ESR investigation on the Breather mode and the Spinon-Breather dynamical crossover in Cu Benzoate

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A new elementary-excitation, the so called "breather excitation", is observed directly by millimeter-submillimeter wave electron spin resonance (ESR) in the Heisenberg quantum spin-chain Cu benzoate, in which a field-induced gap is found recently by specific heat and neutron scattering measurements. Distinct anomalies were found in line width and in resonance field around the "dynamical crossover" regime between the gap-less spinon-regime and the gapped breather-regime. When the temperature becomes sufficiently lower than the energy gap, a new ESR-line with very narrow line-width is found, which is the manifestation of the breather excitation. The non-linear field dependence of the resonance field agrees well with the theoretical formula of the first breather-excitation proposed by Oshikawa and Affleck. The present work establishes experimentally for the first time that a sine-Gordon model is applicable to explain spin dynamics in a $S = 1/2$ Heisenberg spin chain subjected to staggered field even in high fields.

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A magnetic field has been recognized as a unique handling-parameter to control the quantum-critical phenomena in various low-dimensional spin systems. An example of the drastic change of magnetic excitation in high magnetic fields has been found recently in Cu benzoate Cu(C$_6$H$_3$COO)$_2$·3H$_2$O. For a very long time, this compound had been regarded as a good representative of $S = 1/2$ Heisenberg quantum spin chain (HQSC), with an exchange coupling $J = 8.6$ K. More recently, however, intensive measurements performed below 1 K revealed rather unexpected features. Besides the dynamical incommensurability expected in high fields, an unexpected energy-gap $E_g(H)$ in the magnetic excitation spectrum was observed to develop as a function of the applied magnetic field $H$. Based on a field theoretical approach, a description was proposed by Oshikawa and Affleck (OA) and, subsequently by Essler and Tsvelik. They claimed that these effects were caused by the staggered fields acting between neighboring spins in a chain. (Note that some aspects of the field-induced gap has been discussed theoretically by several authors, \cite{9}.) Their most striking theoretical proposal for Cu benzoate is that the particle-like "breather" excitation appears besides solitons, in the extreme low-temperature limit, where the temperature is smaller than the gap.

The "breather" is the soliton-antisoliton bound-state and one of the elementary excitations in a quantum sine-Gordon model. For conventional $S = 1/2$ HQSC, the gap-less spinon excitation develops due to the short-range correlation when the temperature $T$ is much lower than $J$. In case of Cu benzoate subjected to the staggered field, for further decrease of the temperature, a drastic change in spin-fluctuation spectrum arises due to the presence of the field-induced energy gap; i.e. the dynamical crossover takes place between the spinon-regime and the gapped breather-regime. In the gapped breather-regime, it is theoretically proposed by a sine-Gordon model that the excitation spectrum consist of the first "breather", soliton, anti-soliton and a multi-particle continuum. Most important, the exact integrability of this model shows that the ESR intensity is dominated by the first-breather mode in the extreme low-$T$ limit. (Note that, in the Faraday configuration we used in the experiment, a soliton cannot be excited.) For these features, a ESR is considered as one of the most unique and powerful probes to investigate the spin dynamics in Cu benzoate.

The first "anomaly" of the magnetic excitation below 1 K was reported in ESR measurements more than 20 years ago. Although their interpretation for the low temperature ESR as the antiferromagnetic resonance was not compatible with the most recent results as mentioned above, their results are presently reanalyzed in the newly proposed theoretical context. It should be noted that no Néel ordering was found in the specific heat and the neutron scattering measurements, at least down to 0.1 K. It means clearly that the field-induced gap should be attributed purely to the one-dimensional and dynamical character of the system.

The main issue of the present work is the experimental proof of the existence of "breather" as well as to elucidate its dynamical properties, here in Cu benzoate. Our present results also open the possibility to reinterpret the experimental results on this material obtained more than twenty years ago. As the first point we test the theoretically proposed mass-formula of the first-breather ESR mode in wide range of magnetic field $H$ including the high-field condition such as $g\mu_B H \sim 2J$. As second item we examine by ESR, the dynamical spinon-breather crossover originating from the field-induced energy gap in...
a very wide frequency range.

