the laser is more than 200. Backward travelling wave oscillators (BWO) are also employed, especially in 35–190 and 350–400 GHz. It should be noted that this frequency coverage is equivalent to the energy range available to a neutron triple-axis spectrometer installed in a reactor. The data acquisition instrument consists of a digital oscilloscope, pre-amplifiers, a multi-channel delay and a personal computer. The synchronization of the start of digital recording, the radiation source trigger, pulse field generation and shutter–chopper operation can be controlled by the multi-channel delay.

2.2. 1D structure of Cu benzoate

The single crystals used in this work were grown by the diffusion method. The quality of crystals was checked by x-ray diffraction and by magnetic susceptibility measurements in a very low magnetic field for different field orientations. We found no detectable contribution from impurities.

Figures 2(a) and (b) show the crystal structure of Cu benzoate. Cu$^{2+}$ ions form an antiferromagnetic chain along the $c$-axis by sharing two H$_2$O molecules [21]. The exchange interaction $J$ was evaluated to be 8.6 K by fitting magnetic susceptibility with a Bonner–Fisher curve [14]. Note that we use the expression of $2J$ for exchange energy. The good one-dimensionality was also found in $T$-linear specific heat at zero field and no peak of 3D magnetic ordering was found down to 80 mK [22]. The weak inter-chain coupling can be understood by considering the crystal structure as follows.

As shown in figure 2(a), the chains are separated by two benzoate anions along the $b$-axis. In one side, a benzoate anion is connected with the Cu$^{2+}$ ions of the magnetic chain through oxygen atoms. In the other side, two benzene anions are stacked on each other by van der Waals interaction and thus no magnetic coupling is expected along this axis. Along the $a$-axis, chains are connected through the hydrogen bonds. There are two different routes, namely the path going through H$_2$O molecules and the path through both H$_2$O molecules and an oxygen atom. The bond lengths indicate that those bonds are so-called weak hydrogen bonding and the magnetic interactions are expected to be a few mK or less [21]. It should be noted that the effective magnetic coupling along the $a$-axis may be further reduced by the competition between the two routes because the signs of the coupling may be different from each other for the excess oxygen atom in one of the paths. Moreover, the dipolar interaction is expected to be tiny because of the long distance between the chains.

The absence of the magnetic ordering down to 20 mK was established by $\mu$SR experiment [23]. Recently, Karaki et al [24] found a sign of some magnetic ordering below 1 mK by magnetic
susceptibility measurement. The ordering temperature is at $10^{-4}$ in the reduced temperature normalized by the intra-chain exchange coupling. Such extremely good one-dimensionality is essential in the study of 1D properties in very high magnetic fields because a 3D ordering can be induced by even weak magnetic coupling between chains. It is noticed that Cu benzoate may be a unique model compound for such study because of the ideal one-dimensionality.

Finally, we mention the origin of the staggered fields. As shown in figure 2, the principle axes of g-tensors are different between the neighbouring Cu$^{2+}$ sites because of the zig-zag chain structure. There is also the alternation of the DM-vectors along the chain. In such a condition, staggered fields are induced and they are strong in the $c'$- and the $c$-axes and weak in the $a$- and the $b$-axes.

3. Experimental results

3.1. Low field regime

In the following, we show the ESR spectra and the energy diagram in the low field regime below the half of the saturation field. Throughout this work, a magnetic field is applied along
the $c$-axis, because staggered fields are strong and many other experiments are made in this orientation. Figure 3 shows the temperature dependence of the ESR spectrum in conventional Faraday configuration where the propagation vector $k$ is parallel to the external magnetic field $H$. As the temperature is decreased, shift of the resonance field and broadening of the line width are found, which are caused by the development of the short range correlation inside the chain. In fact, the changes start where temperature $T$ is comparable with the exchange coupling $J$. As temperature is decreased further, a new peak appears in the low field side and those two peaks coexist in some temperature ranges. A similar behaviour was reported in the early study, however, the temperature range of the alternation is much higher here [15]. In our previous study, we analysed this phenomenon as the dynamical crossover between spinon ESR mode and breather ESR mode because the crossover occurs when $T$ is comparable with the magnitude of the field-induced gap [8]. This explains why the alternation regime changes with frequency.

