Submillimeter Wave ESR Study of Spin Gap Excitations in CuGeO$_3$

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Transitions between the ground singlet state to the excited triplet state has been observed in CuGeO$_3$ by means of submillimeter wave electron spin resonance. The strong absorption intensity shows the break down of the selection rule. The energy gap at zero field is evaluated to be 570 GHz (2.36 meV) and this value is nearly identical to the gap at the zone center observed by inelastic neutron scattering. The absorption intensity shows strong field orientation dependence but shows no significant dependence on magnetic field intensity. These features have been explained by considering the existence of Dzyaloshinsky-Moriya (DM) antisymmetric exchange interaction. The doping effect on this singlet-triplet excitation has been also studied. A drastic broadening of the absorption line is observed by the doping of only 0.5 % of Si.

KEYWORDS: CuGeO$_3$, submillimeter wave ESR, magnetic excitation, spin gap, high magnetic field

§1. Introduction

CuGeO$_3$ has attracted considerable attentions as the first inorganic material which shows a spin-Peierls transition. A large number of experimental and theoretical studies have been made in these few years on this compound and the study of magnetic excitations has been one of the most interesting subjects. Among many different kinds of experimental methods to study magnetic excitations such as inelastic neutron scattering, Raman scattering or far-infrared spectroscopy, ESR is considered to be a unique tool for the following characteristics:(1) high sensitivity, (2) high energy resolution and (3) possibility of high field measurements by using a pulsed magnetic field. The third feature of ESR enables us to investigate magnetic excitations in all three fundamental magnetic phases such as uniform phase(U-phase), dimerized spin-Peierls phase(SP-phase) and so called magnetic phase(M-phase). As the matter of fact, many ESR investigations have been reported on CuGeO$_3$ and different aspects of magnetic excitations have been discussed in detail.

However, only a few direct observations were made for the spin gap excitation. One of the reasons is that the transition between the ground singlet state and the excited triplet state is forbidden as ESR in principle because the total spin is conserved in magnetic dipole transition. Moreover, the energy gap is as high as a few meV and it requires a special ESR equipment which covers the high frequency submillimeter wave. For these reasons, it was considered that the observation of the singlet-triplet transition was very difficult.

An observation of the singlet-triplet transition in CuGeO$_3$ by ESR was first reported by Brill et al. under magnetic fields parallel to the $a$-axis. The value of the energy gap was reported as $E_{g1}$=63.77 K (5.495 meV) and it was explained as the transition at the $q$=$a$. The field orientation dependence of this singlet-triplet transition were also reported by a different group.

Since the early stage of researches on CuGeO$_3$, we have performed a systematic ESR investigation on three fundamental magnetic phases by using our submillimeter wave ESR equipment which covers both high magnetic field region and wide frequency range. In the course of this study, we have found a new strong singlet-triplet transition with an energy gap of $E_{g2}$=2.36 meV. This gap energy $E_{g2}$ is different from that observed by Brill et al. and it is close to the spin gap energy at zone center [0, 1, 1/2] which was observed by inelastic neutron scattering (INS). The absorption intensity of newly found singlet-triplet transition is very strong and this fact is considered to be strange because the singlet-triplet transition is usually forbidden as explained above. Moreover, the absorption intensity shows a strong field orientation dependence. These features show that the spin-Hamiltonian of the system is much deviated from the simple Heisenberg type and show that a non-secular term such as Dzyaloshinsky-Moriya interaction should be included into that Hamiltonian.

Before proceeding to the experimental results, we describe briefly about the dispersion of magnetic excitation in CuGeO$_3$ observed by INS experiments in dimerized SP phase. A very steep dispersion is observed along the magnetic chain of the $c$-axis. In addition to this, a two-dimensional modulation of the dispersion as shown in Fig. 1 is observed for the non-negligible interchain exchange coupling $J_b$ along the $b$-axis. For the simplicity, we use a notation $q=(k, l)$ which is the wave vector associated with the two dimensional reciprocal space spanned...
by $b^*$ and $c^*$. In this notation the energy gap $E_{g2}=2.36$ meV is related to the gap at $q=(0, \pi)$ or $q=(\pi, 0)$ and the energy gap $E_{g1}=5.50$ meV is related to that at $q=(0, 0)$ or $q=(\pi, \pi)$. This two-dimensional dispersion relation indicates that the newly observed ESR peak is related to the energy gap at the reciprocal lattice point where the wave vector is not zero. This fact implies that the magnetic excitation at $q=(0, \pi)$ or $q=(\pi, 0)$ are folded towards $q=(0, 0)$ in the dimerized SP phase. Another important feature of the magnetic excitation of CuGeO$_3$ is that the existence of the double gap structure where the first excited triplet branch is separated by the second gap from the two magnon spin wave continuum. This separation enables us to apply a simplified singlet-triplet energy scheme to describe the magnetic excitation in dimerized SP phase of CuGeO$_3$.

