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# THz ESR study of peculiar Co pyrochlore system $\text{GeCo}_2\text{O}_4$ using pulsed high magnetic field

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## Abstract

THz electron spin resonance (ESR) measurements of the spinel compound  $\text{GeCo}_2\text{O}_4$ , which consists of the  $\text{Co}^{2+}$  pyrochlore structure, were performed. The temperature dependence measurements revealed new antiferromagnetic phases,  $\text{AF}_1$  and  $\text{AF}_2$ , below  $T_N$ . Moreover, a wide magnetic field range of ESR study using a single crystal at 1.8 K also revealed various field-induced phases due to the competition between the spin-lattice coupling and the spin-frustration. Critical field resonances were observed at 5.0 T, 8.6 T, and 11.0 T for  $B//[111]$  and 5.1 T, 7.7 T, 11.2 T and 13.0 T for  $B//[110]$  at 1.8K. Although it became difficult to observe ESR above 86K, the g-values of  $\text{Co}^{2+}$  ions were estimated to be  $g_{[111]} = 3.34$  and  $g_{[110]} = 3.27$  for  $[111]$  and  $[110]$ , respectively, from the observed ESR mode above the saturation field at 1.8K. Detailed frequency-field diagrams of the ESR modes at 1.8 K suggested the existence of spin-lattice coupling energy of 250 GHz ( $= 1.03 \text{ meV} = 12 \text{ K}$ ) at the critical field resonances. The spin gap mode in the frequency-field diagram at 1.8K showed excitation energies of  $E_{[111]} = 1004 \text{ GHz}$  ( $= 4.15 \text{ meV} = 48 \text{ K}$ ) and  $E_{[110]} = 1044 \text{ GHz}$  ( $= 4.32 \text{ meV} = 50 \text{ K}$ ) for  $[111]$  and  $[110]$ , respectively. These results will be discussed in connection with the di-tetramer model suggested previously.

## 1 Introduction

The concept of frustration in condensed matter physics [1] has attracted much attention recently. Geometrical frustration in particular has been shown to lead to a variety of novel ground states and dynamical phases. The cubic spinel  $\text{AB}_2\text{O}_4$  with the space group  $Fd-3m$ , whose B sites form the pyrochlore lattice known as the typical three-dimensional geometrically frustrated structure, provides fruitful orbital and spin physics, such as the orbital ordering [2], the orbital liquid state [3], the orbital glass [4], and the peculiar lattice distortion coupled to spin [5, 6]. For instance, the  $\text{ACr}_2\text{O}_4$  chromium spinel systems ( $A=\text{Mg, Zn, Cd, and Hg}$ ) have been intensively studied from the viewpoint of competition between magnetic and elastic energies. In fact, these systems show peculiar structural flexibility related to their magnetic structures, which comes from the combination of the magnetic and lattice degrees of freedom, in zero and finite magnetic fields [5-11]. In these chromium compounds, the frustration between magnetic and elastic energies is dissolved by structural transition with antiferromagnetic ordering at  $T_N$ . Moreover, the half magnetization plateau, which is stabilized by the spin-lattice coupling, appears in a wide range of magnetic fields. These complex temperature-magnetic field phases have been interpreted by a release process from frustration [5, 11].

Now we will focus on the  $\text{Co}^{2+}$  ions, because Co systems are expected to have stronger spin-orbit

coupling than the other 3d transition systems and often show successive magnetic transitions within the long range ordering [12]. Co sites in the cubic spinel  $\text{GeCo}_2\text{O}_4$  form a pyrochlore lattice, which consists of corner-sharing Co-tetrahedrons as shown in Figure 1(a) [13]. Tetrahedrons are considered to be the basic components of the three-dimensional geometrically frustrated structure [1]. The magnetic susceptibility at high temperature follows the Curie-Weiss behavior with a positive value of the Weiss temperature,  $\theta = 81.0$  K, which suggests the existence of stronger ferromagnetic (FM) interactions [14, 15]. However, the system turns out to undergo the antiferromagnetic (AF) ordering at  $T_N = 23.0$  K from the DC susceptibility [15], the AC susceptibility [14], the specific heat [16, 17], and the powder neutron diffraction [18] measurements. This antiferromagnetic ordering is accompanied by the cubic-to-tetragonal structural transition [17, 19, 20]. Although it seems that the frustration is dissolved by this structural transition, the axial elongation in tetragonal symmetry is very small, with a value of  $\Delta c/a = 0.116\%$  [15]. Moreover, strong softenings for  $k//[110]$  and  $k//[111]$  at the Néel temperature are observed in the ultrasound measurements [15]. This result also suggests that  $\text{GeCo}_2\text{O}_4$  has a strong spin-lattice coupling. Anisotropic magnetic behavior for  $B//[110]$  and  $B//[111]$  are also observed in the magnetization measurement [20]. The characteristic behaviors for  $[110]$  and  $[111]$  in the pyrochlore lattice suggest that these behaviors come from the kagome-triangular layer structures stacking along the  $[111]$  direction, as shown in Figure 1(c). Accordingly, several researchers have tried to interpret X-ray [21] and neutron [18, 26] structural data in connection with the kagome or the triangular structures. However, studies using ultrasound [23], specific heat [18], magnetization [20, 24], neutron [21], ESR [25], and low-temperature XRD [26] measurements have revealed successive structural and magnetic transitions below  $T_N$  and under the magnetic fields in  $\text{GeCo}_2\text{O}_4$ , suggesting that  $\text{GeCo}_2\text{O}_4$  does not actually have a regular pyrochlore structure. If the deformation occurs in the tetrahedrons in a similar manner as in chromium spinels [5, 11], a consideration of the local Co-tetrahedrons would be more appropriate for understanding the magnetic phases than an analysis of longer-scale structures such as layered kagome and triangular structures. From this viewpoint, Tomiyasu proposed an antiferromagnetically coupled di-tetramers model [27]. This model consists of the two antiferromagnetically coupled ferromagnetic tetramers of Co-tetrahedron.