A schematic dispersion relation of $S = 1/2$ Heisenberg AFC with staggered fields is given in figure 4, where the $z$-axis is defined to be parallel to $H$. Important features are shift of the wave vector of ‘soft mode’, polarization dependence, the field-induced gap and the discretization of the excitation spectrum [1]. The presence of staggered fields changes the gapless soft mode into a gapped minimum with the shift of the wave vector. The dispersion is different between the $S_z$ and $S_{xy}$ components. Those two components can be identified by the polarization dependence of ESR. For instance, in Faraday configuration, the polarization of radiation lies in the $xy$-plane and thus the $S_{xy}$ component can be observed. In Voight configuration, both $S_z$ and $S_{xy}$ components can be observed because the radiation has both field-parallel and perpendicular components. Different modes can be distinguished by comparing ESR spectra measured in two configurations. The excitations are quantized in $S = 1/2$ Heisenberg AFC, which results in the discretization of the excitation spectrum as shown in figure 4.

A $q = 0$ magnetic excitation can be observed by ESR usually because the wave vector of the radiation is nearly zero. We describe here what can be expected in the polarization dependence of ESR. As shown in figure 4, the effect of the field-induced gap is different between the $S_z$ and

Figure 3. Temperature dependence of the ESR spectrum at 325.9 GHz for $H \parallel c$. The ▼ and the □ denote the spinon ESR and breather ESR, respectively.
Figure 4. A schematic view of the lower boundary of magnetic excitation of Cu benzoate in a magnetic field. $S_z$ and $S_{xy}$ denote magnetic excitations parallel and perpendicular to the magnetic field, respectively. The soft mode expected in the absence of the gap is shown by the dashed curve around the incommensurate wave vector $q = q_{\text{inc}}$. The discretization of the magnetic excitation is schematically shown around $q = 0$ and $q = \pi$, where only the two lowest modes are shown.

In the $S_{xy}$ components. In the $S_z$ component, the gap appears at $q = q_{\text{inc}}$ and at $q = \pi$, where $q_{\text{inc}}$ is the incommensurate wave vector proportional to the magnetization. The energy shift at $q = 0$ is the sum of two contributions, namely, Zeeman energy proportional to $H$ and the field-induced gap. If there are no staggered fields, the energy is reduced to the Zeeman energy and the excitation at $q = 0$ corresponds to the spinon excitation (spinon ESR) at a finite magnetic field. The special feature of the spinon mode is the sharp delta-function-like line shape [3].

In the $S_z$ component, the excitation energy at $q = 0$ represents purely the field-induced gap and thus ESR may pick up the gap directly. Such gapped excitation is usually forbidden in ESR because the total spin $S$ is different between the ground and the excited states. In fact, the ground state is a sort of singlet for fully isotropic $S = 1/2$ AFC. When staggered fields are induced, the ground state mixes with the excited states. Consequently, ESR can probe the gap directly. Such breaking of the ESR selection rule by staggered fields has been known in many systems [25, 26]. It should be also noted that staggered fields cause the mixing between $q = 0$ and $q = \pi$ modes. In other words, ESR may pick up the excitation at $q = \pi$. In any case, it is most probable that the field-induced gap can be observed directly by ESR in Voight configuration and that the sum of the Zeeman energy and the gap can be observed in Faraday configuration.

Figure 5 shows the temperature dependence of the ESR spectrum in Voight configuration. The inset shows the spectrum in Faraday configuration measured at comparable frequency. By comparing those spectra, it is found that the intensities of different peaks change with the polarization. In Faraday configuration, the two peaks $B_{1xy}$ and $B_{2xy}$ are strong and the other two
peaks $B_{1z}$ and $B_{2z}$ are weak in intensity. In Voight configuration, the intensity ratio between those two groups is reversed. It is also noticed that the peak $B_{1xy}$ is 15 times as strong as $B_{1z}$ in Faraday configuration. On the other hand, in Voight configuration, the peak heights are comparable between $B_{1z}$ and $B_{1xy}$. This difference is consistent with the fact that the radiation has only perpendicular polarization in Faraday configuration and has the mixed polarization in Voight configuration. Such clear polarization dependence of the modes enables us to classify them into $S_z$ or $S_{xy}$ related excitations.