In the following, we report the results on the newly found singlet-triplet transition of $E_{g2}$ in CuGeO$_3$. The temperature, field intensity and field orientation dependencies of this excitation will be shown. The origin of the breaking of the selection rule will be discussed considering the experimentally observed features. Finally the effect of doping will be also shown.

§2. Experimental

Submillimeter wave ESR measurements have been performed up to 800 GHz in pulsed magnetic fields up to 30 T. A far-infrared laser, backward traveling wave tubes and Gunn oscillators have been employed as the radiation source. An InSb is used as a detector. Both the solenoid and the split type pulsed magnets have been used for the field generation. Single crystal samples were synthesized by the floating zone technique. The concentration of Si is determined by EPMA method.

§3. Results

3.1 Singlet-triplet transition

Figure 2 shows examples of ESR spectra measured at 1.7 K in three different magnetic field orientations. All the measurements were performed in the Faraday configuration where the propagation vector $k$ of the radiation is parallel the external magnetic field.

The absorption lines denoted by TR is the transition within the excited triplet state and the signal is caused by the thermally activated spins across the energy gap. Another transitions marked by M is the ESR mode in the M phase where the energy gap is collapsed by strong magnetic fields. The sharp absorption lines indicated by P are the signal of DPPH used as the field calibration maker. The resonance fields of TR or M absorption lines increase as frequency is increased. Since these two kinds of ESR modes have been already reported in separated papers, we do not explain them further. There is an another type of resonance peak marked by D with broad line width. For the signal D, the resonance field increases as the frequency increases up to 570 GHz and above this frequency the resonance field increases as the frequency is increased. The frequency field diagram of this transition is shown in Fig. 3 for all three magnetic field orientations. This figure shows that signal D is associated with the zero field energy gap of $E_{g2}=570$ GHz(2.36 meV). A large zero field gap shown in Fig. 3 is not expected for a paramagnetic resonance of $S=1/2$ Cu$^{2+}$ ions. Moreover this energy coincide with the value of spin gap obtained by neutron scattering at $q=(\pi, 0)$ or $q=(0, \pi)$ as mentioned before. These facts indicate that the signal D is the direct transition between the ground state and the excited triplet state as shown schematically in the inset of Fig. 3.

To confirm that signal D is the singlet-triplet transition, we have also measured the temperature dependence of the ESR spectra at 342.0 GHz as shown in Fig. 4. The intensity of the signal D located around 8 T increases as the temperature is decreased. This behavior clearly indicates that the signal D is the transition from the ground state and not a transition among the excited states. The temperature dependence of signal TR appears around 12 T is completely opposite to that of signal D. In the case of signal TR, the absorption intensity increases as the temperature is increased showing obviously that this signal is related to the thermally excited states. Table 1 shows the list of zero field energy gap value and $g$-value of each triplet branch. The obtained $g$-values are consistent with the values reported in the references.

To examine the existence of the anisotropic exchange interaction, we carefully check if a zero field energy splitting exists between $S_z=1$ and $S_z=-1$ branches. However, the energy gap of observed six branches are in the range of 570±2 GHz and no significant zero field splitting is found. The $S_z=0$ branch has not been because the frequency of this branch is field independent and thus it cannot be detected by our magnetic field sweep ESR.

Another very important feature of this transition is that the intensity is anisotropic as shown in Fig. 2. The absorption intensity is strongest for $B \parallel c$ and weakest for $B \parallel b$. Since there are two inequivalent Cu$^{2+}$ sites in CuGeO$_3$, a staggered moment can be induced by external magnetic field. However, two sites are equivalent with respect of the magnetic field orientation in the case of $B \parallel c$. Hence, the fact that the absorption intensity is strongest for $B \parallel c$ and a staggered field mechanism as the candidate of the breaking of the selection rule are not compatible. This point will be discussed later.

