High-field ESR on quantum spin systems

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Abstract

High-field electron spin resonance (ESR) experiments have been performed on quantum spin systems. A distinct field-induced crossover between the gap-less spinon regime and the gapped sine-Gordon regime is observed for the Heisenberg quantum spin chain; CuBenzoate. In a Shastry and Sutherland model compound $SrCu_2(BO_3)_2$, a set of multiple-triplet excitations has been resolved by utilizing high-resolution ESR. The splitting of the two-triplet bound state into a few discrete energy levels is considered as the evidence of the extreme localization of the triplet excitations in this compound. The present results indicate the unique and powerful features of ESR in the study of magnetic excitations. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Quantum spin systems have been considered as important models to study the quantum critical behavior in strongly correlated electrons. In a conventional phase transition, critical phenomena are mostly examined as a function of temperature. For quantum spin systems, however, a magnetic field can be used as the unique handling parameter of the quantum spin fluctuation. The influence of magnetic fields on strong quantum fluctuation is manifested as drastic anomalies in the magnetic excitation spectra. These "anomalies" are, in many cases, nontrivial when a system is located near the quantum critical point. Hence, studies of the magnetic excitations in quantum spin systems in high magnetic fields have attracted much interest in this decade.

Electron spin resonance (ESR) is considered to be a unique tool among many different kinds of experimental techniques to study magnetic excitations such as inelastic neutron scattering, Raman scattering and far-infrared spectroscopy, for the following reasons: (1) high sensitivity, (2) high-energy resolution and (3) capability of high-field measurements by using a pulsed magnetic field. The accessible field range, by a non-destructive pulsed field ESR equipment, is more than 40 T and such high fields cannot be used by any means other than mentioned above. Experiments in mega-gauss fields are also possible by using a single-turn coil system. In the following, after a brief description of the experimental setup, several recent examples of the high-field ESR on quantum spin systems are presented.

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2. Experimental

The schematic drawing of the experimental setup of the ESR equipment is shown in Fig. 1. For insulating compounds, a simple transmission method is employed. For metallic materials, several different techniques are used as given in the reference [1]. Three different types of sources are installed to cover the wide frequency range between 35 GHz and 7 THz. For the microwave region, conventional Gunn oscillators are employed. Between 250 GHz and 7 THz, an optical pumped far-infrared laser is used. Backward travelling wave tubes are also used between 100 and 400 GHz. To cover such wide frequency range, four different types of detectors: (a) InSb, (b) GaAs, (c) a magnetic-field-tuned InSb and (d) GeGa, are installed. It should be noted that this frequency coverage is equivalent to that available by a neutron triple-axis spectrometer installed in a reactor. To obtain pulsed fields up to 40 T, a capacitor bank of 100 kJ energy is installed. For the generation of magnetic fields, a conventional wire-wound multi-layer coil is used. The pulse duration time is between 5 and 8 ms. The inner diameter of the cryostat can be changed between 12 and 22 mm depending on the

maximum field. A magnetic field up to 20 T can be generated by a split-type pulsed magnet. The split magnet is used to perform the experiments in Voigt configuration.

Two types of cryostats are installed to control the sample temperature. Below 70 K, a conventional bath-type cryostat is used. The lowest temperature of 0.4 K is obtained by using a ^{3}He insert. Above 70 K, a gas-flow-type cryostat is employed. The highest temperature available is 450 K.

3. Breather excitation in CuBenzoate

A $S = \frac{1}{2}$ Heisenberg spin chain ($S = \frac{1}{2}$HSC) is the most well-know model system showing quantum critical phenomena. A well-known spinon continuum of $S = \frac{1}{2}$HSC is characterized by a diverging zero energy (gap-less) mode with strong quantum fluctuations. In high magnetic fields, a new soft mode develops at the incommensurate wave vector and the excitation spectrum is gap-less up to the saturation of magnetization.