In this paper, we provide the  $g$ -values of the Co local site from high-field EPR measurements. To clarify the spin dynamics of  $\text{GeCo}_2\text{O}_4$ , the temperature dependence ESR measurements were performed over a wide temperature range. Finally, to clarify the magnetic phases, we performed high-field and multi-frequency ESR measurements at 1.8K.

## 2 Experimental

Large single crystals of  $\text{GeCo}_2\text{O}_4$  were grown by the floating zone method [28]. The obtained single

crystals were checked by X-ray measurements. The magnetic susceptibility and magnetization results of the single crystal were published in a previous paper [15]. High-field ESR measurements of  $\text{GeCo}_2\text{O}_4$  single crystals were performed in the temperature range from 1.8 to 265 K using a pulsed magnetic field up to 40 T. ESR measurements above 86 K were performed using a highly sensitive InSb detector (QMC Instruments, Ltd.) and a high-temperature cryostat with temperature control by a nitrogen gas flow from 86 to 265 K [29]. The cryostats with a small-pulsed magnet for low-field measurements up to 16 T were used for temperature dependence measurements in the temperature range from 1.8 to 80 K [30, 31]. High-field and high-frequency ESR measurements were performed using a CuAg pulsed magnet up to 55 T with a highly sensitive InSb detector [32]. Gunn oscillators, backward wave oscillators (BWO), and a far-infrared (FIR) laser were used as light sources [33]. All ESR measurements were performed using the transmission method. The magnetic field was calibrated by the resonance field of DPPH, which is a field maker for  $g = 2.00$  placed on the  $\text{GeCo}_2\text{O}_4$  single crystal. In this paper, the crystal structures were visualized using VESTA [34]. To investigate the magnetic anisotropy of the paramagnetic state, multi-frequency ESR measurements of a single crystal  $\text{GeCo}_2\text{O}_4$  were performed for  $B//[100]$ ,  $[110]$ , and  $[111]$  at 86 K. To investigate the spin dynamics and the magnetic excitation from the ground state, temperature and frequency dependence measurements were carried out for the magnetic field directions  $B//[111]$  and  $[110]$ , which correspond to the applied field perpendicular and parallel to the kagome-triangular plane, respectively.

### 3 Results and discussion

Although we tried to measure ESR spectra of the Co local site in the paramagnetic state at high temperatures using a highly sensitive detector, we could not observe the spectra above 133 K due to the broadening of absorption lines. Consequently, the magnetic anisotropy at high temperature is discussed based on the observable ESR spectra at 86 K. Figure 2 shows the typical frequency dependence of ESR spectra for  $B//[111]$  at 86 K in the frequency range from 160 to 568 GHz. A sharp absorption line at a higher field is a signal of DPPH, which is a field maker of  $g = 2.00$ . A very broad absorption line with a linewidth of 10 T, as indicated by the open circles in the figure, was observed at around  $g \sim 5$ . The novel broad ESR absorption spectra means that the spin relaxation time is very short, possibly due to the strong spin-lattice coupling. It was clear that the whole absorption line could not be observed using the low frequency and the low magnetic field. Similar very broad absorption lines are observed for  $B//[100]$  and  $B//[110]$  at 86 K. Figure 3 shows the frequency-field diagram for  $B//[100]$ ,  $B//[110]$ , and  $B//[111]$  at 86 K. The error bar corresponds to 10% of the linewidth. The  $g$ -value was estimated to be  $g = 5.26 \pm 0.07$  for  $B//[111]$ . The obtained  $g$ -values were  $g = 5.16 \pm 0.12$  and  $g = 4.98 \pm 0.07$  for  $B//[100]$  and  $B//[110]$ ,

respectively. The Co ion is located at the center of the  $\text{CoO}_6$  octahedron, which forms a regular octahedron with a Co-O bond length of 0.125 nm toward the crystal axes. All O-Co-O bond angles are  $90^\circ$  degrees [13], as shown in Figure 1(b). Therefore, the  $\text{Co}^{2+}$  ion is in a cubic field. The ground state of the  $\text{Co}^{2+}$  ion in a cubic field is the  $\Gamma_4$  triplet state whose g-values are expected to be isotropic [35-37]. The directions of applied magnetic fields for  $B//[100]$ ,  $[110]$ , and  $[111]$  correspond to the x-axis and the xy-axis of the quantized axes and trigonal axis, respectively. Therefore, the obtained isotropic g-values coincide with the cubic symmetry field. However, we cannot use the absolute value  $g \sim 5$  at 86 K as the intrinsic g-value. This is because the inverse plot of the magnetic susceptibility deviates from the Curie-Weiss law at around 86 K. This in turn suggests that the spin-spin correlation might be developed at 86 K. We will estimate intrinsic g-values from the high-field ESR measurements in the field-induced ferromagnetic state later.

The temperature dependence of ESR spectra at 160GHz for  $B//[111]$  is shown in Figure 4. Although decreasing baselines at the lower field are observed for higher temperatures above 133 K, it is difficult to estimate the resonance field due to the broad features. Precursory resonance shifts below approximately  $(T_N + 10)$  K are also observed. This suggests the development of a short-range order above  $T_N$ . Such a precursory resonance shift is often observed in the frustrated spin systems due to the development of spin-spin correlations before the long range order [38]. The observed precursory resonance shift is different from that of the chromium spinels such as  $\text{MgCr}_2\text{O}_4$  and  $\text{ZnCr}_2\text{O}_4$  [39], because their resonance fields change abruptly at  $T_N$  [40], accompanied by the first-order structural phase transition. However, in the case of  $\text{GeCo}_2\text{O}_4$ , the gradual change of the resonance field seems to be related to the softening of the longitudinal elastic moduli along the  $[111]$  direction to  $T_N$  [15]. Then the resonance field becomes stable below 15 K, which corresponds to the structural distortion temperature  $T_D = 16$  K [26]. Below  $T_N$ , two new antiferromagnetic resonances (AFMR) appear in the higher field, and its shift to higher field as the temperature decreases. Moreover, several new AFMR appear at  $B_{C1} = 5.0$  T,  $B_{C2} = 8.6$  T, and  $B_{C3} = 11.0$  T below 3 K, as shown in Figure 4. The temperature dependence of the resonance field at 160 GHz for  $B//[111]$  shows clear phase boundaries at  $T_N$  and 3 K, as shown in Figure 4(b). However, no anomalies were observed at around 3 K in the specific heat, the longitudinal elastic moduli at zero magnetic field [15, 17] and the temperature dependence of the magnetization [24]. On the other hand, the existence of complicated magnetic phases at a lower magnetic field for  $B//[110]$  was observed in the ultrasound measurements under the magnetic field [23] and isothermal magnetization measurements [24]. Therefore, the appearance of new resonances in the temperature dependence of ESR spectra suggests the existence of complicated temperature-magnetic phases below  $T_N$ .