3.2 Field dependence

To study the possible softening of the lattice dimerization around the critical field $H_c$ between SP and M phase, we check the non-linear behavior of the triplet branch. If softening occurs, the energy gap depends on field intensity and then the field dependence of the resonance frequency becomes non-linear. We have tried the fitting of the observed $S_z=-1$ branch for $B \parallel c$ assuming a power law field dependence of energy gap as

$$h\nu = \Delta_0 \delta H^\alpha - g\mu_B S_z H \quad (3.1)$$

where $\nu$ is the frequency of ESR, $\Delta_0$ is the energy gap at zero field, $\delta H$ is a normalized magnetic field as $\delta H = (H_c-H)/H_c$, $H_c$ is the critical field between SP and M phases and $H$ is the external magnetic field. The fitting gives a very small value of $\alpha=2.5\times10^{-4}$ when $0 \leq B \leq 12.7$
T. The fitting with different magnetic field range such as $10 \leq B \leq 12.7$ T shows no significant change of $\alpha$. This fact show that there is no field dependence of energy gap at least when $\delta H \geq 0.01$ within the experimental error and indicates that the transition between SP phase and M phase is the first order transition.

This first order nature of the transition is also shown in the hysteresis of the signal $D$ as shown in Fig. 5. At 195.8 GHz, the absorption intensity as well as resonance field changes between increasing and decreasing fields. This change is consistent with the hysteresis of the magnetization process. At slightly lower frequency of 190 GHz, the direct transition suddenly disappears because the spin-Peierls energy gap collapses in the M phase. Considering above mentioned field dependence of the singlet-triplet transition, we conclude that no significant softening of spin gap is induced by magnetic fields in the field range of $0.01 \leq \delta H$.

Another important point is that the down going branch of the excited triplet does not show a level crossing with the ground singlet state at $H_c$ as shown in Fig. 3. It means that the ground state of the system changes from non-magnetic to magnetic states at $H_c$ with a finite energy gap. This behavior is different from that of a simple isolated dimer spin system where the zero field energy gap $E_g$ and the critical field $H_c$ holds a simple relation of $E_g = g \mu_B H_c$. As is well known, the spin-Peierls transition costs the lattice deformation energy $E_d$. Considering this loss, we may rewrite the above relation to $E_g - E_d = g \mu_B H_c$ for the spin-Peierls system. This relation expresses that the critical field is decreased by the lattice dimerization energy loss for spin-Peierls system. This relation is not precise because an incommensurate lattice dimerization exists even above $H_c$. However, we can consider $E_d$ as a measure of lattice dimerization energy of the system at SP phase. If we assume that $E_d$ is identical with the energy difference between $S_z = 1$ branch and the ground state at $H_c$, we obtained $E_d = 193$ GHz. By using this $E_d$, we found a very simple relation between two energy gap $E_{g1}$ and $E_{g2}$ as $E_{g1} = 2E_{g2} + E_d$. This point will be discussed later.

3.3 Impurity effect

The effect of impurity doping for the singlet-triplet transition have been examined using single crystals in which Ge site is partly substituted by Si. The spectra for different Si concentrations are shown in Fig. 6. The Néel temperatures and the spin-Peierls transition temperatures are 2.5 K and 11.5 K for $x = 0.01$ and 0.9 K and 13.5 K for $x = 0.005$ samples, respectively. No additional extrinsic signals are observed for both samples. This fact shows the high quality of the single crystals used for the present experiments.

The drastic change of the spectrum is found by Si doping and no absorption is observed for $x = 0.01$. In the case of $x = 0.005$, only a very weak and broad resonance is observed. The strong suppression of the singlet-triplet transition shows that the density of state of the first excited triplet state is very sensitive to the impurity doping. In the coexisting phase of Si doped sample, a well defined antiferromagnetic resonance(AFMR) has been observed. This AFMR is related to a spin wave excitation at $q = 0$. Thus the suppression of the singlet-triplet transition shows that the spectral weight shifts drastically from the triplet branch to the AFMR mode by a very small amount of Si doping.