Figure 6 shows the frequency–field plot obtained at 0.5 K in $H \parallel c$. The $B_{1z}$ mode can be easily distinguished from other modes by the distinct nonlinear field dependence. The frequency of the $B_{2z}$ mode is almost double that of the $B_{1z}$ mode at the same magnetic field intensity. The mode $B_{1xy}$ slightly deviates from the linear magnetic field dependence shown by the dashed line. The difference between the higher order peak $B_{2xy}$ and the fundamental peak $B_{1xy}$ is small in Faraday configuration. As discussed in previous paragraphs, the excitation energy in Faraday configuration is given by the sum of two contributions: Zeeman energy and the field-induced
Figure 6. Frequency–field plot for $H \parallel c$. The notations are the same as those in figure 5. All points are taken from $T = 0.5$ K data, except for $X_z$ taken at 1.2 and 1.6 K. The dashed line indicates the position of the conventional paramagnetic resonance of $g = 2.25$.

gap. The energy of the ESR mode in Faraday configuration $(h\nu)_F$ is thus given by

$$(h\nu)_F = \sqrt{(g\mu_B H)^2 + E_{xy}(H)^2},$$

where, $\nu$, $g$, $E_{xy}(H)$ are frequency, $g$-value and the field-induced gap (excitation energy of soliton/breather), respectively [7]. The field dependence of the gap is evaluated by using equation (1) from the measured data set of $\nu$ and $H$ plotted in figure 6. The known $g$-value along the $c$-axis of 2.25 is used [15]. It should be noted that excitation energies are obtained by the subtraction of Zeeman energy for both $B_{1xy}$ and $B_{2xy}$ modes. The evaluated pure excitation gaps are plotted in figure 7 as the function of magnetic field. For Voight configuration, the energy of the ESR mode corresponds directly to the excitation gap and thus the values in figure 6 are re-plotted in figure 7.

In the following, we use a notation of $E_{1xy}$ as the energy of the mode $B_{1xy}$. Similar notations are used for other modes. Below 7 T, both $E_{1xy}$ and $E_{1z}$ follow the same power-law curve 1 expected in the SG model [6]. The ESR result is in good agreement with the gap evaluated by specific heat as shown in figure 7. A finite deviation is found between $E_{1xy}$ and $E_{1z}$ above 7 T. It may be caused by the different nature of excitation at $q = 0$ between $S_{xy}$ and $S_z$ components. For higher order excitations $E_{2xy}$ and $E_{2z}$, the difference is small as shown in figure 7. The degeneracy of those two modes suggests that the deviation between $xy$- and $z$- components becomes distinct only in higher magnetic fields. This point will be discussed later.
Figure 7. The field dependences of the excitation energies for different modes. The notations are same as those in figures 5 and 6. \( C_p \) is the gap evaluated by specific heat taken from the [5]. The curves 1 and 2 are eye-guides for power-law \( E(\text{GHz}) = a B(T)^{3/2} \), where the proportional constants are 25.7 and 46.2 for curves 1 and 2, respectively. The curve 3 is the difference between curve 2 and curve 1.

It is also noticed that the coefficient of the curve 2 is 1.8 times as large as that of the curve 1. In other words, the \( E_{2z} \) is a little smaller than the double of \( E_{1z} \). It means that the higher order excitation is not caused by the simultaneous generation of two-solitons/two-breathers. In fact, the energy of \( E_{2xy} \) and \( E_{2z} \) agrees with the expected energy of a higher order breather, which is discussed in the next section.

Finally, we mention the signal \( X_z \) appearing around 10.5 T in figure 5. This signal is found only in the temperature range between 2.3 and 1.2 K. It is suggestive that the low temperature peak shown in figure 3 becomes dominant around this temperature range. Moreover, the disappearance of the signal at lower temperature indicates that the \( X_z \) is the transition within the excited states. The absence of the signal at high temperature is due to the fact that the field-induced gap is not well established above 3 K. From those features, we assign the \( X_z \) to be the transition between \( B_{1z} \) and \( B_{2z} \). In fact, the energy fits nicely with the difference of the curve 2 and the curve 1 as shown in figure 7. The observation of such inter-breather excitation is a clear evidence of the discretization of the energy spectrum.

