Direct observation of the multiple spin gap excitations in two-dimensional dimer system SrCu$_2$(BO$_3$)$_2$

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Various spin gap excitations have been observed in the two-dimensional dimer system SrCu$_2$(BO$_3$)$_2$ by means of submillimeter wave ESR. The zero-field energy gap of the lowest spin gap excitation shows a splitting into two triplet modes and the energy splitting clearly depends on the magnetic field orientation when a field is rotated in the ac-plane. A zero-field splitting is also found between the $S_z=+1$ and $S_z=-1$ branches of each triplet. These behaviors are qualitatively explained by considering the anisotropic exchange coupling of inter-dimer and intra-dimer, respectively. The averaged value of the lowest spin gap energy is determined to be $722\pm2$ GHz ($34.7$ K). We have also found the second spin gap excitation at $1140$ GHz ($54.7$ K), which indicates that the inter-dimer coupling is significantly strong. Besides these modes, a number of gapped ESR absorption are found and we propose that these multiple magnetic excitations are caused by the localized nature of the excited state in the present system.

KEYWORDS: SrCu$_2$(BO$_3$)$_2$, spin gap, ESR, magnetic excitation, high magnetic field

Low-dimensional quantum spin systems with a finite spin gap have been a subject of intense and advancing research in this decade. One of the factors lies in prominent progress in solid state chemistry enabling a tailoring of various low-dimensional spin systems for the experimental verification of a concept brought by a theoretical study. Recently, a strontium copper boron oxide SrCu$_2$(BO$_3$)$_2$ with a layered structure has been added to the list of two-dimensional(2D) system with a spin-gapped ground state. A prominent characteristic is that this material can be regarded as a model system with an exactly known ground state. SrCu$_2$(BO$_3$)$_2$ has a tetragonal unit cell and all Cu$^{2+}$ ions that carry spin $S=1/2$ are located at equivalent sites. In a CuBO$_3$ layer sandwiched by layers of Sr ions, a dimer unit is made up of the neighboring pair of planer rectangular CuO$_4$ and these dimers connect orthogonally by way of a triangular planer BO$_3$, providing a unique 2D network of $S=1/2$ as shown in the inset of Fig. 1. This 2D lattice is topologically equivalent to a 2D square lattice with additional alternating diagonal interactions, for which the direct product of the singlet pairs is the exact eigenstate as proven by Shastry and Sutherland. This model for SrCu$_2$(BO$_3$)$_2$ thus can be considered as a 2D analogue of the Majumdar-Ghosh model for a one-dimensional zigzag spin chain with some stringent conditions. The role of the next-nearest-neighbor interaction in the ac-plane $J_2$, which brings a frustration into the system, has been also studied theoretically by Miyahara and Ueda. They 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 of 30 K. It should be noted that the ratio $J_2/J=0.68$ is just below the critical value of $J_2/J=0.70$ between the spin gap state and the Néel-ordered state. Thus this material resides near the border between these two states.

Another interesting feature of this material appears in the magnetization curve with quantized plateaux at one-quarter, one-eighth and possibly one-tenth of the saturated moment. These magnetic plateaux have been realized in terms of the extremely localized nature of the low-lying excited triplets. It means that excited triplets cannot propagate freely in the 2D lattice. As a result, it is considered that these triplets organize a regular lattice made up of spatially separated triplets.

Hence, it will be very interesting to study the field dependence of the magnetic excitation of this system. However, since the critical field is above 20 T, only a few methods can be applied to investigate of the magnetic excitation in such high fields. Among many different methods, ESR has been established its unique status as a probe of a magnetic excitation especially to study its field variation. Thus we have performed a systematic study of magnetic excitations of SrCu$_2$(BO$_3$)$_2$ by using a submillimeter wave electron spin resonance. The present work is the first paper of our successive articles for the experimental procedure and finally the energy diagram and localized nature of magnetic excitation is discussed.

Submillimeter wave ESR measurements have been performed up to 1 THz and in pulsed magnetic fields up to 30 T. A far-infrared laser, backward travelling wave tubes and Gunn oscillators have been employed as the radiation source. An InSb is used as a detector. High-
purity bulk single crystals of SrCu$_2$(BO$_3$)$_2$ were grown by the travelling solvent floating zone (TSFZ) method. By means of Laue X-ray back-reflection, the grown materials was checked and the crystal axes were determined.