§4. Discussion

4.1 Dzyaloshinsky-Moriya interaction

As mentioned previously, the intensity of a singlet-triplet transition is supposed to be very weak. However, present results show that the absorption intensity of this forbidden transition is strong in CuGeO$_3$. As is well known, a non-secular term should be included into spin-Hamiltonian to cause a singlet-triplet transition. Possible candidates for such a non-secular term are the following:(1) DM interaction, (2) Staggered moments caused by the alteration of $g$-tensors (3) Anisotropic exchange(AE) interaction. The staggered field effect can be excluded for following reasons. As was shown by Shiba and Sakai for a Haldane gap system NENP, two distinct features are expected for this mechanism. Firstly, since the staggered magnetic moments are induced by uniform magnetic fields, the intensity of the singlet-triplet transition should increase as the field is increased. Secondly, the induced moments are coupled with radiation for Voight configuration where $k \perp B$. In the present case, no strong field dependence of absorption intensity is observed as shown in Fig. 2. To evaluate the relationship between the intensity of singlet-triplet excitation and the direction of a magnetic field or propagation vector, we have also performed the experiments in Voight configuration as shown in Fig. 7. The results for both Faraday and Voight configurations are summarized in table 2. As shown in table 2, the transition is observed for both Faraday and Voight configurations. For example, the transition is very strong for $B \parallel k \parallel c$. In this configuration, as mentioned in previous section, the staggered moment is not expected. Thus we conclude that the staggered field mechanism cannot be applied to the present case.

Next we consider the possible breaking of selection rule due to DM interaction. As is well known, both DM interaction and AE interaction are related to the spin-orbit coupling $\lambda$. It should be noted that DM interaction causes a stronger effect than AE interaction because the former term is the first order correction of spin-orbit coupling $\lambda$ while the latter is the second order correction. Thus if DM interaction exists in CuGeO$_3$, this will be a leading term as the origin of the experimentally observed singlet-triplet transition. Moreover, the fact that the zero field splitting of energy gap due to AE was not found shows that AE may be small in the present system. The existence of the DM interaction for U phase was first proposed by Yamada et al. by considering the characteristic behavior of the line width of EPR. Although the known crystal structure at that time was not compatible with the existence of DM interaction, a reexamination of crystal structure was made by X-ray diffraction and it was shown that the new crystal structure allows the existence of DM interaction. According to the proposal of Yamada et al, $D$-vectors are parallel to one another.
along the $a$-axis and they are alternated along the $b$-axis with an angle of about 100 degree pointing to one of the principal axes of CuO$_6$ octahedron as depicted in the inset of Fig. 7. This complicated arrangement is caused by the existence of inequivalent Cu sites. Next we consider the direction of $D$-vectors in dimerized SP phase. Considering the lattice deformation in SP phase determined by neutron scattering, we can expect that the direction of $D$-vectors are not changed by the dimerization. Thus the existence of $D$-vectors are justified for SP phase.

Recently Kokado and Suzuki have made a theoretical calculation of ESR intensity considering DM interaction and proposed the following features: (1) the absorption intensity shows no strong field dependence, (2) The transition can be observed in the Faraday configuration (3) The intensity is strongest when $D \perp B$ and weakest when $D \parallel B$. As mentioned before, the theoretically expected two features (1) and (2) are clearly consistent with our experiments. We now discuss the third point considering the direction of the proposed $D$-vectors. For simplicity, we discuss the results in the Faraday configuration. In the experiment, the intensity is strongest for $B \parallel c$ and weakest for $B \parallel b$. In the $B \parallel c$ configuration the condition $D \perp B$ is satisfied because the $D$ vectors are in the $ab$-plane. Thus we can expect the strong singlet-triplet transition for this configuration. If we compare two configurations $B \parallel a$ and $B \parallel b$, the component of the $D$-vector in the plane normal to the magnetic field is larger for $B \parallel a$ and smaller for $B \parallel b$. Thus we can expect that the intensity is stronger for $B \parallel a$ and weaker for $B \parallel b$. Although the intensity of the transition may depend on the details of the spin-Hamiltonian used for the calculation, above mentioned fundamental and qualitative features shows a good agreement with the present experimental results. Hence we can conclude that the strong singlet-triplet transition is caused by the DM interaction. Finally we mention that we can not exclude the possible small contribution of the AE interaction in the present case. However, as discussed above, we find that the AE is small for CuGeO$_3$ and thus we conclude that the DM interaction is the leading term.