Figure 5 shows the frequency dependence of ESR spectra up to (a) 16 T and (b) 40 T for  $B//[111]$  at

1.8 K in the frequency range from 60 to 785 GHz. Frequency-independent absorption lines are observed at  $B_{C1}=5.0$  T,  $B_{C2}=8.6$  T, and  $B_{C3}=11.0$  T up to 250 GHz for  $B//[111]$ . Above 250 GHz, frequency-dependent AFMR modes appear from  $B_{C1} \sim B_{C3}$ . Stronger absorption lines of  $\omega_1$  and  $\omega_3$  are observed at around 5 T in Figure 5(a). On the other hand, a broad absorption line with some structure is observed in  $\omega_4$  and  $\omega_6$  at around 10 T in Figure 5(b). Moreover, a sharp and weak absorption line  $\omega_7$  is observed at a higher field than the saturation field of 12 T. Figure 6 (a) shows the frequency-field diagram for  $B//[111]$  at 1.8 K in the frequency range up to 785 GHz and the magnetic field range up to 35 T. Thus the existence of frequency-independent modes, also known as critical field resonances, becomes clear; these modes are found at  $B_{C1} = 5.0$  T,  $B_{C2} = 8.6$  T and  $B_{C3} = 11.0$  T for  $B//[111]$ . The critical field resonance<sup>1</sup> can be observed at magnetic transitions in single crystal measurements, when the applied magnetic field cants slightly from the easy axis [7, 41–43]. ESR modes for  $B//[111]$  are split and shifted from the critical field resonances at  $B_{C1}$ ,  $B_{C2}$ , and  $B_{C3}$  above approximately 250 GHz. Linear extrapolation of the AFMR mode  $\omega_1$  reaches 1254 GHz at zero field with  $g = 13.1$ . The slopes of the AFMR modes for  $\omega_3$ ,  $\omega_4$ ,  $\omega_5$ , and  $\omega_6$  change simultaneously at around 450 GHz. The high-field ESR mode  $\omega_7$  appears above the saturation field. Its  $g$ -value is estimated to be  $g = 3.34$  by the linear fitting. If we extrapolate the  $\omega_7$  mode to zero frequency, it will cross at 14.5 T. On the other hand, ESR spectra for  $B//[110]$  at 1.8 K appear rather complicated, with more absorption lines in the lower field than for  $B//[111]$ . Therefore, we show the frequency-field diagram without minor absorption lines for  $B//[110]$  at 1.8 K in the frequency range up to 720 GHz in Figure 6(b). The critical field resonances are also observed at  $B_{C1} = 5.10$  T,  $B_{C2} = 7.71$  T,  $B_{C3} = 11.2$  T, and  $B_{C4} = 13.0$  T for  $B//[110]$ . The ESR modes are also split and shifted above 250 GHz. The AFMR mode  $\omega_1$  reaches 1294 GHz at zero field and linearly down to  $B_{C1}$  with  $g = 14.1$ . The high-field ESR mode  $\omega_7$  mode appears above the saturation field, and it has the  $g$ -value of  $g = 3.27$ .

Now we will discuss these complicated AFMR modes in connection with magnetization curve of a single crystal and the proposed model by Tomiyasu. Generally, the critical field resonances are observed at the critical field of the magnetic transition. According to Figure 2(b) in ref. [20], the differential magnetization curve for  $B//[111]$  at 1.5 K has peaks at 4.6 T and 10.2 T. Although the critical field resonances  $B_{C1} = 5.0$  T and  $B_{C3} = 11.0$  T for  $B//[111]$  are close to these peaks, somehow they are a bit higher than the peaks of the differential magnetization. Moreover, there are no anomalies in the differential magnetization curve at  $B_{C2} = 8.6$  T. Similar discrepancy between the differential

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<sup>1</sup> The critical field resonance has been pointed out theoretically by Nagamiya, and T. Nagamiya [41] and has been observed experimentally by M. Data group [42]. The detailed angular dependence measurements of the critical field resonance for antiferromagnet  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  has been reported by K. Nagata. The absorption intensity of the critical field resonance decreases abruptly, when the applied magnetic field parallels absolutely the easy axis within  $0.1^\circ$  [43].

magnetization peaks and the critical field resonances is also observed for  $B//[110]$ . The differential magnetization for  $B//[110]$  at 1.5 K has peaks at 4.2 T and 9.4 T, and anomalies at 4.8 T, 7.4 T and 11.0 T. The critical field resonances of  $B_{C1} = 5.1$  T,  $B_{C2} = 7.7$  T and  $B_{C3} = 11.2$  T are close to anomalies of the differential magnetization rather than the peaks. The differential magnetization distinguishes clear changes in magnetization. However, the magnetization measurements may not be sensitive to the lattice distortion. On the other hand, ESR is a more sensitive method to detect local symmetry of the magnetic moment. The discrepancy between the differential magnetization peaks and the critical field resonances may come from the difference in the sensitivity for each measurement. Indeed, different critical fields were reported from the specific heat measurements of the  $\text{GeCo}_2\text{O}_4$  single crystal under a magnetic field [44]. In the case of chromium spinels  $\text{MCr}_2\text{O}_4$ , a complicated field-temperature phase diagram due to a strong spin-lattice correlation was proposed [5]. And the magnetic phase boundary, which could not be detected by the magnetization measurements [10], was detected by ESR measurements [46]. Therefore, the critical field resonances suggest hidden magnetic transitions related to the lattice distortion, which does not change the total magnetization.