ESR spectra at 1.6 K are depicted in Fig. 1 for $H$||a. Among many different kinds of ESR signals, a set of two resonance peaks marked by arrows shows characteristic frequency dependence. Namely, as the frequency is increased, the resonance field first decreases and then increases again at higher frequency. The resonance fields measured up to 1 THz are summarized as the frequency field diagram in figures 2(a) and 2(b) for $H$||c and $H$||a, respectively. As shown in these figures, the above mentioned ESR signals marked by closed circles(T1$_u$ and T1$_d$) and closed rectangles(T2$_u$ and T2$_d$) are associated with a zero-field energy gap of about 720 GHz. The value of the energy gap is close to the gap estimated so far by different methods. These facts indicate clearly that the two modes correspond to the transitions between the ground singlet state and the first excited triplet state we call these modes singlet-triplet transition hereafter). As shown in Figs. 2(a) and 2(b), we have observed two branches of $S_z=+1$ and $S_z=-1$ for each triplet mode T1 or T2(we use the notation such as T1 when we treat the T1$_u$ and T1$_d$ as a set of triplet). The $S_z=0$ branch cannot be detected by our field scanning ESR. The lowest spin gap excitations T1 and T2 shows a complicated structure. For $H$||a, a zero-field splitting exists between two branches of $S_z=+1$ and $S_z=-1$. The modes T1$_u$ and T2$_u$ or T1$_d$ and T2$_d$ are degenerated at zero-field and the center of $S_z=+1$ and $S_z=-1$ branches are identical between T1 and T2 modes. A small splitting observed at high fields between T1$_u$ and T2$_u$ or between T1$_d$ and T2$_d$ cannot be explained by the anisotropy of $g$-value in the c-plane because all Cu sites are equivalent with respect to magnetic fields for $H$||a in the known crystal structure at room temperature. Thus we infer that a small lattice distortion occurs at low temperature, however a detailed structure analysis at low temperature is required to clarify this point. On the other hand, for $H$||c, no zero-field splitting exists between two branches of $S_z=+1$ and $S_z=-1$, while two triplets T1 and T2 show a splitting at zero-field. These characteristic behaviors will be explained later by considering the anisotropic exchange coupling of inter-dimer and intra-dimer. The slope of these modes for each field direction is nearly identical with that of the paramagnetic resonance signals indicated by the dashed lines in Figs. 2(a) and 2(b). The $g$-value are determined as $g_a=2.05$ and $g_c=2.28$ by the paramagnetic resonance peak positions at 25 K. From Figs. 2(a) and 2(b), we determine the average value of the lowest spin gap as 722±22 GHz(34.7 K).

This assignment of T1 and T2 to the singlet-triplet transition is further confirmed by the temperature dependence of ESR spectra as shown in Fig. 3. The intensity of two peaks marked by the arrow decreases as the temperature is increased. This behavior indicates that these signals are the transitions from the ground state of the system. As is well known, the transition between the ground singlet state and the excited triplet state is forbidden in principle as the magnetic dipole transition observed in ESR. However, the presence of a non-secular term such as Dzyaloshinsky-Moriya(DM) interaction, non-equivalent $g$-tensors or anisotropic exchange interaction makes it possible to observe this transition by means of ESR. We speculate that the anisotropic exchange is the origin of the breaking down of the selection rule in the present system and the reason is given in the following.