In the last three decades, CuBenzoate $Cu(C_6H_5COO)_2 3H_2O$ (CBZ) had been known as a good model of $S = \frac{1}{2}$HSC with an exchange coupling $J = 8.6$ K [2]. Recently, the presence of a field-induced energy gap was found in the specific heat, neutron scattering and susceptibility by Dender et al. [3]. This unexpected observation is very surprising, because the magnetic excitation of $S = \frac{1}{2}$HSC should be governed by the gap-less spinon mode even in high magnetic fields. Since no Néel ordering was found at least down to 0.1 K, the field-induced gap cannot be attributed to the field-induced ordering. Moreover, it is found that the magnitude of the gap increases with magnetic field intensity H as $H^{2/3}$. This power–law dependence on H indicates that the critical phenomenon of the system is controlled by the application of magnetic fields.

By using field-theoretical approaches, it has been claimed that the gap is caused by the staggered fields acting between neighboring spins in a chain due to the presence of Dzyaloshinsky–Moriya (DM) interactions which alternate their directions between the neighboring sites [4,5]. The most important point is that CBZ is classified as a quantum sine-Gordon system. As it is well known,
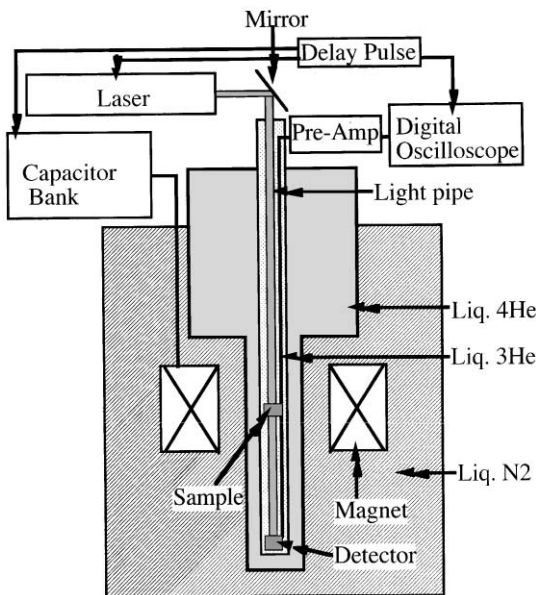

Fig. 1. Schematic view of the high-field ESR system.

a sine-Gordon model is the best-known system that contains non-linear excitations such as solitons, antisolitons, and their bound states, the so-called "breather excitations". The integrability of the model enables us to calculate many kinds of physical quantities exactly and thus it is very important to find out a good model compound representing this model.

ESR measurements on this compound below 1 K were reported more than 20 years ago and a new ESR peak was found at lowest temperature [6]. This ESR signal was interpreted as the antiferromagnetic resonance, which is not compatible with the present results as mentioned above. It has been proposed by Oshikawa and Affleck, that this new ESR signal is the manifestation of a breather excitation [7]. A characteristic feature of this mode is the non-linear field dependence of the resonance frequency v as

$$hv = [(g\mu_{\mathbf{B}}H)^2 + M_1^2]^{1/2}, \tag{1}$$

where g is the g-value and M_1 is the mass of the first breather. Since the first breather B_1 is the lowest energy excitation in a sine-Gordon model, the M_1 (energy of B_1) is identical to the magnitude of the field-induced gap. In the present ESR experiments, v and H can be precisely measured and thus, the field dependence of M_1 can be determined very accurately.

Fig. 2 shows an example of the temperature dependence of ESR spectra for $H\|c$. As the temperature is decreased, the resonance field shifts and the line width shows a broadening. Such changes are commonly observed for a $S = \frac{1}{2}$ HSC and the origin is considered as the development of the correlation length of the spinon excitation towards $T = 0$. Below 1.6 K, a new peak appears in low-field side besides the conventional spinon ESR mode (see Ref. [8] for more details). This behavior is similar to that observed in the previous ESR experiment performed at much lower frequency. This difference originates in the different magnitude of the gap as a function of H. To examine the nature of this new mode, the frequency dependence of the resonance field is examined at 0.5 K.