### 3.2. High field regime

Figure 8 shows the ESR spectra measured in the high field regime between 10 and 30 T. Between 119.8 and 135 GHz, three peaks are found, while only one peak is found for 150.7 GHz. The frequency–field plot is given in figure 9, where the peaks in figure 8 are marked as \( B_{1z} \). This mode
Three peaks are identified and two of them tend to merge around 18 T with increasing frequency. For the other peak appearing in the high field side, the resonance field steadily increases with increasing frequency.

As shown in figure 8, two peaks are nearly merged at 135 GHz, which supports the re-entrant behaviour around 18 T. In pulsed field ESR, a scan is made along the horizontal line in the frequency–field diagram, since the magnetic field is swept at a certain fixed frequency of radiation. When a mode is flat in the frequency–field diagram, the horizontal cut of the mode results in the broad line width.

The observed complicated behaviour of $B_{1z}$ can be explained by considering the origins of the gap in two regimes, namely above and below the saturation field. Above the saturation field, spins align parallel to the external magnetic field and a flip of the spin costs a finite energy. The gap observed above the saturation is similar to the excitation gap in an Ising ferromagnetic chain. The difference here is that the anisotropy is caused by a strong external magnetic field and not by built-in anisotropy. It should be also noted that the effective field applying to this ‘Ising chain’ is zero at the saturation field because the external field and the antiferromagnetic exchange coupling cancel each other. It is easily understood that the energy of spin flip is proportional to the deviation from the saturation field, which is consistent with the present result. Below the saturation field, the decrease of the gap above 18 T is caused by the reduction of the staggered field. It is because the uniform magnetization overwhelms the staggered moments in such a high magnetic field. In such a condition, the energy of the field-induced gap becomes comparable with $E_{\text{max2}}$ as shown in figure 10. The perturbative treatment of the SG model should show the
Figure 9. The frequency–field diagram up to 30 T. The notations are the same as those in figure 7. The mode above the saturation field is also marked as $B_{1z}$, though the nature of the excitation is different from the $B_{1z}$ observed below the saturation. The diamonds show the result of DMRG calculation for the c-axis [27]. The dotted black, dashed black, solid blue and solid black curves are the second breather $B_2$, soliton, the first breather $B_1$ and the inter-breather ($B_2 - B_1$) excitations respectively, which are calculated by using the equation (3) [28]. The dashed blue curve is the $B_1$ calculated by the equation (2) [20]. All theoretical curves are plotted up to $0.97H_s$, where $H_s$ is the saturation field.

complete breakdown in this regime. The discussion on different theoretical approaches will be made in the next section.

Finally we mention that the gap does not close completely around the saturation field. As is well known, the energy states are mixed when non-secular terms such as DM interaction or staggered field exist. The mixing leads to the opening of the gap instead of the gap closing at the saturation field. A consequence of such mixing is the rounding of the magnetization around the saturation field. In such a case, the polarization of spin is not perfect and staggered moments remain finite, which may cause the orthogonal order of uniform and staggered moments as mentioned by Zhao et al [27].

4. Discussion

As shown in the previous section, the field dependence of the magnetic excitation mode is obtained in the whole range of the magnetic field. In the following, we compare the present results with some of the theoretical results so far published.
In figure 10, we present the qualitative difference of the dispersion curves (of the lower bound of magnetic excitations) between the low field regime and the high field regime. In the low field regime, the field-induced gap is small and then the dispersion curve is modified only slightly from that of the fully isotropic Heisenberg chain. On the other hand, the sinusoidal dispersion is heavily distorted in the high field regime. The ratio of the field-induced gap to the maximum of the dispersion such as $E_{g2}/E_{\text{max}2}$ is a good indicator to separate these two regimes. At 3 T, $E_{g1}/E_{\text{max}1} \sim 0.1$ and thus a perturbative treatment can be used. In fact, an SG model has been successfully applied for the analysis of field-induced gap in Cu benzoate below 7 T. The SG model should break down in the higher field regime, because the dispersion cannot be calculated by any perturbation theory when the dispersion of the unperturbated isotropic Heisenberg chain is completely modified as shown in figure 10.