One of the evidence of the anisotropic intra-dimer exchange interaction is the zero-field splitting between the two branches of $S_z=+1$ and $S_z=-1$ for each triplet mode(for example between T1$_u$ and T1$_d$ or between T2$_u$ and T2$_d$) for $H$||a as shown in Fig. 2(b). Let us consider an isolated dimer of $S=1/2$ coupled by an antiferromagnetic exchange interaction with exchange anisotropy. Since each Cu is bridged by a planer CuO$_4$ unist which lies parallel in the c-plane, we can expect that $J_{cc}$ deviates from $J_{aa}$ in the present system, where $J_{cc}$ and $J_{aa}$ are the components of exchange coupling along the c-axis and a-axis, respectively. By diagonalizing the Hamiltonian of a dimer with such anisotropic exchange coupling, we can show that the splitting at a zero-field exists between $S_z=+1$ and $S_z=-1$ branches for $H$∥c and that no splitting exists for $H$||c between these two branches. This field orientation dependence is consistent with the experimental results of the splitting between $S_z=1$ and $S_z=-1$ branches shown in Figs. 2(a) and 2(b). As is well known, the order of the anisotropic exchange AE can be estimated roughly by the relation $AE \approx -(\Delta g/g)^2 J_1$, where $\Delta g/g$ is the anisotropy of the $g$-value normalized by the average of $g$ and $J_1$ is the isotropic part of exchange constant. By using $g_a=2.05$, $g_c=2.28$ and $J_1 \approx 100$ K, we evaluate $AE \approx 1$ K. This value is comparable with the zero-field splitting of about 30 GHz in Fig. 2(b) and thus we consider that the anisotropic exchange is the origin of the above mentioned splitting and this term makes the singlet-triplet transition allowable for ESR.

Next let us discuss the parallel splitting of the lowest energy spin gap excitation for $H$||c into T1 and T2 modes. The splitting between T1 and T2 cannot be attributed to the difference of $g$-value because the splitting exists even at zero-fields for $H$||c and both modes are parallel to each other as shown in Fig. 2(a). Such splitting can be expected when an inter-dimer interaction $J'$ exists. Since the splitting depends on the field orientation, we speculate that the splitting is caused by the anisotropy of $J'$ and it is not related to the absolute total value of $J'$. To confirm this point, we have measured angular dependence of two peaks T1$_d$ and T2$_d$ at 428.9 GHz as shown in Fig. 4. By using the angular dependence of $g$-value, the zero-field energy of two triplet is evaluated as a function of field orientation as shown in the inset of Fig. 4. It should be noted that the splitting shows a sinusoidal angular dependence. Thus we confirmed that the splitting between T1 and T2 for $H$||c is caused by the anisotropic inter-dimer exchange interaction.

When a finite $J'$ exists, we can expect a second excited state which shows a splitting of about $J'$ from
the lowest triplet state. In practice, the second lowest singlet-triplet transition is found and the energy gap is about 1140 GHz (see closed triangles in Figs. 2(a) and 2(b)). This second triplet state can be understood by using a simple model as follows. When $J' < J$, we can treat a two dimer coupled by $J'$ as a dimer of two $S=1$ spins. In this case, the ground state ($E=0$), the first excited state ($E=J'$) and the second excited state ($E=3J'$) are $S=0$ singlet, $S=1$ triplet and $S=2$ quintet, respectively, where $E$ is the energy of each level. Thus we can expect that the second triplet state is located at the $E=J'$ above the lowest triplet state. The experimentally observed splitting of 418 GHz = 1140 GHz - 722 GHz is the measure of inter-dimer coupling. If we neglect the third-neighbor interaction in the $c$-plane, $J'$ is roughly the half of $J_2$ = 68 K (1416 GHz). The agreement between these two estimations of $J'$ are very poor because our model is too simple. However, these results show that inter-dimer interaction is considerably large in the present material. This second energy gap was also observed by the neutron scattering experiments which was made very recently. Thus we can conclude that the splitting between $T_1$ and $T_2$ for $H \parallel c$ as well as the existence of the second spin gap for both $H \parallel c$ and $H \parallel a$ are attributable to the large $J'$ in the present system.