For this work, single crystals were grown by the diffusion method and rectangular shaped samples with a typical dimension of $5\times4\times0.1$ mm$^3$ were used for the measurements. The quality of crystals was checked by X-ray diffraction and by magnetic susceptibility measurements. The crystal structure belongs to the monoclinic space group $I2/c$ and magnetic chains made up of Cu$^{2+}$ ions are lined up along the $c$-axis. The details for the ESR system were given in references. All measurements were performed in the Faraday configuration where a propagation vector of the light is parallel to the external magnetic field.

Examples of ESR spectra for $H\parallel c$ are shown in Fig. 1 at different frequencies. Drastic changes in spectra, shift of the resonance field and broadening of the line width, appear when $T<J$. The origin of the $T$-dependence is the increase of the spinon correlation-length $\xi_{\text{spinon}}$ that develops as $\xi_{\text{spinon}} \sim J/T$. The development of $\xi_{\text{spinon}}$ is a common feature of a HQSC and causes the remarkable changes of ESR spectra. However, the temperature dependences of the shift and the line width depend on the type of the anisotropic-term in the spin-Hamiltonian. For Cu benzoate, it is proposed that a staggered field gives rise to the anomalies of ESR and that the shift and the line width follow the relations as $(H/T)^{\eta}$ and $(H/T)^{\kappa}$, respectively. In fact, as shown in Fig. 1, the shift and the line width drastically increase as the temperature is decreased.

As the temperature is decreased further, a novel crossover takes place. While the width of the spinon ESR line $S$ increases continuously, the integrated intensity of this signal decreases gradually. At the same time, the new ESR line $B_1$ appears in the low field side. The lines $S$ and the $B_1$ coexist in some temperature regime and, in this regime, the spectral weight shifts gradually from the line $S$ to the line $B_1$. At 0.5 K, finally, the absorption intensity of the $B_1$ becomes dominant. These behaviors of ESR spectra clearly exhibit that the change should be considered as "crossover" rather than a phase transition associated with a well defined phase boundary. To examine the nature of this crossover, we performed a fit consisting of two Lorentzian for each spectra and evaluated the width of the ESR line $S$ and that of the line $B_1$ independently as a function of temperature as shown in Fig. 2.

The solid lines represent the best fit curves for the ESR line $S$. The leading term of the fitting function is $\alpha(H/T)^2$, the parameter chosen is as $\alpha = 0.087 [K^2\text{Tesla}^{-1}]$. This term expresses the broadening of the line width caused by the staggered field, which was proposed by OA in the simplest approximation. In addition to this main term, a small line width as $\beta H$ ($\beta = 0.007$, dimensionless) is added, which is caused by other mechanisms. Surprisingly, the data at all frequencies are satisfactorily reproduced with only two universal parameters in the wide temperature range, except for the very vicinity of the crossover regime. Since the term $\alpha(H/T)^2$ clearly dominates the line widths, we can say that the functional form predicted by OA for the spinon-regime is applicable for a very wide field-temperature range. It should be noted that the existing low frequency data are consistently reproduced by using the same parameters we are proposing here (Note that a small $T$-linear term in the previous data is negligible compared to the $\beta H$ term). The shift of the resonance field also follows the theoretical proposal as $(H/T)^{\eta}$ mentioned before, although some deviation was found around the crossover regime. For the limited space of the paper, the results will be discussed separately.