4.2 Zone folding

As discussed above, we can expect a finite transition matrix element between the ground singlet state and the excited triplet states by including the DM interaction in to the Hamiltonian. However, the gap observed in the present work is related the gap at the non zero wave vector such as $q=(\pi,0)$ or $q=(0,\pi)$. Since only the mode at $q=0$ can be excited by electromagnetic wave, we cannot relate our spin gap excitation directly to the result of INS experiments. A possible explanation to overcome this difficulty is to consider the folding of the magnetic excitation branch by DM interaction or by lattice dimerization. If the magnetic excitation at $q=(\pi,0)$ or $q=(0,\pi)$ is folded to $q=(0,0)$ in the dimerized SP phase, we can observe this folded magnetic excitation by ESR. Recently J. E. Lorenzo et al. found the folding of magnetic excitation in CuGeO$_3$ by neutron diffraction experiments. They found that two triplet peaks exist at $q=(\pi,3/2\pi)$ and $q=(0,3/2\pi)$. Although it is difficult to observe the magnetic excitation at $q=(0,0)$ directly by neutron, this observation shows clearly that the zone folding exist in the SP phase of CuGeO$_3$. This fact supports our explanation that the zone folding makes it possible to observe two spin gap excitations at $q=0$ by means of ESR.

4.3 Relation of two energy gaps

As mentioned in the previous section, we have found a simple relation $E_{g1}=2E_{g2}+E_d$ experimentally between two energy gaps $E_{g1}=1329$ GHz and $E_{g2}=570$ GHz. Figure 8 shows a schematic energy diagram for two energy gaps. As the values of gaps are determined by ESR, the error is less than a few GHz. In the present experiments, the disappearance of the singlet-triplet transition occurs between 195.8 and 190 GHz. Then we can evaluate $E_d$ as the average of these two frequencies and it turned out to be $E_d=193$ GHz. If we calculate $2E_{g2}+E_d$ by using our experimental values, we obtain $2E_{g2}+E_d=1333$ GHz. This is identical to $E_{g1}=1329$ GHz obtained by Brill et al. within the experimental errors. Moreover, it is surprising that up-going branch of the lower triplet and the down-going branch of the higher triplet crosses at the critical field $H$, as shown schematically in Fig. 8. Although we have no good explanation for this unexpected relation between and $E_{g1}$ and $E_{g2}$, we speculate that this simple relation between two spin gaps is not accidental. In the theoretical investigations of magnetic excitations in CuGeO$_3$, the dispersion along the $b$-axis has been treated so far as a modification for the one-dimensional system. However, the present results show that two dimensional nature of CuGeO$_3$ is essential and should be considered more seriously.

Finally we would propose a possible candidate to explain the broad line width. As is shown in Fig. 2, the line width of a direct transition is broader than that of TR transition. These two signals are both related to the triplet state. However, the coupling to the lattice may be different between two cases. The triplet state caused by electromagnetic radiation may not be followed by releasing of a lattice dimerization because the frequency of the radiation is much faster that that of phonon which cause the deformation of the lattice. On he other hand, the thermally activated transitions is coupled with the lattice relaxation through phonon. In another word, former process can be adiabatic with respect to the lattice. If this speculation is correct, the life time of the triplet excited electromagnetically is expected to be short and as a result the line width becomes broad.

To summarize, a strong transition from the ground singlet to the excited triplet has been observed for the first time by ESR. The energy gap at zero field is isotropic and it turned out to be $570\pm2$ GHz. The characteristic features of this transition can be understood by considering DM interaction. The observation of the spin gap transition related to the gap other than $q=0$ indicate the folding of the magnetic excitations in the SP phase.