When we look at the frequency field diagram shown in Figs. 2(a) and 2(b), we notice that a number of ESR signals are observed besides the lowest and the second lowest energy modes of the singlet-triplet transition. We categorize these signals into following two types: (1) strong ESR absorption appearing just below the critical field (closed diamond), and (2) other weak ESR signals marked by open rectangles. To investigate the origin of the strong ESR mode (1), we measured the temperature dependence of ESR spectra as shown in Fig. 3. The signal located at 22 T is a paramagnetic resonance. Since the intensity of all ESR peaks observed at 1.6 K decreases as the temperature is increased, these signals are considered as the excitations from the ground state. It should be also noted that the intensity of the peaks appearing around 15-17 T is much stronger than that of the singlet-triplet transition and is comparable with that of paramagnetic signal. Moreover, these signals are not related to the magnetic excitations at a plateau because the fields are well below the critical field $H_c$, where the lowest triplet state crosses with the singlet ground state. These facts indicate that the strong signals are related to the ground state but are not a forbidden transition such as singlet-triplet transition. Hence, we infer that the ground state of the system near the critical field is not a perfect nonmagnetic singlet state; i.e., a part of the singlet is broken and as a consequence a magnetic ground state is recovered locally in some part of the system for the finite mixing between the ground singlet state and the excited states. In practice, the bending of triplet mode $T_{1d}$ and $T_{2g}$ are observed above 15 T as shown in Fig. 2(a) and the magnetization is non-zero even at 0.5 K in the field well below $H_c$.

Finally, we discuss the origin of the weak signals marked by open rectangles which are categorized as (2). It seems that many of them lie almost parallel to the singlet-triplet transition $T_1$ or $T_2$. It means that these ESR signals have finite zero-field energy gap and thus they are the transitions between the ground state and the excited state. We speculate that these weak absorption are the localized multiple spin gap excitation caused by the extremely localized nature of the excited state proposed theoretically. Usually, an excited triplet in the dimerized spin-gap system can propagate for the finite inter-dimer coupling and thus a significant dispersion is observed. In the present system, a triplet excitation is extremely localized and its propagation is very limited. In this case, we expect that a dispersive mode may be replaced by a number of excitations, which consists of nearly degenerated discrete energy levels. Namely, we can expect a state that triplets are coupled as dimer, trimer, quadramer etc. In this case, the excitation energy of each level may be given by a sum of the formation energy of the isolated triplet, the interactions with other triplets located nearby and the Zeeman energy. This idea can explain why the most of weak ESR peaks appear above the $S_z=1$ branch of the second lowest singlet-triplet transition (closed triangles). It also explains that the number of the peaks increases when a field approach to the critical field $H_c$. It is because the number of the surrounding triplets are increased around the $H_c$. As is well known, such localized excitations with discrete energy levels have been known as a spin cluster excitation for Ising system, however, it is found for the first time for Heisenberg system. A further theoretical and experimental investigation is desirable to clarify our proposal.

To summarize, we have directly found the singlet-triplet transition of the SrCu$_2$(BO$_3$)$_2$ by submillimeter wave ESR. Two sets of well-defined triplet modes are found and the energy gaps are evaluated to be $722\pm2$ GHz (34.7 K) and 1140 GHz (54.7 K). In additions to these transitions, we have also observed multiple spin gap excitations, which may be realized by the extremely localized nature of the excited state.

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Figure captions

Fig. 1. Examples of ESR spectra at 1.6 K for $H \parallel a$. Arrows indicate two lowest triplets T1 and T2. The suffix u and d indicate the $S_z =+1$ and $S_z =-1$ branches, respectively. Closed triangle and open rectangles are the second lowest triplet and other multiple weak signals, respectively. The inset shows the schematic crystal structure in the $c$-plane. The dotted lines shows the unit cell.

Fig. 2. The frequency-field diagrams at 1.6 K for $H \parallel c$ (a) and for $H \parallel a$ (b). The dashed line indicates the position of paramagnetic resonance. Closed circles and closed rectangles are the two triplet modes T1 and T2. Closed triangle is the second lowest triplet. Closed diamond and open rectangles are other strong and weak signals, respectively as mentioned in the text. The magnetization curve of single crystal measured at 0.5 K taken from Ref. 8 is also plotted for $H \parallel a$.

Fig. 3. Temperature dependence of ESR spectra at 716.7 GHz. Arrows show T1 and T2 modes.

Fig. 4. The angular dependence of the T1 and T2 modes at 1.6 K in the $ac$-plane. Numbers for each spectrum is the angle $\theta$ between magnetic field and the $a$-axis. The inset shows the angular dependence of zero-field energy gaps of T1(closed circle) mode and T2(closed rectangles) mode.
Fig 1 Nojiri et al.
Nojiri et al. Fig 2 (a) and (b)
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