Fig. 3 shows the field dependence of the gap (M_1) as a function of H derived from Eq. (1) in the present work. In Eq. (1), g-value, v, and H are
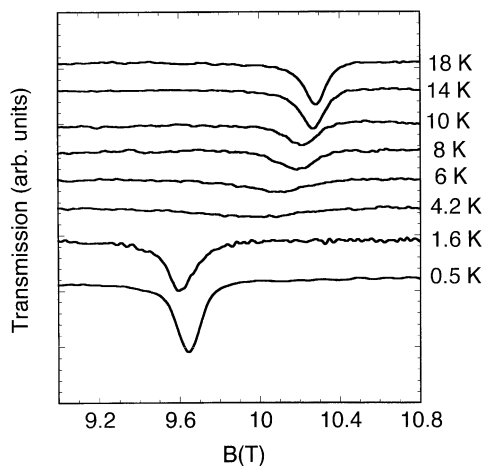

Fig. 2. Temperature dependence of ESR spectra observed at 326 GHz for $H\|c$.
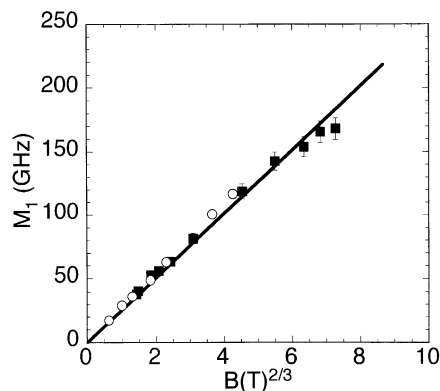

Fig. 3. Field dependence of M_1 determined by ESR at $T = 0.5$ K (closed rectangles). Open circles denote the value of M_1 given in Ref. [3]. The horizontal axis is scaled as $\frac{2}{3}$-power in magnetic field. The solid line is an eye-guide.

experimentally determined precisely and thus M_1 is determined without any adjustable parameters. The field dependence of the M_1 agrees well with that derived from the previous heat capacity measurement [3]. Moreover, the magnitude of the field-induced gap changes as $H^{2/3}$ as proposed by theory. This agreement indicates that the new ESR mode is the manifestation of a breather excitation. It should be noted that the high-energy resolution of ESR enables us to examine the field dependence of the gap very accurately.
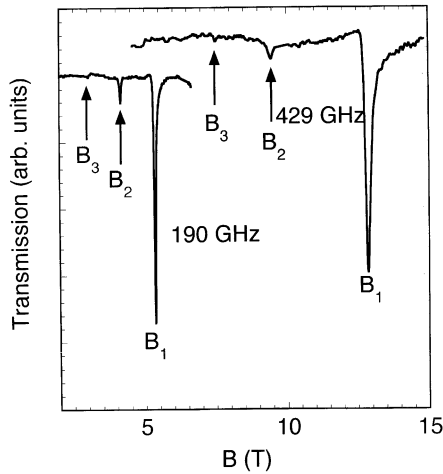
Fig. 4. Examples of ESR spectra observed at 0.5 K foe $H\|c$.

Fig. 5. Schematic spin arrangement in the c-plane. Closed circles and thick solid line show the Cu^{2+} ions and a dimer unit respectively. Line with arrows denotes a bond for J_2.

Finally, we show an unexpected observation of higher-order excitations other than the first breather mode B_1 as depicted in Fig. 4. In the low-field side of B_1, very small signals marked by B_2 and B_3 are observed. The energies of these modes are higher than that of B_1 at the identical field intensity. Therefore, it is speculated that these modes are related to the higher order breathers. Although there is no quantitative interpretation of these higher-order modes, we believe that the present results stimulate further theoretical investigations. The present results demonstrate the high sensitivity of ESR. Since the spectral weights of B_2 and B_3 are very small, it is difficult to obtain these modes from the thermodynamic quantities such as heat capacity. Moreover, these modes were not found, for the limited sensitivity, in the previous neutron scattering experiments.