Next we will consider the frequency-field diagram for  $B//[111]$  at 1.8 K in Figure 6(a). The ESR mode above the saturation field has the same  $g$ -value of the paramagnetic state, because the saturated state is the field-induced ferromagnetic state. Therefore, the  $g$ -value for  $B//[111]$  can be estimated to be  $g_{[111]} = 3.34$  from the high-field mode  $\omega_7$ . Similarly, the  $g$ -value for  $B//[110]$  is estimated to be  $g_{[110]} = 3.27$  from the high-field mode  $\omega_7$  for  $B//[110]$  in Figure 6(b). This isotropic  $g$ -value  $g \sim 3.3$  from the field-induced ferromagnetic state is consistent with the isotropic feature of  $g$ -values observed for  $B//[111]$ ,  $[110]$ , and  $[100]$  at 86 K. In addition,  $g \sim 3.3$  also coincides with the theoretical estimation [35].

Now we will discuss the critical field resonance. The critical field resonances of  $[111]$  and  $[110]$  disappear at 250 GHz in unison. Such synchronized behavior is often observed in strong spin-lattice coupled systems. For example, for the inorganic spin-Peierls material  $\text{CuGeO}_3$ , the ESR of singlet-triplet transition, which is observable due to the Dzyaloshinsky-Moriya interaction, disappears below 200 GHz [45], because  $\text{CuGeO}_3$  has a strong spin-lattice coupling. Because a strong spin-lattice coupling is expected in  $\text{GeCo}_2\text{O}_4$  [15, 23], we can assume that the magnetic phase transition has a lattice deformation energy cost similar to that observed in  $\text{CuGeO}_3$ . Therefore, the lattice deformation energy of  $\text{GeCo}_2\text{O}_4$  is estimated to be 250 GHz ( $= 12$  K  $= 1.03$  meV). And the critical field  $B_{C1} \sim B_{C3}$  can be considered as the critical field of magnetic phase boundaries. Since the spin arrangement and lattice deformation of the Co tetrahedron determine the total energy, the critical field is considered to be dependent on the direction of the applied magnetic field to the Co tetrahedron.

Here, we will discuss the low field mode in the frequency-field diagrams in Figure 6 because the low

field mode is related to a zero-field gap, which is easy to compare with other zero-field measurement results. The ESR mode  $\omega_1$  appears from 250 GHz below the critical field  $B_{C1}$  for both  $B//[111]$  and  $B//[110]$  at 1.8 K. If the ESR mode  $\omega_1$  is linearly extrapolated to the lower magnetic field, the mode  $\omega_1$  has a zero-field gap of 1254 GHz ( $=5.2$  meV= $60.2$  K) for  $B//[111]$  and that of 1294 GHz ( $=5.4$  meV= $62.1$  K) for  $B//[110]$ , which coincide well within the error bar of ESR. The zero-field gap obtained by our ESR results is rather comparable with the 4 meV mode proposed by Tomiyasu *et al.* based on their powder inelastic neutron scattering (INS) findings under a zero magnetic field at 4 K [24] with consideration for the possible error bar in INS. Tomiyasu *et al.* observed a magnetic excitation of about 4 meV in the INS measurements below  $T_N$ , and they interpreted this excitation as the singlet ( $J_{\text{di-tetra}}=0$ ) to the first excited triplet ( $J_{\text{di-tetra}}=1$ ) excitation by the di-tetramer model for  $\text{GeCo}_2\text{O}_4$  [24]. Here, the tetramer consists of four ferromagnetically coupled  $\text{Co}^{2+}$  ions with a fictitious spin  $S=1/2$  for each  $\text{Co}^{2+}$  ion, and two tetramers are antiferromagnetically coupled in the di-tetramer model. The origin of allowed ESR transition from singlet ( $J_{\text{di-tetra}}=0$ ) to the triplet ( $J_{\text{di-tetra}}=1$ ) may be due to the Dzyaloshinsky-Moriya interaction, because there is no inversion center between two tetramers from the crystal symmetry (Figure 1 (a)), or due to the mixing of states discussed below. Therefore, the observed zero-field gap looks rather consistent between ESR and INS, and appears to support the di-tetramer model proposed by Tomiyasu *et al.* [24]. On the other hand, the field dependences of  $\omega_1$  give the effective g-values  $g_{[111]}^t=13.1$  for  $B//[111]$  and  $g_{[110]}^t=14.1$  for  $B//[110]$  as shown in Figure 6. These observed field dependences by ESR are rather surprising for the di-tetramer model because the slope of the triplet ( $J_{\text{di-tetramer}}=1$ ) is expected to be  $g_{[111]}=3.34$  for  $B//[111]$  and  $g_{[110]}=3.27$  for  $B//[110]$  in the naive picture with the strong ferromagnetic interaction regime in the tetramer. In fact, the intra-tetramer ferromagnetic exchange interaction and inter-tetramer antiferromagnetic interaction in  $\text{GeCo}_2\text{O}_4$  were estimated to be  $J_1^{(\text{ex})}=-8$  meV and  $J_3^{(\text{ex})}=10$  meV, respectively, and these absolute values were comparable to those from the analyses of INS [24]. Therefore, because the mixing of states among the  $J_{\text{di-tetramer}}=0, 1, 2, 3, 4$  states is expected, the g-values may be larger than  $g_{[111]}=3.34$  and  $g_{[110]}=3.27$ , but an approximate 4-fold increase in the g-value, such as  $g_{[111]}^t=13.1$  or  $g_{[110]}^t=14.1$ , would be unlikely. These observed large g-values of the  $\omega_1$  mode may thus suggest something new beyond the di-tetramer model, but this possibility remains for a future investigation.

