Magnetoelectric properties of Ca$_2$CoSi$_2$O$_7$ studied by high-field electron spin resonance

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Abstract. We have performed electron spin resonance (ESR) experiments of multiferroic Ca$_2$CoSi$_2$O$_7$ single crystals in high magnetic fields perpendicular to the easy plane. We observed many ESR absorption signals in the magnetization plateau phase below the saturation field which form branches with a linear magnetic field dependence. At zero magnetic field, large energy gaps with $\Delta = 1.7 \sim 1.8$ THz are identified by linear extrapolations of the resonance branches. We speculate that the high-energy ESR modes would be caused by electromagnons. With increasing magnetic field, some of these ESR modes decrease linearly with field even within the magnetization plateau phase and intersect the zero-frequency line at the magnetic field where the magnetization plateau terminates, suggesting a relationship between these energy gaps and the magnetization plateau.

1. Introduction
Magnetoelectric multiferroic materials have attracted both experimental and theoretical interest [1, 2, 3]. The mechanism of spin-dependent electric polarization is well explained by several microscopic models [4, 5, 6, 7]. A well-known model is the spin-current mechanism in which ferroelectricity originates from a cycloidal spin structure (e.g., TbMnO$_3$ [8]). On the other hand, up-up-down-down spin order induces electric polarization through exchange striction. This type of ferroelectricity is realized in highly-distorted orthorhombic $R$MnO$_3$ compounds ($R$=Y, Ho, ..., Lu) with $E$-type antiferromagnetism [9], DyFeO$_3$ [10], and Ca$_3$(Co,Mn)$_2$O$_6$ [11]. The third mechanism is the spin-dependent $p$-$d$ hybridization mechanism, where the hybridization between transition-metal $d$ and ligand $p$ orbitals is affected by the spin orientation relative to the bond direction between the transition metal and the ligand ions through the spin-orbit interaction. The variation of the hybridization generates a local electric dipole moment, and the sum of the local electric dipole moments is observed as spontaneous electric polarization. The remarkable feature of this mechanism is that the electric polarization is induced by one spin and its ligand ions without considering the spin-spin interactions. Therefore, the magnetic-field induced electric polarization caused by the $p$-$d$ hybridization mechanism has been observed not only in a magnetically long-range ordered state but also in a paramagnetic state [12]. In contrast, the other two mechanisms induce an electric polarization only in the magnetically ordered state because of the spin-spin interactions.

Recently, the Co åkermanite family, such as Ca$_2$CoSi$_2$O$_7$ [13, 14], Sr$_2$CoSi$_2$O$_7$ [12], Ba$_2$CoGe$_2$O$_7$ [15, 16], and Sr$_2$CoGe$_2$O$_7$ [17], have attracted attention as typical multiferroic examples of the $p$-$d$ hybridization mechanism. As seen from the schematic crystal structure...
Figure 1. The crystal structure of Ca$_2$CoSi$_2$O$_7$ projected onto the $ab$-plane in (a) high temperature phase and (b) low temperature phase. Space group of high (low) temperature phase is $P4_21m$ ($P2_12_12$).

of akermanite illustrated in Fig. 1(a), corner sharing CoO$_4$ and SiO$_4$ (GeO$_4$) tetrahedra form layers alternating with intervening layers of alkaline earth metal ions along the $c$-axis. The Co$^{2+}$ magnetic ions form diagonal square lattices. Among them, Ca$_2$CoSi$_2$O$_7$ undergoes a series of structural phase transitions as a function of temperature [18, 19, 20]. Above 500 K, it shows the normal akermanite structure with tetragonal $P4_21m$ space group, as shown in Fig. 1(a). Between 150 and 500 K, the structure is incommensurate (IC). At 150 K, an IC-C (commensurate) transition occurs, and a $3 \times 3 \times 1$ supercell structure with orthorhombic $P2_12_12$ space group develops at lower temperatures, as shown in Fig. 1(b).

The magnetoelectric behavior is also complicated [13, 14]. An antiferromagnetic order takes place at the Neel temperature $T_N = 5.7$ K in Ca$_2$CoSi$_2$O$_7$. Magnetization processes for magnetic fields along the $a$- and $b$-axes show some anomalies. The magnetization along the $[110]$ direction exhibits a steep increase at 11 T, accompanied by a reversal of electric polarization. As shown in Fig. 3(a), the magnetization along the $c$-axis increases linearly up to 18 T. Between 18 T and 50 T a magnetization plateau develops, the magnitude of which is slightly smaller ($\sim$85%) than the saturation magnetization, and a step-like increase to the saturation value at 60 T. To clarify the origin of this anomalous magnetization plateau state from a microscopic viewpoint, we have performed electron spin resonance (ESR) experiments of single crystals of Ca$_2$CoSi$_2$O$_7$ in high magnetic fields.