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References

[1] M. Hase, I. Terasaki and K. Uchinokura:Phys. Rev. Lett 70 (1993)3651.
[2] M. Nishi, O. Fujita and J. Akimitsu:Phys. Rev. B 50 (1994)6508.
[3] M. C. Martin, G. Shirane, Y. Fujii, M. Nishi, O. Fujita, J. Akimitsu, M. Hase and K. Uchinokura:Phys. Rev. B 53 (1996)R14713.
[4] M. Arai, M. Fujita, M. Motokawa, J. Akimitsu and S. M. Bennington:Phys. Rev. Lett. 77 (1996)3649.
[5] L. P. Regnault, M. Ain, B. Hennion, G. Dhaleinne and A. Revcolevschi:Phys. Rev. B 53 (1996)5579.
[6] M. A in, J. E. Lorenzo, L. P. Regnault, G. Dhaleinne, A. Revcolevschi, B. Hennion and Th. Jolicoeur:Phys. Rev. Lett. 78 (1997)1560.
[7] P. H. M. van Loosdrecht, S. Huant, G. Martinez, G. Dhaleinne and A. Revcolevschi:Phys. Rev. B 54 (1996)R3730.
[8] T. M. Brill, J. P. Boucher, J. Voiron, G. Dhaleinne, A. Revcolevschi and J. P. Renard:Phys. Rev. Lett. 73(1994)1545.
[9] H. Ohta, S. Imagawa, Y. Yamamoto, M. Motokawa, O. Fujita and J. Akimitsu:J. Phys. Soc. Jpn. 63 (1994)2870.
[10] W. Palme, G. Ambert, J. P. Boucher, G. Dhaleinne and A. Revcolevschi:Phys. Rev. Lett. 76 (1996)4817.
[11] H. Nojiri, T. Hamamoto, O. Fujita, J. Akimitsu, S. Takagi and M. Motokawa:J. Magn. Magn. Mat. 177-181(1998)687.
[12] H. Nojiri, Y. Shimamoto, N. Miura, M. Hase, K. Uchinokura, H. Kojima, I. Tanaka and Y. Shibuya:Phys. Rev. B 57 (1998)10276.
[13] I. Yamada, M. Nishi and J. Akimitsu:J. Phys. Condens. Matter. 8 (1996)2625.
[14] H. Nojiri, N. Miura, M. Hase, K. Uchinokura, H. Kojima, I. Tanaka, Y. Shibuya, S. Luther and M. von Ortenberg:unpublished.
[15] H. Nojiri, H. Ohta, N. Miura and M. Motokawa:Physica B 246 (1998)169.
[16] H. Nojiri, T. Hamamoto, Z. J. Wang, S. Mitsudo, M. Motokawa, S. Kimura, H. Ohta, A. Ogawa, O. Fujita and J. Akimitsu:J. Phys. Condens. Matter 9 (1997)1331.
[17] W. Lu, J. Tuchendler, M. von Ortenberg and J. P. Renard:Phys. Rev. Lett. 67 (1991)3716.
[18] T. Sakai and H. Shibata:Physica B201 (1994)182.
[19] M. Hidaka, M. Hase, I. Yamada, M. Nishi and J. Akimitsu:J. Phys. Condens. Matter. 9(1997)809.
[20] K. Hirota, D. E. Cox, J. E. Lorenzo, G. Shirane and J. M. Tranquada:Phys. Rev. Lett. 73 (1994)736.
[21] S. Kokado and N. Suzuki:proceeding for APF-4(Tsukuba, 1999) and S. Kokado:Dr Thesis.
[22] J. E. Lorenzo, L. P. Regnault, J. P. Boucher, B. Hennion, G. Dhaleinne and A. Revcolevschi:Europhysics. Lett. 45 (1999)619.

§5. Figure captions

Fig.1 A schematic dispersion curve of the lowest triplet branch in the $b'c'$-plane. Two different energy gap $E_{g1} = 5.50$ meV and $E_{g2} = 2.36$ meV exist for the inter-chain coupling $J_b$.

Fig. 2 Examples of ESR spectra at 1.7 K. TR and M denote the transition among the excited triplet states and ESR in the M phase, respectively. Broad resonance lines D are the singlet-triplet transition. Mark P indicate the signals of DPPH used for the field calibration. Number attached to each spectrum is the frequency in the unit of GHz. The baseline of each spectrum is shifted vertically for convenience.

Fig. 3 The frequency field diagram for the signal D. The up-going branch and down-going branch are related to $S_z = 1$ branch and $S_z = -1$ branch of the excited triplet state, respectively.