#### 4 Summary

High-field and wide frequency ESR measurements of the Co cubic spinel compound  $\text{GeCo}_2\text{O}_4$  have been performed. Isotropic feature of g-values is obtained for  $B//[111]$ ,  $[110]$  and  $[100]$  at 86 K, and the

absolute values of  $g$  for  $B//[111]$  and  $[110]$  are estimated to be  $g_{[111]} = 3.34$  and  $g_{[110]} = 3.27$  from the ESR measurements in the field-induced ferromagnetic state at 1.8 K. The critical field resonances are observed at  $B_{C1} = 5.0$  T,  $B_{C2} = 8.6$  T and  $B_{C3} = 11.0$  T for  $B//[111]$ , and they are also observed at  $B_{C1} = 5.1$  T,  $B_{C2} = 7.7$  T,  $B_{C3} = 11.2$  T and  $B_{C4} = 13.0$  T for  $B//[110]$ . Most field-dependent ESR branches appear at these critical field resonances above 250 GHz ( $= 1.03$  meV  $= 12$  K), which can be interpreted as the lattice deformation energy coming from the strong spin-lattice coupling. Moreover, the critical resonances suggest hidden magnetic transitions related to the lattice distortion, which does not change the total magnetization. The linearly extrapolated  $\omega_1$  modes observed by ESR for  $B//[111]$  and  $B//[110]$  at 1.8 K suggest the zero-field gaps of 1254 GHz ( $= 5.2$  meV  $= 60.2$  K) and 1294 GHz ( $= 5.4$  meV  $= 62.1$  K), which are in good agreement with the lowest magnetic excitation 4 meV mode observed by the powder INS in consideration of the experimental errors, and these results appear to support the di-tetramer model proposed by Tomiyasu *et al.* [24]. However, the observed effective  $g$ -values of the  $\omega_1$  modes are  $g_{[111]}^t = 13.1$  for  $B//[111]$  and  $g_{[110]}^t = 14.1$  for  $B//[110]$ , which are much larger than the expected values for the triplet ( $J_{\text{di-tetramer}} = 1$ ) state. It is difficult to interpret such large effective  $g$ -values, even if we consider the mixing of higher energy states. Therefore, further studies of the magnetic field dependence will be needed.

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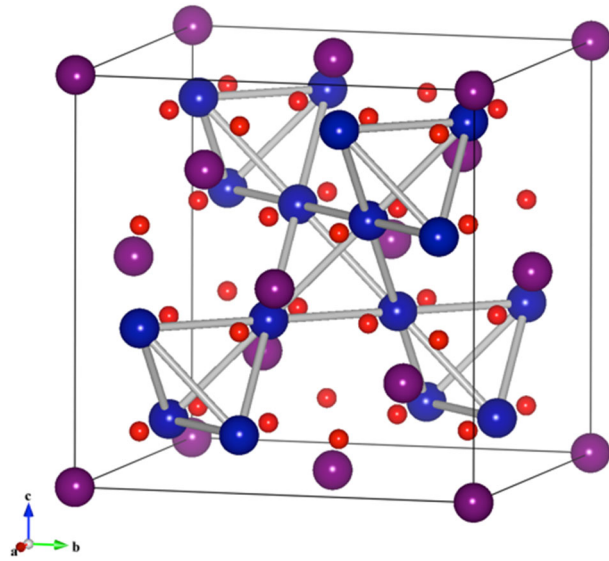
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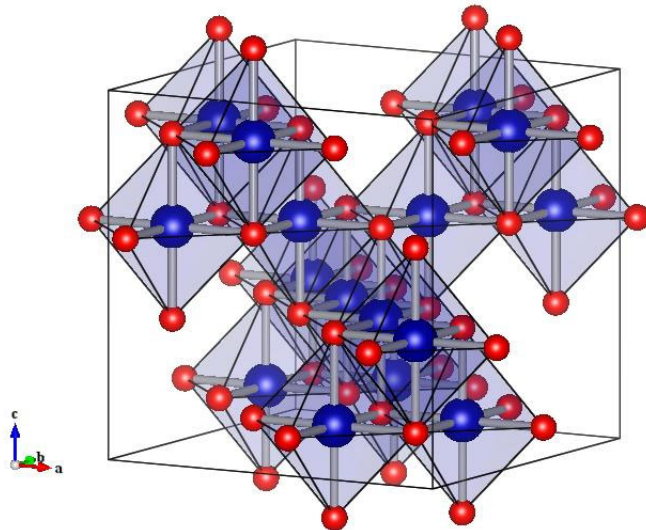
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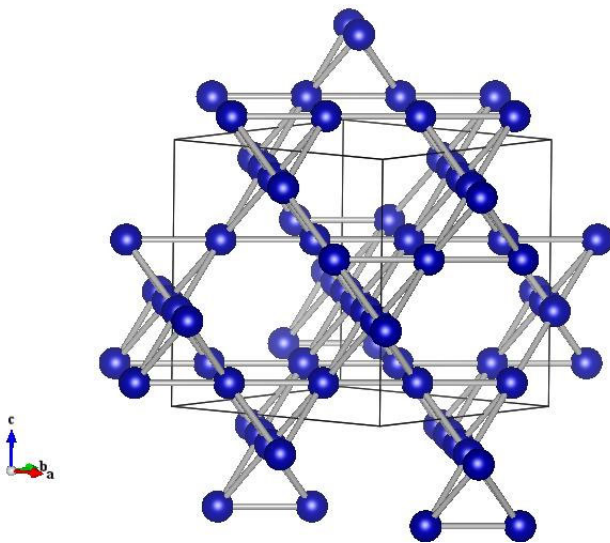
## Figures



(a)



(b)



(c)

Fig. 1 Crystal structure of  $\text{GeCo}_2\text{O}_4$  (a) (b) (c).