4. Multiple-triplet excitation in $SrCu_2(BO_3)_2$

Recently, a two-dimensional (2D) spin-gapped system $SrCu_2(BO_3)_2$ with tetragonal symmetry has been studied intensively as a realization of the Shastry and Sutherland model [8]. The Cu^{2+} ions form a unique 2D-network of $S = \frac{1}{2}$ spins as shown in Fig. 5. Each antiferromagnetic dimer unit is made up of two neighboring pairs of Cu^{2+} ions and these dimers are orthogonally arranged with re-
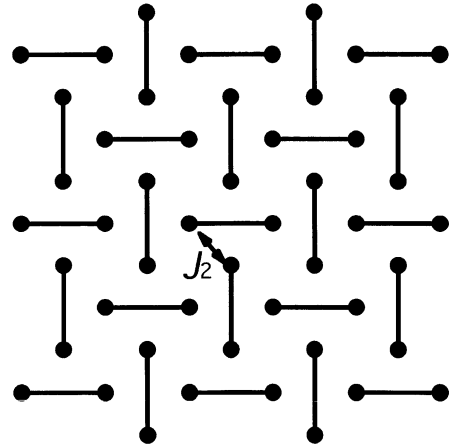
spect to each other. This 2D lattice is topologically equivalent to a 2D square lattice with additional alternating diagonal interactions, the so-called Shastry and Sutherland model [9].

The orthogonal dimer arrangement of the system leads to interesting ground state and excited state properties. First of all, the exact ground state is given by the direct product of the singlet dimer state. As the second point, the propagation of an excited triplet on a dimer bond to the nearest sites is considerably suppressed. It has been shown that the hopping of a triplet is possible only from the sixth order in the perturbation and thus a triplet excitation is extremely localized [10]. It should be noted that this feature originates from the frustration between the intra-dimer interaction (J) and inter-dimer interaction (J_2) and is not caused by the smallness of the inter-dimer interaction. In fact, the ratio $J_2/J \sim 0.63$ is very close to the critical value of $J_2/J \sim 0.70$ between the spin gap state and the Néel ordered state [11]. The strong suppression of the hopping of a triplet is essential for the appearance of quantized plateaux in the magnetization observed in high fields [12].

The magnetic excitations of $SrCu_2(BO_3)_2$ have been intensively studied by different experimental techniques [13–16]. In the previous work, we have investigated the spin-gap excitation in the singlet ground state and found the lowest spin-gap excitation to excite one triplet from the singlet ground

state to the excited state. We have also found a "multiple-triplet" excitation, which is related to the generation of a bound state of triplets. Usually, one triple excitation is dominant in a magnetic excitation spectrum of a spin-gap compound. Therefore, the observation of such higher order excitation is very surprising. As it was pointed out theoretically, a correlated hopping of two-triplets is possible from the second order in perturbation theory, for one-triplet the sixth order is necessary [17]. Hence, the appearance of a "multiple-triplet" excitation is evidence for the extreme localization of the one-triplet excitation.

In the present work, we present the results of high-sensitive ESR measurements for the two-triplet excitations. Because of the high resolution of our equipment, a broad two-triplet band, which is observed in neutron scattering, is resolved into several independent modes. Moreover, a quintuplet excitation is observed, which is the direct evidence for the existence of a two-triplet bound state.

Before proceeding to the results, we discuss briefly the selection rule for ESR. As is well known, the transition between the ground singlet state and the excited triplet state is forbidden in principle. However, a non-secular term in a spin Hamiltonian breaks this selection rule. As a candidate, DM interaction and a staggered field should be considered. As discussed in the previous work, the staggered field mechanism can be ruled out [13]. Recently, it has been proposed that the DM interaction breaks the selection rule for $SrCu_2(BO_3)_2$ [18,19]. The observation of the spin-gap excitations in Faraday configuration is consistent with this proposal, however, the angular dependence of intensity and the zero field splitting between the $S_z = 1$ and $S_z = -1$ branches may not be compatible with this model. We speculate that the combined effect of DM interaction and anisotropic exchange interaction is important.

Fig. 6 shows the ESR spectrum taken at 1042 GHz. The schematic energy diagram is also given in the inset. Since the temperature is much lower than the energy gap of 34.7 K, the signals are identified as the transitions between the singlet ground state and the excited states. Since the O mode was reported in the previous work, we focus on T and Q modes in the following. It is
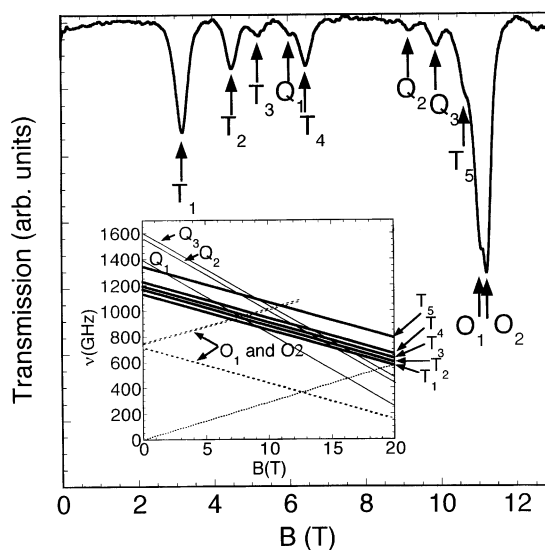