2. Experiment
We grew single crystalline samples of Ca$_2$CoSi$_2$O$_7$ using the floating zone method. X-ray diffraction measurements at room temperature assigned the crystal structure to the tetragonal $P4_21m$. All specimens used in the experiments were cut along the crystallographic principal
axes into platelike shapes by means of the X-ray back reflection Laue technique. High-field multi-frequency ESR measurements at 1.4 K in pulsed magnetic fields of up to 50 T were conducted by utilizing a far-infrared laser and Gunn oscillators with a frequency doubler to generate submillimeter and millimeter waves. We used a magnetically tuned InSb hot-electron bolometer as a detector. All the experiments were carried out using unpolarized light.

3. Results and Discussion
Figure 2 displays the ESR absorption spectra of Ca$_2$CoSi$_2$O$_7$ for magnetic fields parallel to the c direction. Several absorption signals were observed in the magnetization plateau phase (Fig. 3(a)). In contrast, below 17 T, absorption signals were detected mostly above 1 THz. The resonance fields are plotted on the frequency-magnetic field diagram as shown in Fig. 3(b). Resonance modes observed in the magnetization plateau phase are linear in magnetic fields (H) with $g = 2.2$. This $g$ value is consistent with the value of the saturation magnetization as shown in Fig. 3(a). The gap frequencies of these linear modes $\Delta_{pi}$ ($i = 0 - 5$) at the transition field into the magnetization plateau phase are 0, 0.14, 0.25, 0.34, 0.43, 0.53 THz. The origin of these split linear modes may be the different magnetic anisotropy at each site due to the distortion of the CoO$_4$ tetrahedra in the $3 \times 3 \times 1$ supercell.

Moreover, two-magnon excitation modes emerge in high-frequency region above 0.5 THz in the magnetization plateau phase and near zero field at about 1.7 THz. Similar excitation was observed in the high field saturated phase of Sr$_2$CoGe$_2$O$_7$ [17]. In Sr$_2$CoGe$_2$O$_7$, this mode is explained by a spin-quadrupolar excitation and could be observed due to electromagnetic
coupling. Therefore, the two-magnon excitation modes in Ca$_2$CoSi$_2$O$_7$ are probably attributed to spin-quadrupolar excitations.

A weak signal with the zero field energy gap of 0.4 THz was observed in THz absorption spectroscopy [21]. However, this gapped mode could not be observed in our measurements, because the signal intensity must be too weak to be detected with our bolometer or this mode must be field independent along the [001] direction. In contrast, we observed other zero field energy gaps at $\Delta = 1.7 \sim 1.8$ THz by extrapolating the resonance modes to 0 T. In Ba$_2$CoGe$_2$O$_7$ ($\Delta = 0.5$ THz) [22] and Sr$_2$CoGe$_2$O$_7$ ($\Delta = 0.2$ THz) [17], the zero field energy gaps are explained by easy-plane type anisotropy. According to the spin-wave theory for the antiferromagnet with easy-plane anisotropy, the energy gap $\Delta$ is proportional to $\sqrt{2J\Lambda}$, where $J$ is the exchange constant between the nearest neighbor spins and $\Lambda$ is the single ion anisotropy constant. The antiferromagnetic transition temperatures $T_N$ are 5.7 K, 6.5 K and 6.7 K for Ca$_2$CoSi$_2$O$_7$ [14], Sr$_2$CoGe$_2$O$_7$ [23] and Ba$_2$CoGe$_2$O$_7$ [15], respectively. These similar values of $T_N$ suggest that the $J$ of Ca$_2$CoSi$_2$O$_7$ is not largely different from the $J$s in other Co åkermanite materials. On the other hand, the $\Lambda$ of Ca$_2$CoSi$_2$O$_7$ is probably small, because isotropic behavior was observed in its magnetization [13]. Therefore, the large zero-field energy gaps of $\Delta = 1.7 \sim 1.8$ THz are difficult to be understood as usual magnetic excitations, whereas the zero field gap of 0.4 THz is probably explained by the antiferromagnetic resonance mode with easy-plane type anisotropy. On applying magnetic fields, some ESR modes decrease linearly from the energy gaps of about $\Delta$. Assuming a linear field dependence with a slope $g=2.2$, these modes intersect the frequency-zero line at the magnetic fields between 54 and 58 T, which are in the vicinity of the magnetic field where the plateau terminates. Accordingly, this gapped resonance mode may be a clue to understand the emergence of magnetization plateau.
4. Conclusions
In conclusion, electromagnetic properties of Ca$_2$CoSi$_2$O$_7$ single crystals were investigated by high-field multi-frequency electron spin resonance (ESR) technique. Several ESR straight branches with $g = 2.2$ were observed in the magnetization plateau phase. We have found ESR modes with large zero-field energy gaps $\Delta = 1.7 \sim 1.8$ THz. These gapped ESR modes, which may be electromagnon excitations, suggest a strong relationship between this energy gap and the magnetization plateau. The studies of light polarization dependence of the ESR signals are necessary to clarify whether these high-energy gapped ESR modes are caused by electromagnons.

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