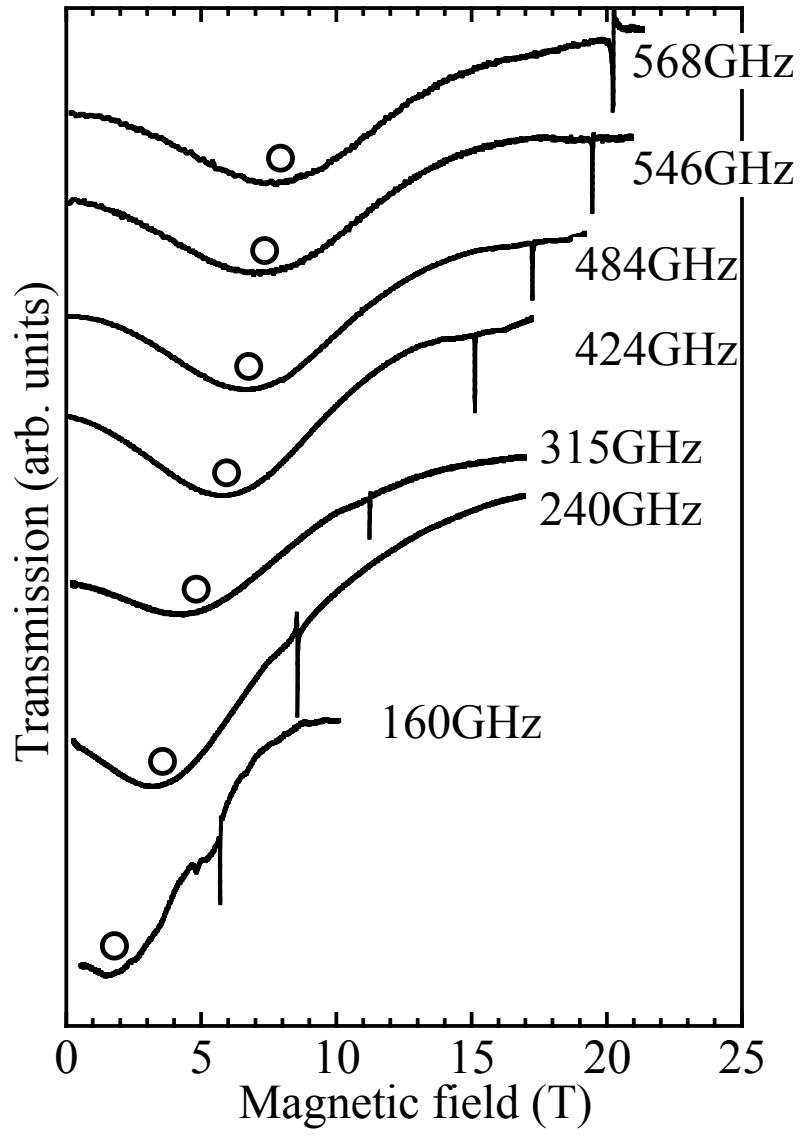
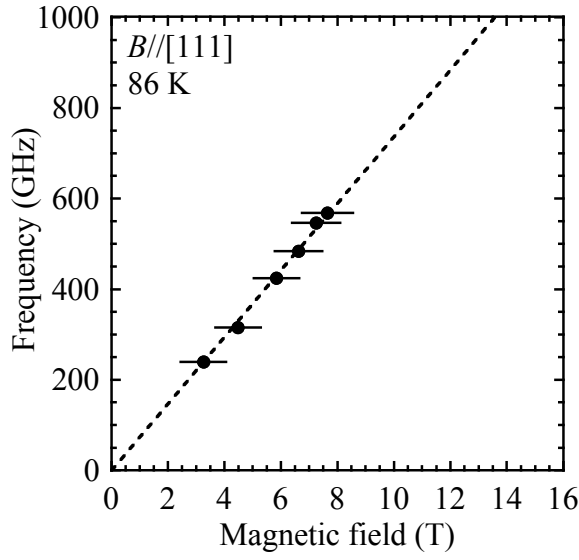
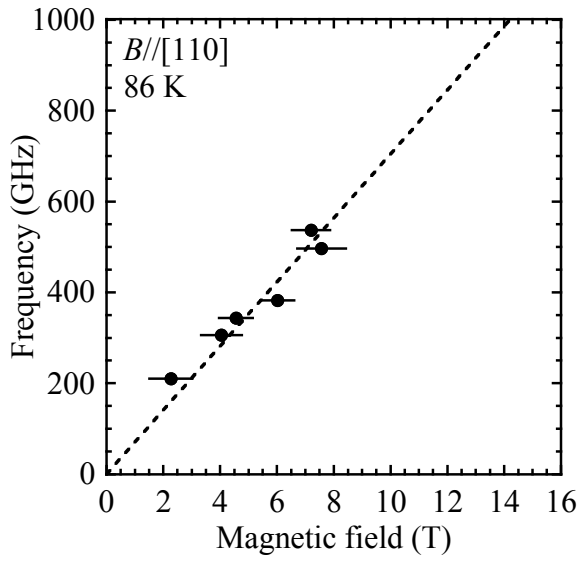


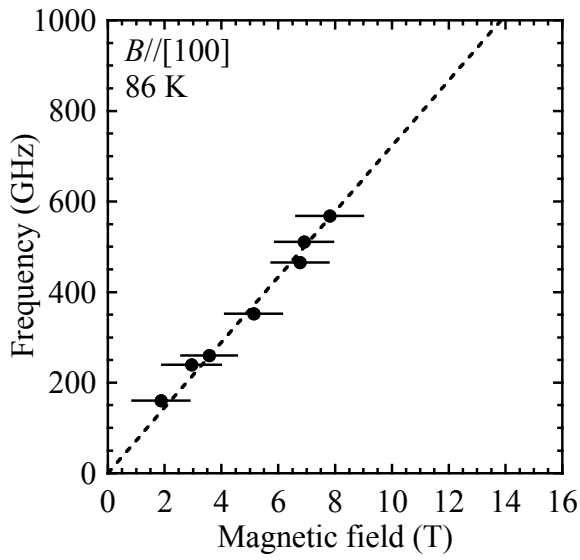
Fig. 2 Frequency dependence of ESR spectra for  $B//[111]$  at 86K.