Fig. 6. ESR spectrum measured at 1.5 K for $H \| a$ O, T, and Q denote, one-triplet, two-triplet and quintuplet, respectively. In the inset, dashed, thick solid, thin solid and dotted lines are O, T, Q and paramagnetic resonance (not observed at low temperature), respectively.

noticed that the second spin-gap excitations observed as a broad band by neutron scattering experiments are resolved into five discrete levels. The high resolution shows an advantage to use ESR to observe magnetic excitations. The values of the energy gaps (in the unit of GHz) are obtained by extrapolating the modes to zero field as follows: $1140(T_1)$, $1170(T_2)$, $1190(T_3)$, $1225(T_4)$, $1350(T_5)$, $1390(Q_1)$, $1560(Q_2)$ and $1600(Q_3)$. It should be noted that linear extrapolation may cause an error of about 10 GHz for T-modes and about 30 GHz for Q-mode, for the possible bending of the modes around zero field as observed for the O-modes (neglected in Fig. 6).

In Fig. 6, it is noticed that the relative magnitudes of T-modes to O-modes are not very small. As mentioned before, the strong suppression of the one-triplet excitation may cause the shift of the spectral weight from the O-modes to the T-modes. The geometrical constraint of the triplet hopping may cause another effect; the spectral weight spreading over the continuum concentrate onto several discrete levels. Next, we discuss the Q-modes. As is well known, a two-triplet bound state
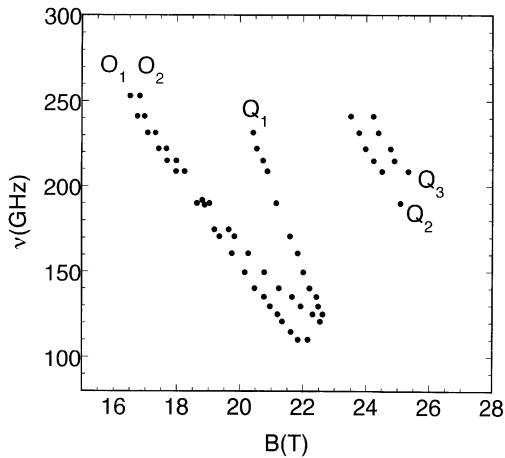
Fig. 7. Frequency–field diagram for $H \| a$.

is an object containing four spins. In the simple dimer model of four spins with antiferromagentic couplings, we can expect three different states, such as singlet ($S = 0$), triplet ($S = 1$), and quintuplet ($S = 2$). It should be noted that the singlet state of a two-triplet bound state is different from the singlet ground state of the whole system. Singlet states observed by means of Raman scattering at finite energy may relate to such a level. In a quintuplet, Zeeman splitting is doubled for $S_z = 2$ and $S_z = -2$ branches compared to that of the triplet. Therefore, a Q-mode can be easily identified.

Fig. 7 shows the frequency–field diagram obtained at lower frequencies. Besides O-modes, a mode with the steep slope is also observed. Since its slope is twice that of the O-mode, this mode is identified as the $S_z = +2$ branch of the quintuplet. The intensity of the Q-mode is roughly 1% of that of the O-mode. It should be noted that the observation of Q-mode is the direct evidence of the formation of a two-triplet bound state.

In summary, high-field ESR investigations have been performed for the low-dimensional quantum spin systems CuBeozoate and $SrCu_2(BO_3)_2$. The unique features of ESR such as high resolution and high sensitivity enabled us to examine the details of the interesting non-linear magnetic excitations in these systems.

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