Fig. 4 Temperature dependence of the ESR spectrum at $\nu = 342.0$ GHz. The signal located around 8 T is the singlet-triplet transition D and the signal TR is also observed around 12 T. Arrows indicate the signals of DPPH used for the field calibration. The baseline of each spectrum is vertically shifted for convenience.

Fig. 5 Hysteres of the singlet-triplet transition observed around the phase boundary between the SP and M phases. The upper trace and lower trace correspond to the increasing field and the decreasing field processes, respectively. The broad absorption lines marked as D are the singlet-triplet transition and the sharp absorption lines TR beside the DPPH signals are the transition with in the excited triplet states. The baseline of each spectrum is vertically shifted.

Fig. 6 The change of the singlet-triplet transition spectrum by Si doping. The $x$ denotes the concentration of Si. The vertical scale is magnified ten times for lower two traces. The baseline of each spectrum is vertically shifted.

Fig. 7 An example of field orientation dependence of the singlet-triplet transition. The measurement was made in Voight configuration where $B \perp k$. The number indicate the angle from the $a$-axis in $ab$-plane. The inset shows the schematic view of the direction of DM vectors $D$ which are denoted by thick arrows. Two inequivalent CuO$_6$ octahedrons are marked by $\sharp 1$ and $\sharp 2$. Shadowed and open circles show the Copper and Oxygen, respectively. The baseline of each spectrum is vertically shifted.

Fig. 8 A schematic energy diagram of two set of triplets with zero field gaps of $E_{g1}$ and $E_{g2}$. The $g$-value is normalized to 2. The dashed line shows the critical field $H_c$ between SP phase and M phase and it is also normalized by using experimentally obtained $g$-values listed in table 1.

Table 1. The list of the zero field energy gap and $g$-value

| Field Orientation | $S_z$ | Energy Gap(GHz) | $g$-value |
|-------------------|------|-----------------|-----------|
| $B|a$             | 1    | 570.0           | 2.15      |
| $B|a$             | -1   | 571.7           | 2.16      |
| $B|b$             | 1    | 568.2           | 2.23      |
| $B|b$             | -1   | 569.3           | 2.26      |
| $B|c$             | 1    | 571.9           | 2.05      |
| $B|c$             | -1   | 570.4           | 2.07      |
Table II. The list of intensity of the singlet-triplet transition for different magnetic field orientation and for different direction of a propagation vector. The diagonal components are related to the Faraday configuration and others are related to the Voight configuration. S, M, W show that the intensity of the singlet-triplet transition is strong, moderate and weak, respectively.

| Polarization | $B\parallel a$ | $B\parallel b$ | $B\parallel c$ |
|--------------|----------------|----------------|----------------|
| $k\parallel a$ | M              | M              | M              |
| $k\parallel b$ | M              | W              | S              |
| $k\parallel c$ | S              | W              | S              |
This figure "figure1.GIF" is available in "GIF" format from:

http://arxiv.org/ps/cond-mat/9906074v1
Fig. 2 H. Nojiri et al.
Fig. 3  H. Nojiri et al.

T=1.7 K

• B//a
• B//b
• B//c

Frequency (GHz) vs. B(T)

$S_z = 1$
$S_z = 0$
$S_z = -1$

(Typical labels and values for scientific data presentation)
Fig. 4 H. Nojiri et al.

Transmission (arb. unit)

B(T)

B//c

ν = 342.0 GHz

13.6K

9.7K

7.5K

5.5K

4.2K

1.8K
Fig. 5 H. Nojiri et al.

Transmission (arb. unit) vs. $B(T)$

- TR
- DPPH
- D
- $B//c \, T=1.7 \, K$
- $\nu=195.8 \, GHz$
Fig. 6 H. Nojiri et al.

Transmission (arb. unit) vs. $B(T)$ for $x=0$, $x=0.005$, and $x=0.01$. The graph shows the variation of transmission with increasing magnetic field $B$ for different dopant concentrations $x$. The data is presented for $T=1.7$ K and $\nu=370.4$ GHz. The transmission is scaled by a factor of 10 for clarity.
This figure "figure7.GIF" is available in "GIF" format from:

http://arxiv.org/ps/cond-mat/9906074v1
H. Nojiri et al. Fig. 8

- $E_{g_1} = 1329$ GHz
- $E_{g_2} = 570$ GHz
- $E_d = 193$ GHz
- $H_c$