The line width of the ESR line $B_1$ shows a completely different $T$-dependence from that for the line $S$. For the line $B_1$, the width very rapidly decreases as $T$ is lowered below the crossover regime. (Note that the abscissa of Fig. 2 is a logarithmic temperature scale) This characteristic $T$-dependence can be explained as the effect of the field-induced gap as follows. For the gapped breather-regime, the magnetic excitation is dominated by the particle-like breather-excitation and thus, the ESR line width is caused by the collisions between the thermally excited particles. Since the number of excited particles exponentially decreases toward $T=0$, the line width is expected to follow the function as $\delta H \propto exp(-E_g(H)/T)$, which is represented by the dashed lines in Fig. 2. Here, we use the experimentally determined gap $E_g(H)$ from the resonance fields by using the mass-formula of the first-breather mode(see Fig. 3(c) for the value of $E_g(H)$). We also add a residual line width $\kappa$ as small as 0.04 Tesla, which is the line width at low- $T$ limit.

Since the transition matrix element to excite the breather mode is the staggered field, we can expect that the prefactor is approximately linear in $H$. It is remarkable that the data at different frequencies are fitted by only two universal parameters $\eta$ and $\kappa$. Note that $E_g(H)$ is not an adjustable parameter. The most important point in this analysis is that the experimentally observed decrease of the line width can be quantitatively explained by using the experimentally obtained value of the gap. It means that experimental data, the resonance fields and the line widths, show the overall agreement with the breather picture proposed by OA. Hence we can conclude clearly that the mode $B_1$ is the manifestation of the breather excitation.

In the inset of Fig. 2, it is instructive to point out that the crossover regime, represented by a horizontal bar, is located besides the solid line which represents the curve $k_B T = E_g(H)$. This finding strongly indicates that the drastic anomaly of the $\delta H$ is caused by the field induced gap i.e. the line width probes the essential difference of...
the spin fluctuation spectrum between the two regimes with and without an energy gap. Consequently, it is convincing that the novel anomaly of the ESR signal observed in the present work is the manifestation of the "spinon-breather crossover". It should be stressed that such dynamical crossover is observed here for the first time directly by means of ESR.

Let us proceed to the discussion of the field dependence of the first breather mode $B_1$ at the lowest temperature $T=0.5$ K. The frequency-field plots for different field orientations are depicted in Fig. 3(a). To examine the field dependence clearly, the deviation $\Delta$ from the linear Zeeman-effect is depicted in Fig. 3(b) as a function of external field.

According to OA, the frequency-field relation of the first breather mode observed by ESR is given by [10]

$$ h\nu = \sqrt{(g\mu_B H)^2 + E_g^2(H)^2}, \quad (1) $$

where $\nu$ and $g$ are the frequency of ESR and the $g$-value, respectively. It should be noticed that the field dependence of this breather mode is different from that observed by neutron scattering at $q = \pi$. This difference is originated by the fact that the first breather mode observed by ESR is a uniform mode at $q = 0$. The equation means that a non-linear frequency-field relation is caused by the presence of $E_g^2(H)$ and thus the deviation from the linear Zeeman-effect is directly related to the magnitude of the gap. This deviation gives rise to the non-linear shift of the resonance field for the low-field side, which is consistent with the experimental results as shown in Fig. 3(b).

In Fig. 3(b), it is found that $\Delta$ is large for $H \parallel c$ and $H \parallel c''$, and small for $H \parallel a$ and $H \parallel b$ in accordance with the angular dependence of the field-induced gap. This finding shows that, for $H \parallel a$ and $H \parallel b$, the induced gap is not large enough to satisfy the condition as $k_B T \ll E_g(H)$ even at 0.5 K. Accordingly, we analyze the data only for $H \parallel c$ and $H \parallel c''$ in the following.

To calculate $E_g^2(H)$ from the experimental data of the frequency-field dependence, we rewrite the eq(1) as

$$ E_g(H) = \sqrt{(h\nu)^2 - (g\mu_B H)^2}. \quad (2) $$

By putting the experimental values of $\nu$ and $H$ and $g_v=2.25$ or $g_v'=2.29$ into eq(2), we determine the energy gap $E_g^2(H)$ as a function of magnetic field without any adjustable parameters. It should be noted that this process is very straightforward as long as the condition $k_B T \ll E_g^2(H)$ is satisfied and thus eq(1) is applicable. The results are depicted in Fig. 3(c) together with the gap for $H \parallel c''$ evaluated by the specific heat measurements. The gap obtained by the ESR shows a very good agreement with that obtained by the specific-heat measurements. It is remarkable that the validity of the eq(1) is clearly confirmed experimentally by the present work, in the wide field range including a high field condition as $g\mu_B H \sim 2J$.