(a)

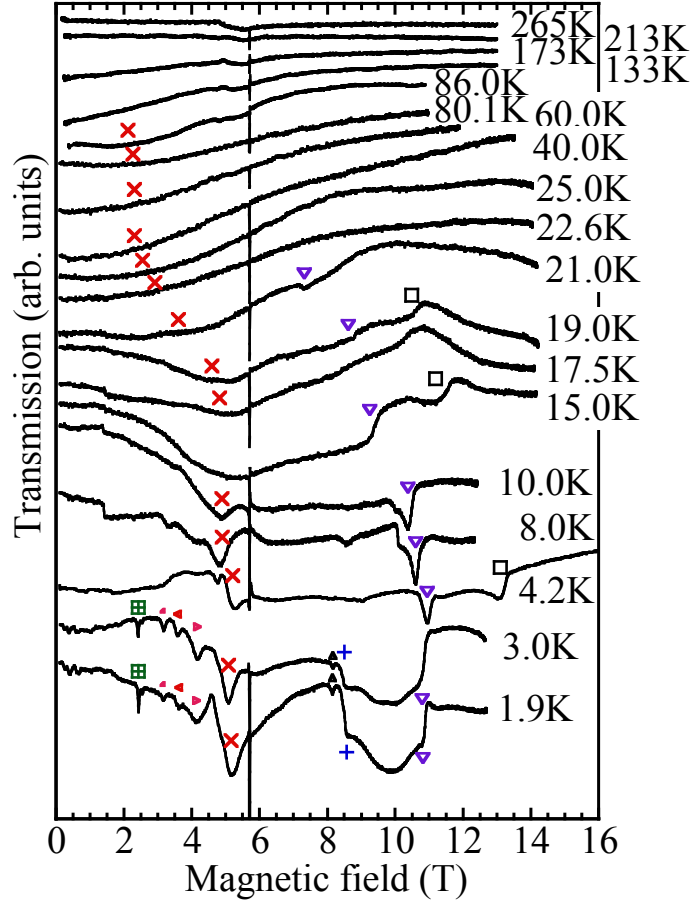


(b)

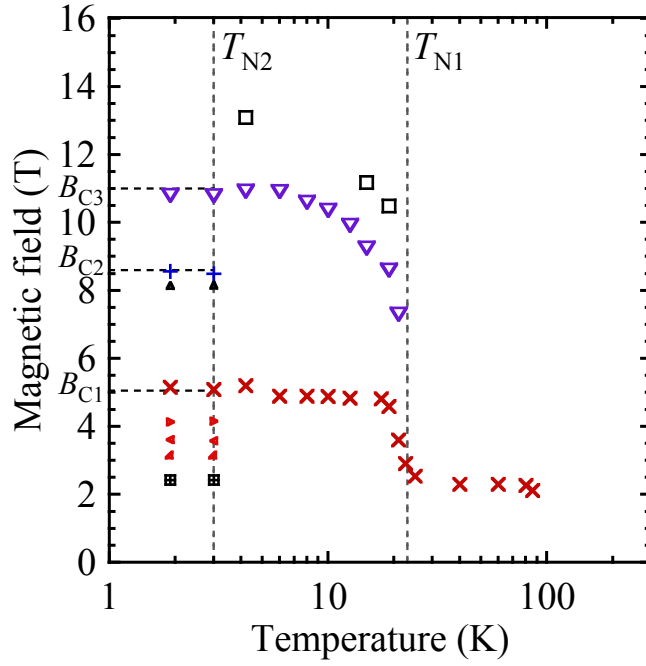


(c)

Fig. 3 Frequency-field diagram at 86K. (a)  $B//[111]$ , (b)  $B//[110]$ , (c)  $B//[100]$ .

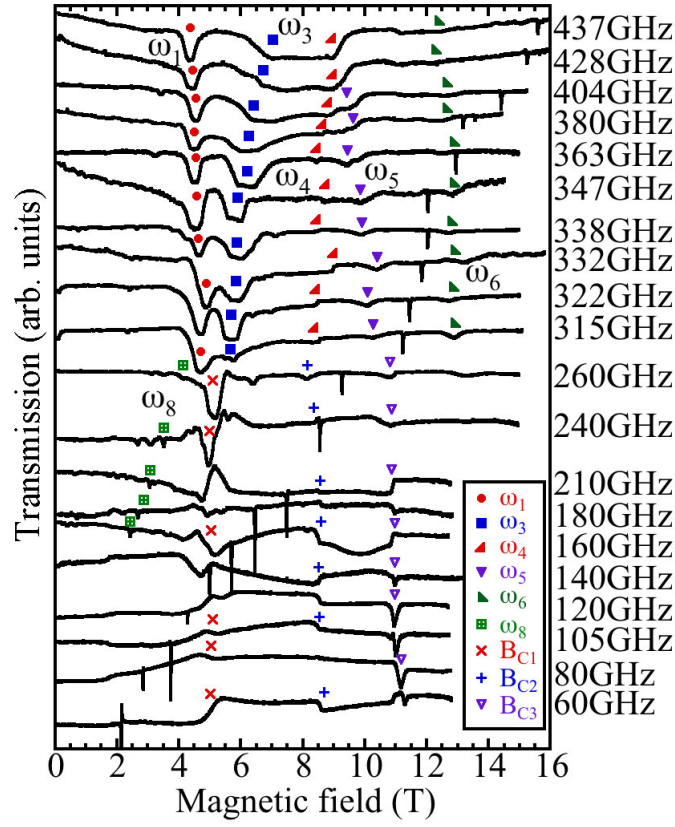


(a)

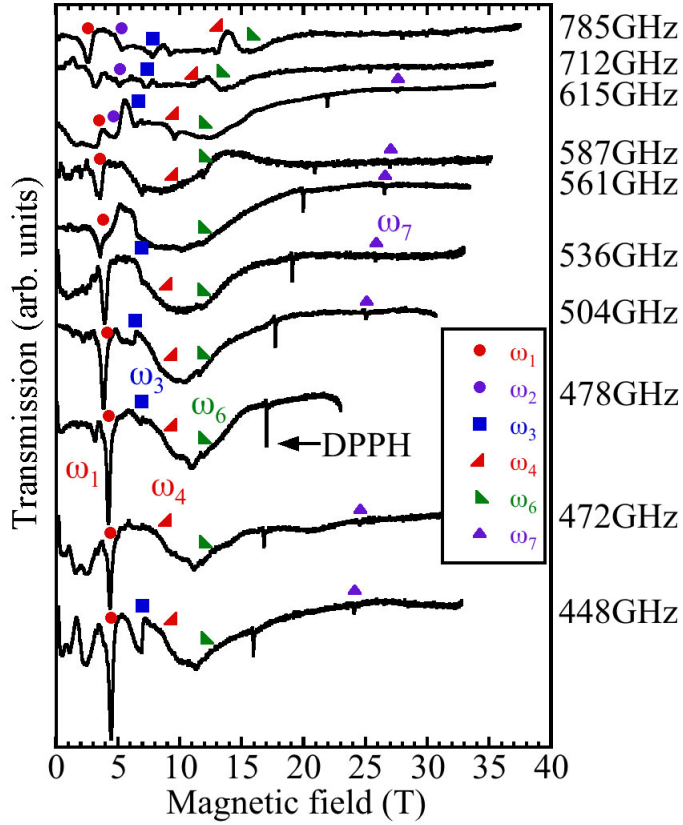


(b)