Affleck and Oshikawa [20] give the following formula of the field-induced gap: $\Delta$ in the region of $\Delta \ll H$.

$$\frac{\Delta}{J} \approx \left(\frac{\hbar}{J}\right)^{(1+\xi)/2} \left[ B\left(\frac{J}{H}\right)^{(2\pi-\beta^2)/4\pi} \left(2 - \frac{\beta^2}{\pi}\right) \right]^{1/4} \left(\frac{1+\xi}{2}\right)^{1/2},$$

(2)
where $\xi$ is a parameter given by the relation $\xi = \beta^2/(8\pi - \beta^2)$ with the coupling constant $\beta$ in the SG model and $B = 0.422169$ is a constant. The magnetic field $H$ and staggered field $h$ are normalized with the exchange coupling $J$ and the relation $h = bH$ holds with a proportional constant $b$. The curve calculated by using equation (2) is shown by the dashed blue curve in figure 9, where $b = 0.08$ is used. It should be noted that the equation (2) can be applied in very low field regions where the energies of solitons and breathers are nearly degenerated. In other words, equation (2) should be used in a magnetic field below 2–3 T. An application of the equation in a narrow field range may result in the inaccuracy of a parameter such as the proportional constant $b$, though a seeming agreement can be obtained even in higher field regimes.

To extend the applicable range of the SG model, it is useful to consider the field dependence of parameters, such as a spin wave velocity $v$, the amplitude $c$ corresponding to the staggered field’s amplitude as well as the coupling constant $\beta$. In the present study, we use the formula and parameter given by Essler et al [28]. They claimed that the field dependence of the soliton mass is given by

$$\frac{\Delta}{J} \approx \frac{2v}{\sqrt{\pi}} \frac{\Gamma\left(\frac{\xi}{2}\right)}{\Gamma\left(1 + \frac{\xi}{2}\right)} \left[\frac{c\pi}{2v} \frac{\Gamma\left(\frac{1}{1 + \xi}\right)}{\Gamma\left(\frac{\xi}{1 + \xi}\right)} \frac{bH}{J}\right]^{(1+\xi)/2}.$$  
(3)

The mass of the $n$-breather is then given by

$$\Delta_n = 2\Delta \sin\left(\frac{\pi \xi n}{2}\right), \quad n = 1, ..., \frac{1}{\xi},$$  
(4)

where $n$ is an integer. For $c$, we use the result of numerical calculation given in the above reference. The parameters $v$ and $\beta$ calculated by using the Bethe ansatz are also given in [29].

The energies of the first and the second breathers are plotted in figure 9, which are calculated by using equations (3) and (4). As the proportional constant of the staggered fields, $b = 0.08$ is used. Below 15 T, the agreement between the theory and the experiment is good for $B_{1z}$ and $B_{2z}$ as well as the inter-breather transition $X_z$. The negative field dependence of the $B_{1z}$ observed above 18 T is seemingly simulated also by the equation (3). This reduction of the $B_{1z}$ is mainly caused by renormalization of $v$ which goes to zero at the saturation field. Although an apparent agreement is found with the theory, the following differences are noticed: (i) discrepancy of the peak field position of $B_{1z}$, (ii) residual gap at $H_s$ and (iii) the discrepancy between $B_{1xy}$ and $B_{1z}$. In figure 9, the results of DMRG calculations made by Zhao et al [27] are also plotted. It should be noted that the calculation is made for $H \parallel c'$, where the staggered fields are larger than those in $H \parallel c$. It is found that the numerical and the experimental curves are quite similar in their characteristic shapes. Considering this fact, it is convincing that the DMRG result can simulate the behaviour of the breather over the whole range of the magnetic field, especially the points (i) and (ii), which are not interpreted by the SG model.