Finally we briefly discuss the unexpected new ESR lines $B_2$ and $B_3$ observed at 0.5 K. As shown in the inset of Fig. 4, weak but definite ESR lines $B_2$ and $B_3$ appear besides the first breather $B_1$. The slope of $B_2$ and $B_3$ modes are 1.42 $g$ and 1.65 $g$, respectively, where $g=2.25$ is the slope of the $B_1$ mode. It should be noted that such large $g$-values of $B_2$ and $B_3$ modes cannot be attributed to the $g$-values of possible impurities. Since the energies of $B_2$ and $B_3$ modes are higher than that of the $B_1$ mode, possible candidates for these signals are the higher breather-excitations or the transition associated with multiple breather-excitations. For a trial, we simply assume that the energy to excite $n$-breather is $nE_g(H)$ and put this mass into eq(1). The results are shown in Fig. 4 for $n=1\sim4$ and some of data points are not so far from the curves. Although no definite interpretation for the origin of those extra signals is found at present, we hope that our observation of the new ESR modes stimulates further theoretical investigations for the elementary excitation in a quantum sine-Gordon model.

To conclude, a well defined breather excitation has been observed by means of ESR for the first time, in a very wide field range for Cu benzoate exposed to a staggered field. The field dependence of the energy gap agrees well with the results of the previously reported specific-heat measurements. The present results establish the validity of the mass-formula of the uniform first-breather mode at $q = 0$ in a wide field range. We have also observed the dynamical crossover between the spinon-regime and the gapped breather-regime. This crossover takes place when the temperature is comparable to the magnitude of the gap. The essential difference of spin fluctuation spectrum between these two regimes are observed very clearly by the characteristic temperature dependence of ESR line width.

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FIG. 1. Examples of ESR spectra at (a) 190 GHz and at (b) 428.9 GHz for $H \parallel c$. The closed circles and the closed triangles represent spinon ESR line (S) and the first-breather ESR line (B$_1$), respectively.

FIG. 2. The temperature dependence of the line width $\delta H$ for the ESR line S (closed circles) and for the ESR line B$_1$ (closed triangles). The line width is defined as a full width at the half maximum. The solid line and the dashed line represent the functions given in the text. In the inset, horizontal bars represent the crossover regime where the lines S and B$_1$ coexist. The solid line is the curve of $k_B T = E_g(H)$, where value of $E_g(H)$ is taken from Fig. 3(c). The dotted line is an eye-guide.

FIG. 3. (a) Frequency-field plot of the main ESR line for different field orientations. The marks used in the panel are identical to those used in other two panels. Thin lines are eye-guides. (b) The deviation $\Delta$ defined as the difference between the resonance field at 60 K and that at 0.5 K. The positive value relates to the shift to the lower field side. The $c''$-axis is in the $ac$-plane and tilts 21° from $a$-axis. (for more detail, see fig. 1 of Ref. [9]) (c) The plot of $E_g(H)$ as a function of external field. Open rectangles and closed triangles represent the values obtained by the present work. Open circles show the value determined by the specific-heat measurements taken from Ref. [3]. Dashed line and solid line are the theoretical curves of $E_g(H) \propto H^{2/3}$, the prefactor for $H \parallel c''$ is taken from Ref. [5].

FIG. 4. Frequency-field plot of the first-breather B$_1$ (closed triangles) together with the new ESR lines B$_2$ (closed rectangles) and B$_3$ (closed diamonds) for $H \parallel c$ and at 0.5 K. Thin lines are the theoretical curves given in the text. Dashed lines are eye-guides. An example of ESR spectrum taken at 190 GHz is given in the inset.
Fig. 1 Asano et al.
Fig. 2 Asano et al.
Fig. 3 Asano et al.
Fig. 4 Asano et al.