Fig. 4 (a) Temperature dependence of ESR spectra for 160 GHz for  $B//[111]$ . (b) Temperature dependence of resonance field for 160GHz for  $B//[111]$ .



(a)



(b)

Fig. 5 Frequency dependence of ESR spectra for  $B//[111]$  at 1.8K. (a) In the case of transmission below 440 GHz (b) In the case of transmission above 440 GHz.

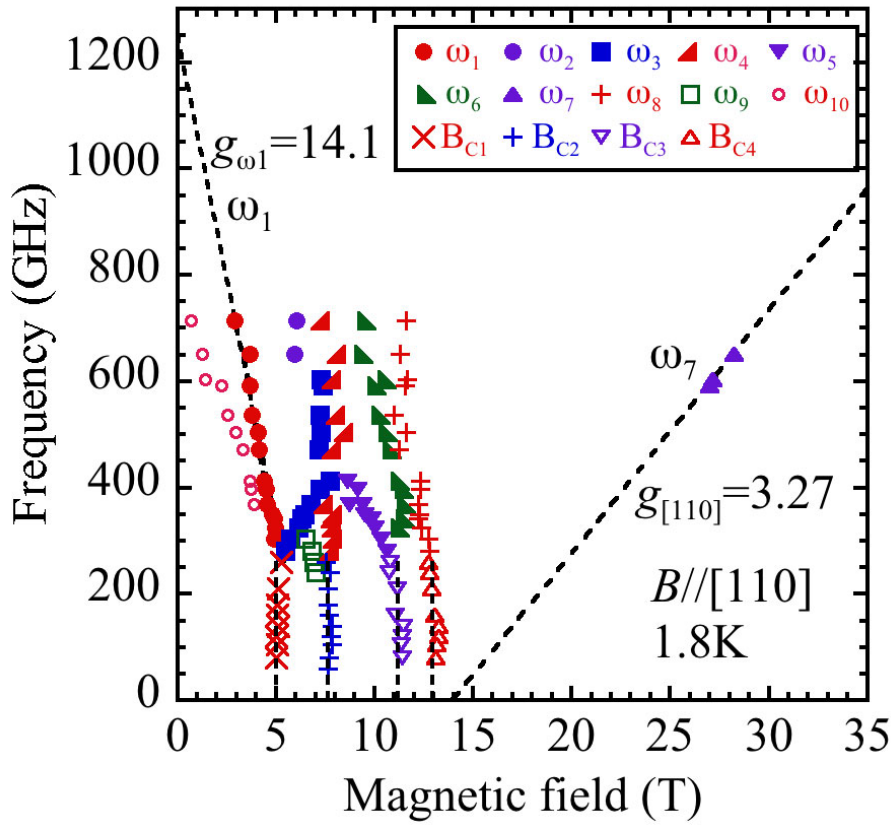
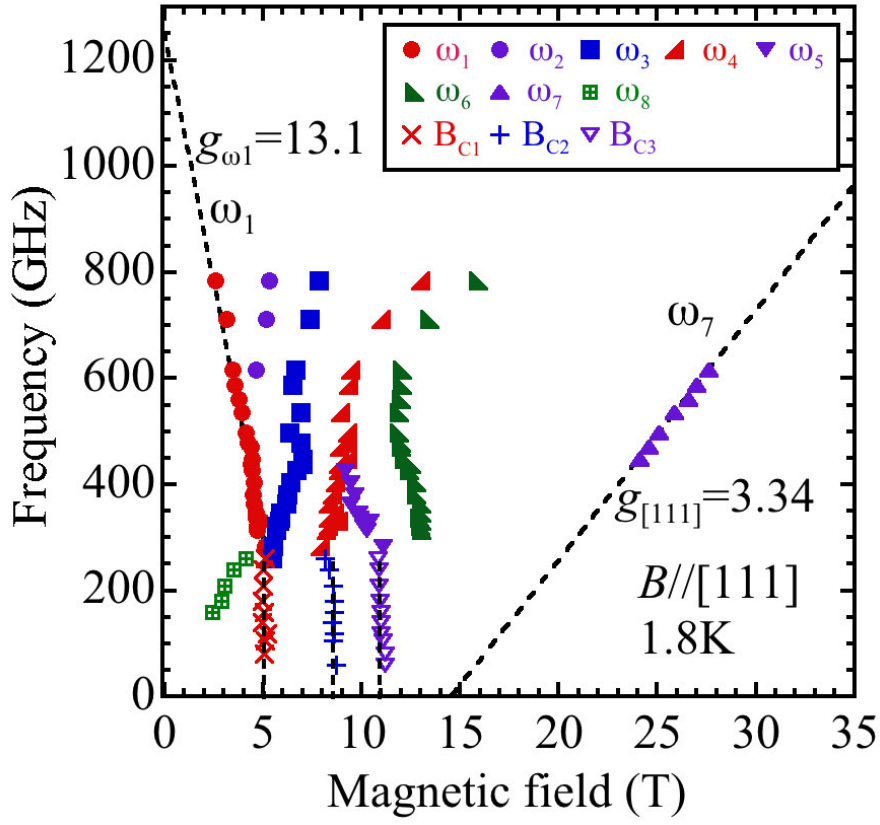


Fig. 6 (a) Frequency-field diagram for  $B//[111]$  at 1.8K. (b) Frequency-field diagram for  $B//[110]$ .