Now let us discuss the physical origin of the breakdown of the SG mode in high magnetic fields. As shown in figure 10, the dispersion curve at 18 T is completely distorted from that of the isotropic system without staggered fields. In such a condition, the use of the SG model may not be justified even if the field dependences of a parameter such as $v$ is considered. The velocity
\( v \) is given by Bethe ansatz and it is the slope of the gapless sinusoidal mode at \( q = 0 \). When the staggered fields are present, ESR probes the excitation at finite energy. In this case, we have to use \( v \) at finite energy instead of that at zero energy. At 18 T, for example, the \( v \) at \( q = q_{Eg} \) of the unperturbative dispersion curve is about 60\% of that at \( q = 0 \). On the other hand, the difference is only 5\% at 3 T. If we consider the fact that the \( v \) is a sort of Fermi velocity of the system, the use of the \( v \) at the energy of the field-induced gap may be justified. It is also noticed that, at 18 T, the gap is nearly comparable with the maximum of the dispersion \( E_{\text{max}2} \). In much higher fields, it is expected that the gap energy exceeds the top of the sinusoidal curve. In such conditions, perturbative treatment of the SG model is not applicable anymore. Hence, the condition \( E_{q2}/E_{\text{max}2} \sim 1 \) gives the rough criterion of breaking down of the SG model, which corresponds to the turning point of the field dependence of the gap at around 18 T. As discussed above, the applicability of the equation (3) must be limited below 18 T and the decrease of the calculated \( B_{1z} \) seems to be insubstantial.

Finally, we discuss the discrepancy between \( B_{1xy} \) and \( B_{1z} \) found above 10 T. In the recent ESR study on Cu–pyrimidine–dinitrate, Zvyagin et al [13] claimed that both solitons and breathers are detected for the mixing of the polarizations. If we consider the different symmetry between this material and Cu benzoate, namely, the difference in the directions of the staggered fields, the absence of the soliton mode in the present study is not surprising. In the present study, it is most probable that we observe breathers in both \( xy \)- and \( z \)-polarizations. Clear support for this is the fact that we observe the higher order mode of \( B_{2xy} \) for \( xy \)-polarization, which is not expected for solitons.

The next point is how we can interpret the mass difference of the breathers between \( xy \)- and \( z \)-polarizations in the high field regime. In figure 10, it is noticed that the curvature of the gapped mode is different between \( q = 0 \) and \( q = q_{c2} \) because of the asymmetry of the dispersion around \( q = q_{c2} \). In the \( S_z \) component, ESR probes mostly the mode at \( q = 0 \) and the mass of the breather is corresponding to the curvature of the dispersion at this point. For the \( S_{xy} \) component, ESR also probes the breather mode at \( q = 0 \). It should be noted that the breather mass of the \( S_{xy} \) component at \( q = 0 \) is affected by the gap at \( q = q_{\text{inc}} \), rather than the gap at \( q = \pi \). As shown in figure 4, the dispersion of the \( S_{xy} \) component around \( q = q_{\text{inc}} \) is similar to that of the \( S_z \) component around \( q = 1 - q_{\text{inc}} \). This means that the contribution of the field-induced gap is different between \( xy \)- and \( z \)-components at \( q = 0 \). It is probable that this difference is the origin of the difference between \( B_{1xy} \) and \( B_{1z} \). This interpretation is consistent with the fact that the deviation becomes apparent only in very high magnetic fields. In low magnetic fields, the dispersion is symmetric around the incommensurate wave vectors such as \( q = q_{Eg} \) and thus no deviation is expected. For quantitative discussion, it may be necessary to develop a more sophisticated formula instead of the equation (3) to separate the contribution of Zeeman energy from the observed \( B_{1xy} \), which remains for further theoretical investigations.

5. Summary

To summarize, the field dependence of magnetic excitations in \( S = 1/2 \) Heisenberg AFC Cu benzoate have been investigated over the whole magnetic field regime. The first and second breather excitations as well as inter-breather excitation are clearly detected, which are the manifestation of the discretization of the excitation spectrum. Below the half of the saturation field, the SG model successfully simulates the observed ESR modes by taking
the field dependence of the parameter into account. In the higher field regime, the breakdown of the SG model is found and the possible interpretation is given in terms of the strong modification of the magnetic dispersion. Moreover, the polarization dependence of the breather excitation energies are found, and the origin is attributed to the development of the asymmetry in magnetic dispersion.

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